Ambient and Indoor Air Sampling for Per- and Poly-Fluorinated Alkyl Substances (PFAS)

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LECO

PFAS in Air – Outline

- **PFAS Background**
  - PFAS in Air Testing
- **Source Air Sampling**
  - OTM-45 overview
  - ASE extraction
- **Ambient and Indoor Air**
  - Small volume sampler
  - Breakthrough
  - Fluorotelomer Alcohols by GC-MS/SIM

PFAS in Air – Outline

- **High Resolution GC-MSTOF analysis**
  - Deconvolution tools
  - Library matching and mass accuracy
  - EI and CI data

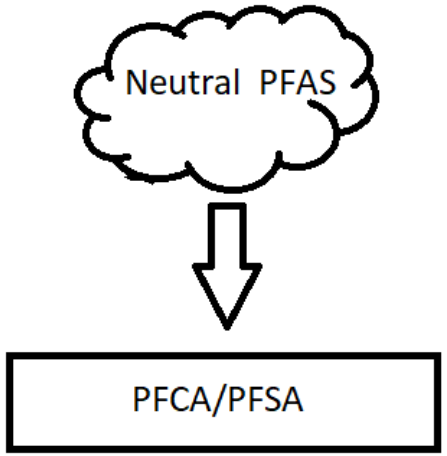
PFAS in Air Testing

- **Source emissions can spread volatile and semi-volatile PFAS**
  - PFAS can be dispersed in vapor phase or on particulates

- **Combustion can create both short chain and large fluorinated molecules**
  - Combustion and incineration processes can create short chain PFAS such as trifluoroacetic acid (TFA) and carbon tetrafluoride (CF_4)
  - At ≤ 800°C fluorinated dioxins and furans can be created

PFAS in Air Testing

- **Volatile PFAS are present in air**
  - Neutral PFAS such as fluorotelomer alcohols (FTOH), perfluorinated sulfonamides (FOSA) and sulfonamide ethanols (FOSE) are volatile and capable of long-range atmospheric transport
  - Neutral PFAS are precursors to ionic PFAS compounds such as perfluoroalkyl carboxylates (PFCA) and perfluoroalkane sulfonates (PFSA)



Annika Jahnke, Urs Berger, Trace analysis of per- and polyfluorinated alkyl substances in various matrices—How do current methods perform?, Journal of Chromatography A, Volume 1216, Issue 3, 2009, Pages 410-421

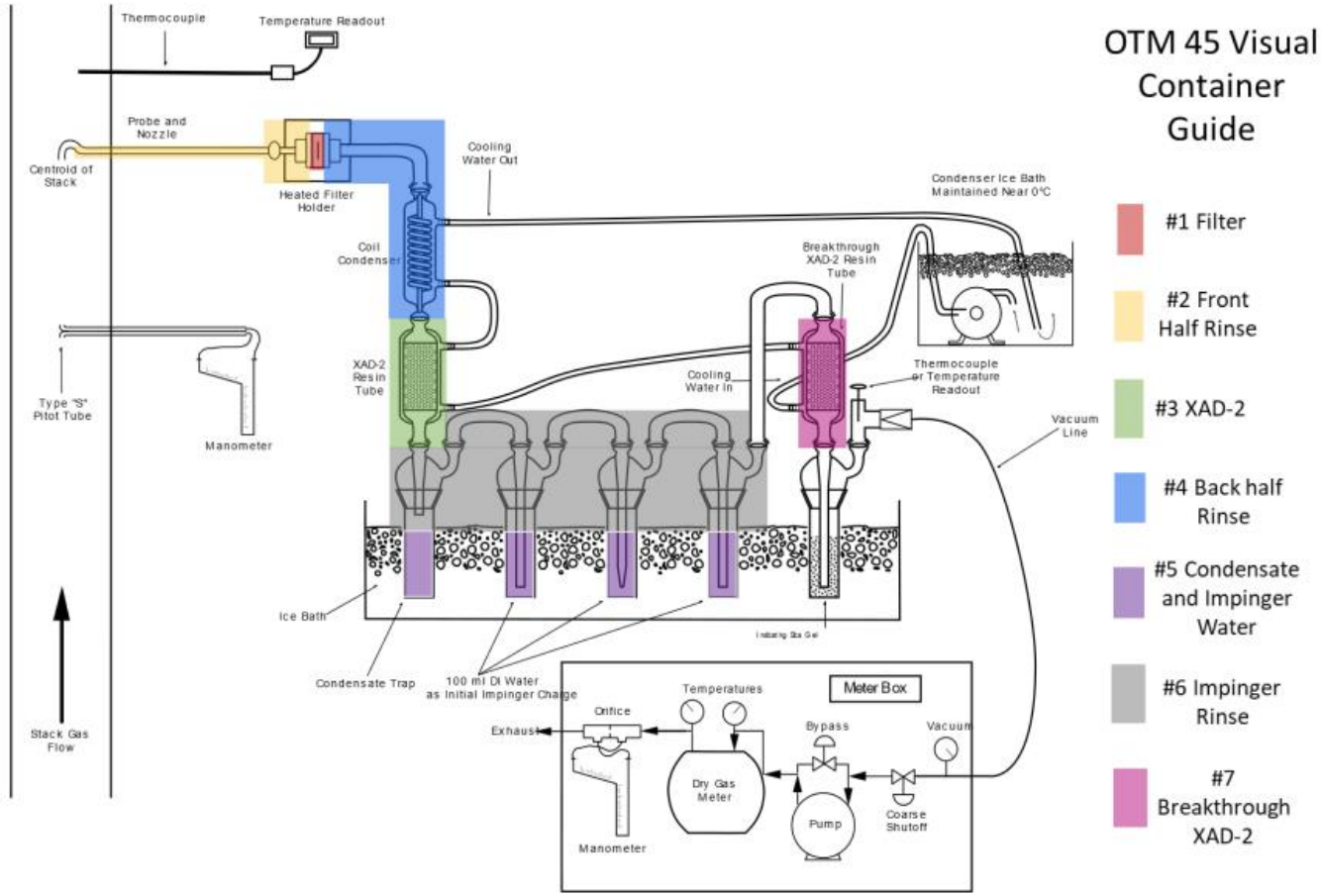
PFAS in Air Testing

- **PFAS can be present in indoor air**
  - Off gassing of volatile PFAS from consumer products
  - Airborne dust containing PFAS from product wear and tear

Kerstin Winkens et al,Perfluoroalkyl acids and their precursors in floor dust of children's bedrooms – Implications for indoor exposure, Environmental International, Volume 119, 2018, Pages 493-502

Source Air Sampling – OTM-45

- **Combines filter, XAD-2, and liquid impingers**
- **Suitable for C_4 to C_{18} PFAS compounds**
- **Many different PFAS classes (PFCA, PFSA, FOSA, FOSE, etc.)**

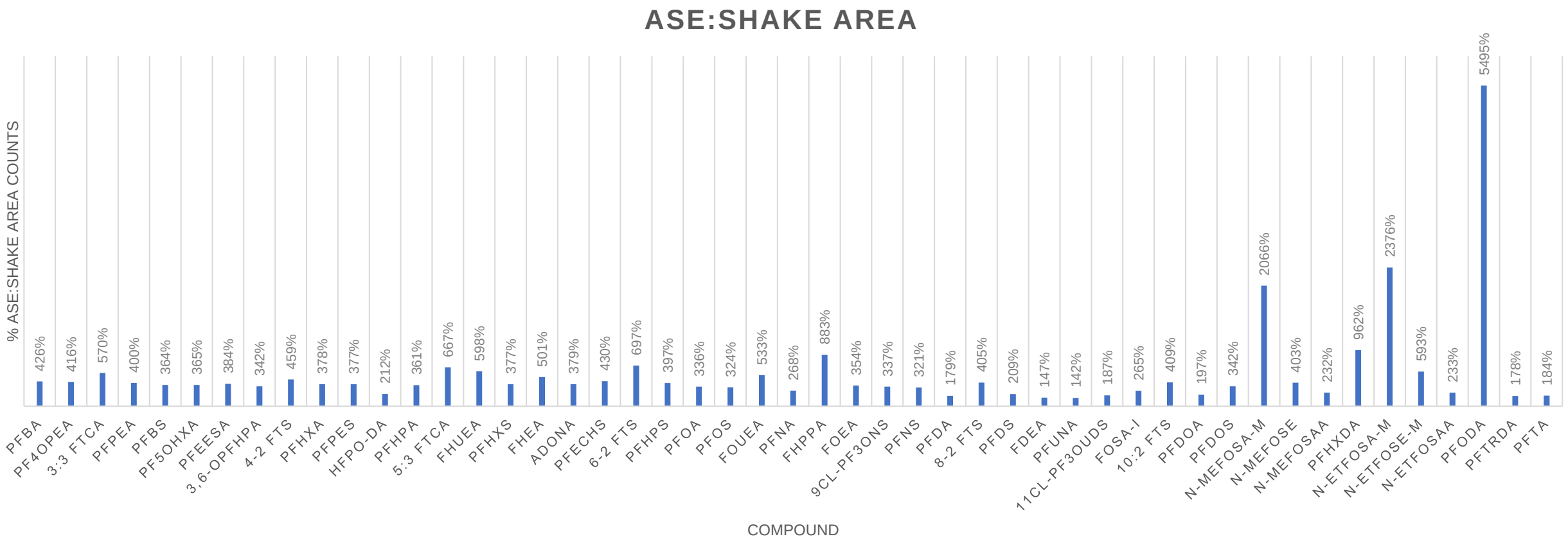


OTM-45 – ASE Extraction

- **OTM-45 sample prep for XAD-2 fraction is two rounds of 16-hour shakeouts using 360 mL total solvent**
  - 32-hour extraction plus time for solvent blowdown

- **Accelerated Solvent Extraction (ASE) advantages**
  - Reduced time – ~45 minutes/sample
  - Reduced solvent use – <100mL solvent/sample
  - Higher extraction efficiency – 1.4 to 55 times more response on ASE

OTM-45 – ASE Extraction



OTM-45 – MDL

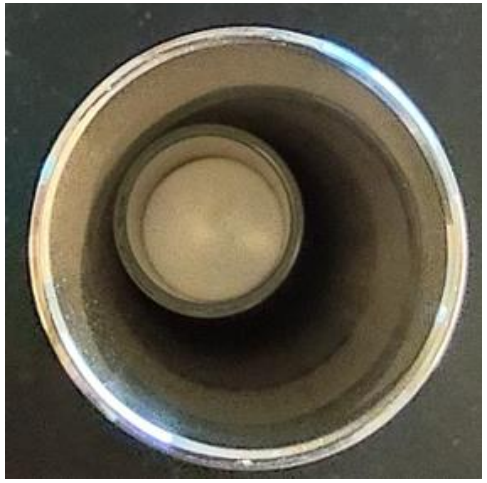
Name	OTM-45 MDL	Restek MDL	Name	OTM-45 MDL	Restek MDL	Name	OTM-45 MDL	Restek MDL
PFBA	2.08	0.06	FHEA		0.09	FDEA		0.07
PF4OPeA		0.02	ADONA	0.14	0.02	PFUnA	0.33	0.08
3:3 FTCA		0.05	PFeCHS		0.03	11Cl-PF3OUdS	0.18	0.04
PFPeA	0.2	0.03	6-2 FTS	0.29	0.02	FOSA-I	0.27	0.13
PFBS	0.17	0.07	PFHpS	0.08	0.03	10:2 FTS		0.04
PF5OHxA		0.01	PFOA	0.43	0.22	PFDoA	0.12	0.10
PFEESA		0.01	PFOS	0.35	0.04	PFDoS		0.06
3,6-OPFHpA		0.02	FOUEA		0.07	N-MeFOSA-M		0.07
4-2 FTS	0.20	0.02	PFNA	0.15	0.06	N-Me-FOSE-M		0.07
PFHxA	0.31	0.02	FHpPA		0.14	N-MeFOSAA	0.4	0.05
PFPeS	0.14	0.02	FOEA		0.18	PFHxDA		0.05
HFPO-DA	2.77	0.22	9Cl-PF3ONS	0.17	0.03	N-EtFOSA-M		0.17
PFHpA	0.21	0.10	PFNS	0.14	0.18	N-EtFOSE-M		0.05
5:3 FTCA		0.07	PFDA	0.13	0.05	N-EtFOSAA	0.39	0.08
FHUEA		0.06	8-2 FTS	0.27	0.07	PFODA		0.05
PFHxS	0.17	0.06	PFDS	0.17	0.32	PFTrDA	0.12	0.8
MDL values in ng/m3 air						PFTA	0.19	0.05

Ambient and Indoor Air Sampling

- Resin sampling from OTM-45 can be adapted to ambient and indoor air
- 8 g of Ultra-Clean Resin was packed into a small volume air sampler
- 20 µm frit to catch particulates
- TD tube used to catch any potential breakthrough compounds

Ambient and Indoor Air Sampling

- **Small volume sampler can be fit into a 100 mL ASE cell for cleaning and extraction**
- **Removes the need to separately clean and extract resin, frits, and glass holder**



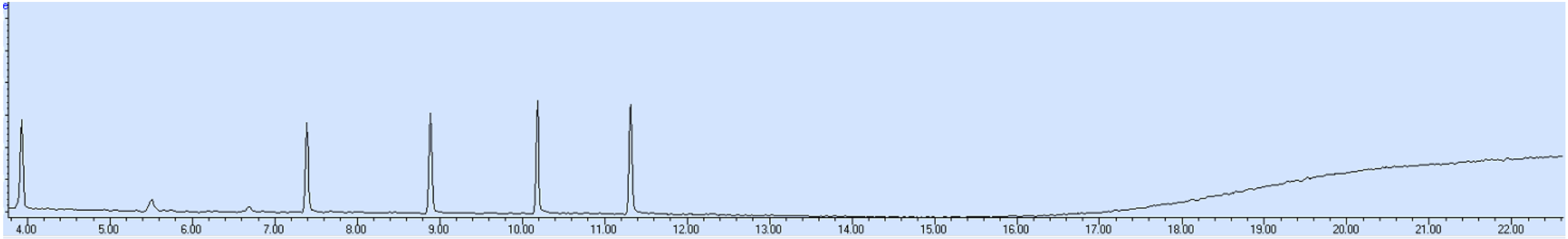
Ambient and Indoor Air Sampling

- Initial testing shows no breakthrough for OTM-45 compounds
- FTOH also tested and showed no breakthrough when spiked on resin
- Sample spiked and air pulled through for 24 hours at 300 mL/min
- 432 L/0.432 m^3 of air sampled

FTOH by GC-MS SIM

- Agilent 7890B
- Rtx 624Sil-MS 60 x 0.25 x 1.4
- Inlet
  - 250C
  - 5:1 split
  - 2 mL/min flow
- Oven
  - 80C hold 3min
  - 15C/min to 300C, hold 5 minutes
- MSD transfer line
  - 250C
- Agilent 5977
- Mass Spec SIM mode
- SIM
  - m/z 45, 69, 95, 119, 131
  - Dwell time 50
- MS Source
  - 350C
- MS Quad
  - 200C

FTOH by GC-MS SIM



- 4:2 FTOH – 7.391 min
- 6:2 FTOH – 8.889 min
- 8:2 FTOH – 10.187 min
- 10:2 FTOH – 11.317 min

FTOH by GC-MS SIM

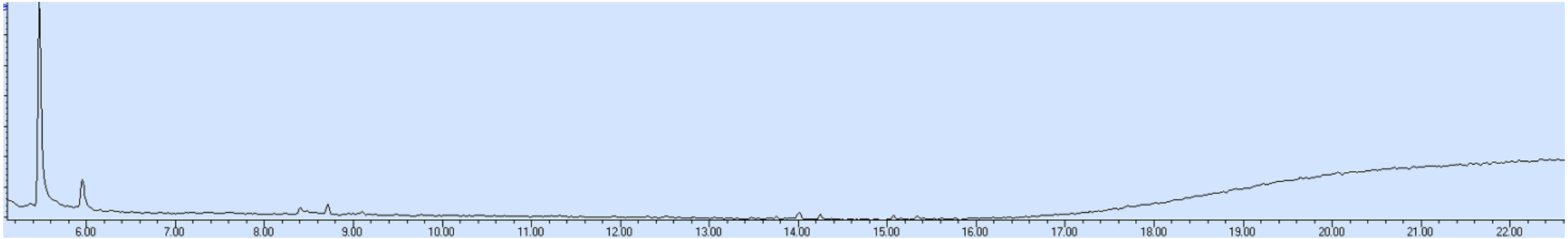
- Calibration from 400-5000 ppb in solution
- 0.9-4.5 ng/ m^3 at 432 L of air sampled

Name	% RSE	MDL (ng/m3)	Avg. Recovery (@ 1.4 ng/m3)	% RSD (@ 1.4 ng/m3)
4:2 FTOH	20%	0.25	90%	7%
6:2 FTOH	16%	0.23	102%	5%
8:2 FTOH	19%	0.38	92%	10%
10:2 FTOH	21%	0.31	111%	7%

Ambient and Indoor Air Sampling

- Real world samples from a residential home
- Downstairs dining room, upstairs office, basement, and outside porch
- Sampled at 200 mL/min for 24 hours, 288 L or 0.288 m^3

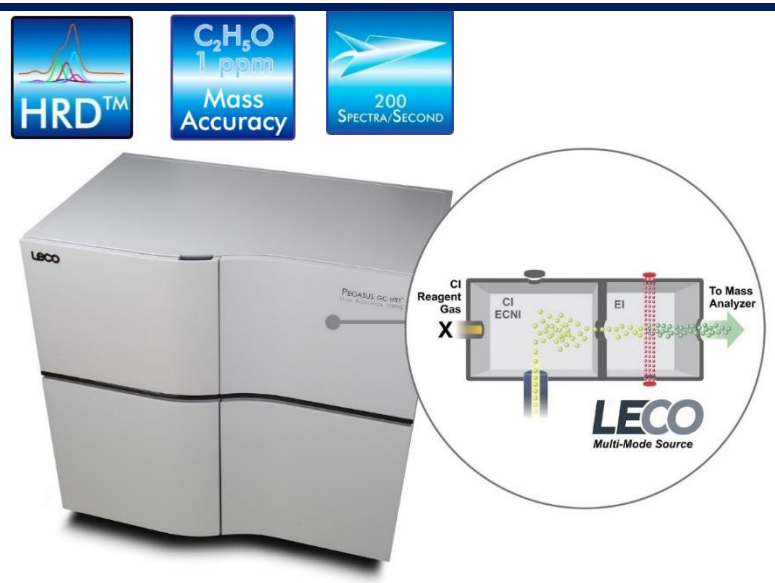
Ambient and Indoor Air Sampling



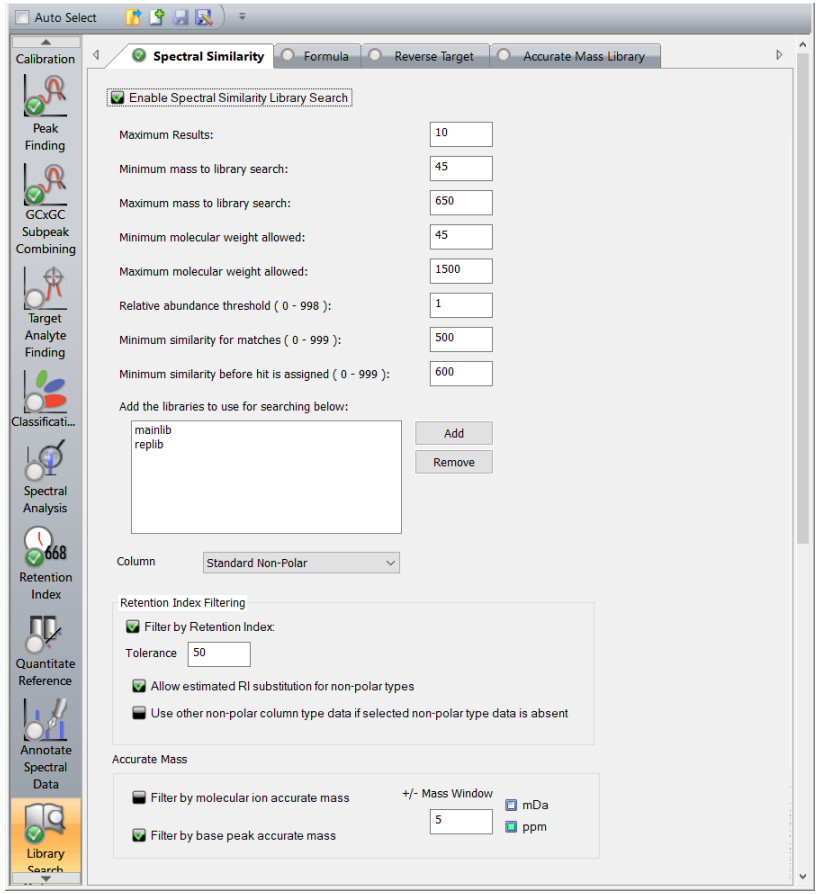
- **No PFAS present in targeted GC-MS SIM or LC-MS/MS analysis**

High-Resolution GC-TOFMS

LECO Pegasus® HRT+ 4D

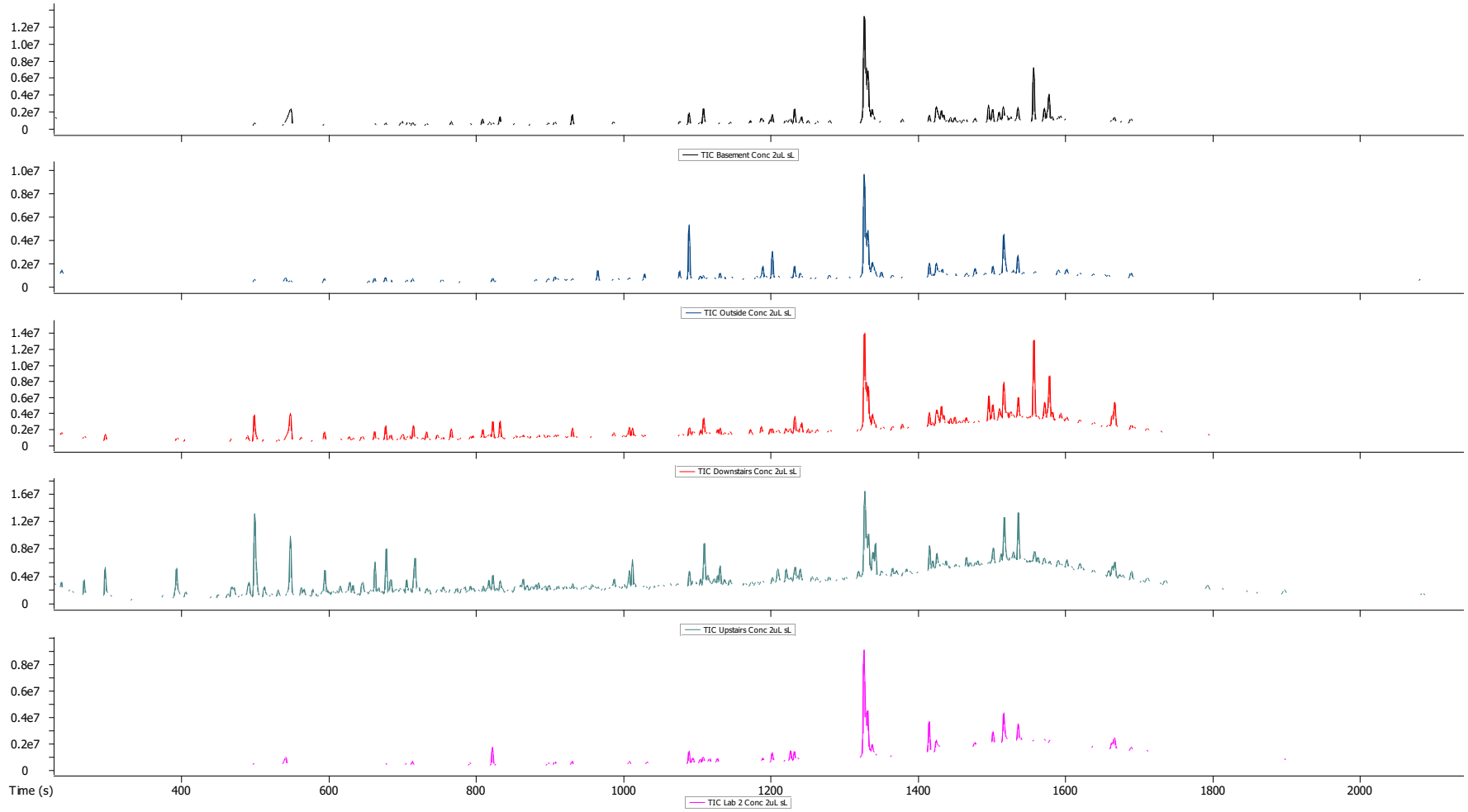


- Mass Accuracy: 1 PPM
- Resolution: Up to 50,000
- Acquisition Speed: up to 200 sps
- Ionization: EI, PCI, ECNI

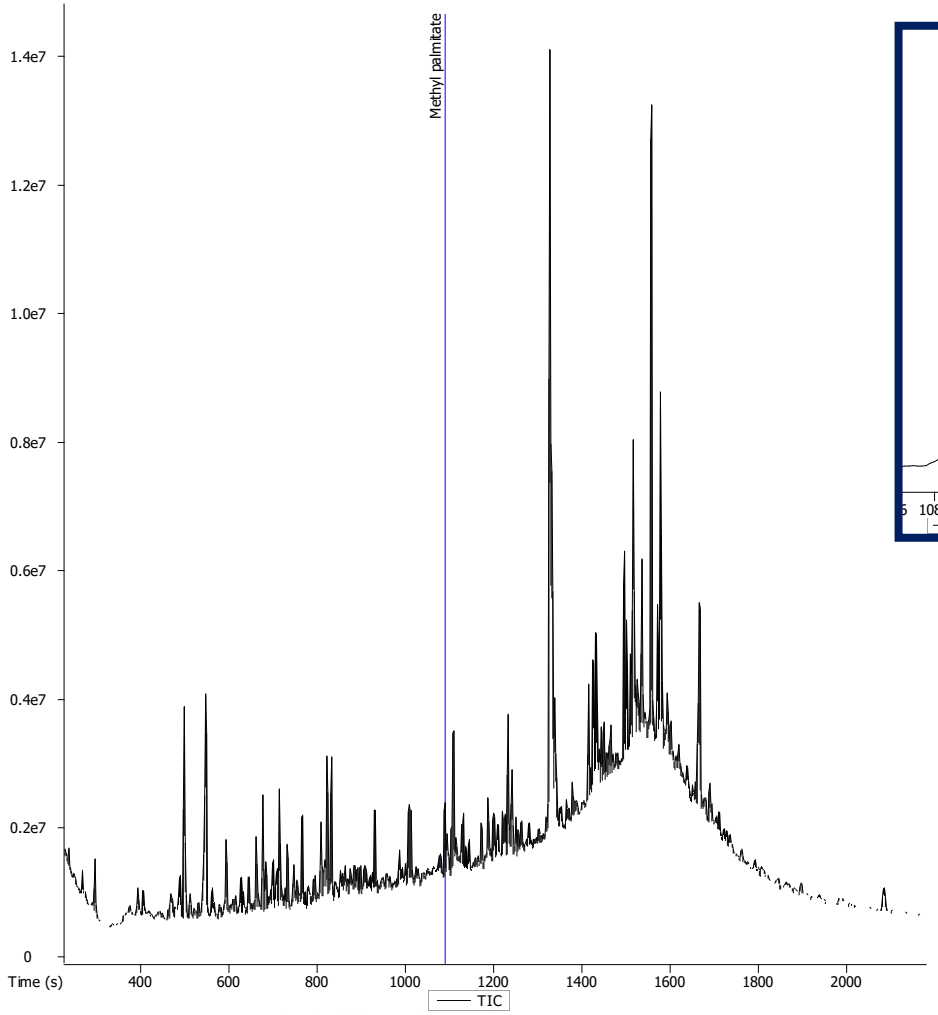


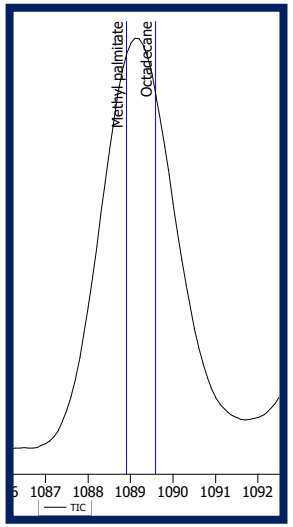
- ✓Peak Finding
- ✓Deconvolution
- ✓Spectral Database Comparisons
- ✓Mass Δ and Mass Accuracy
- ✓Calculations → Formula Determinations

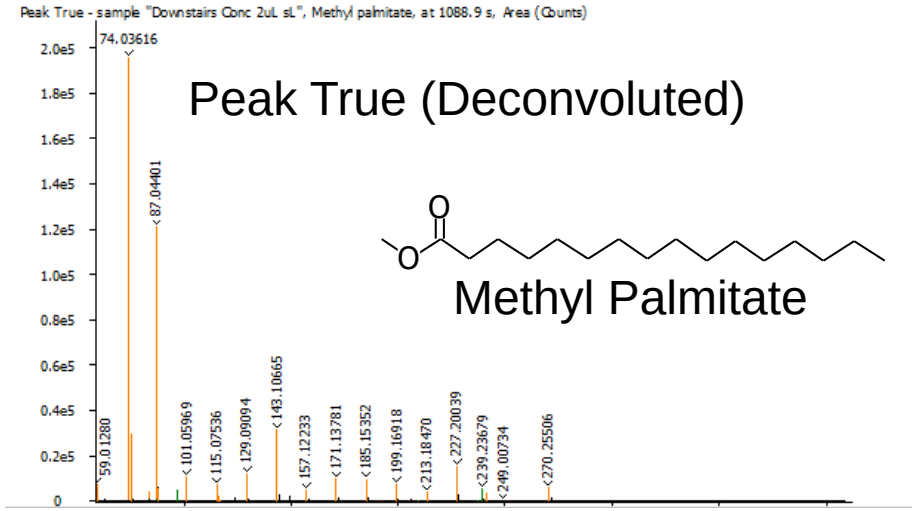
High-Resolution GC-TOFMS

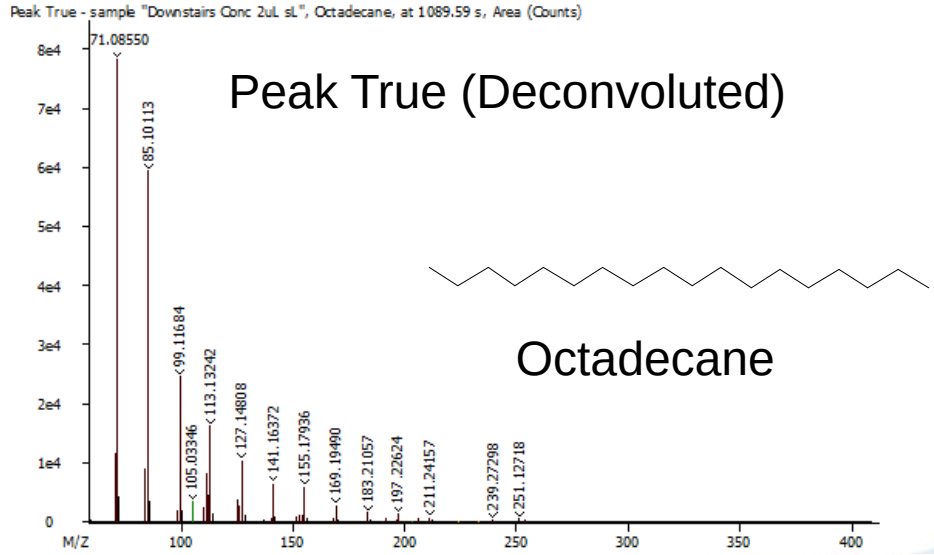


Deconvolution of Spectra

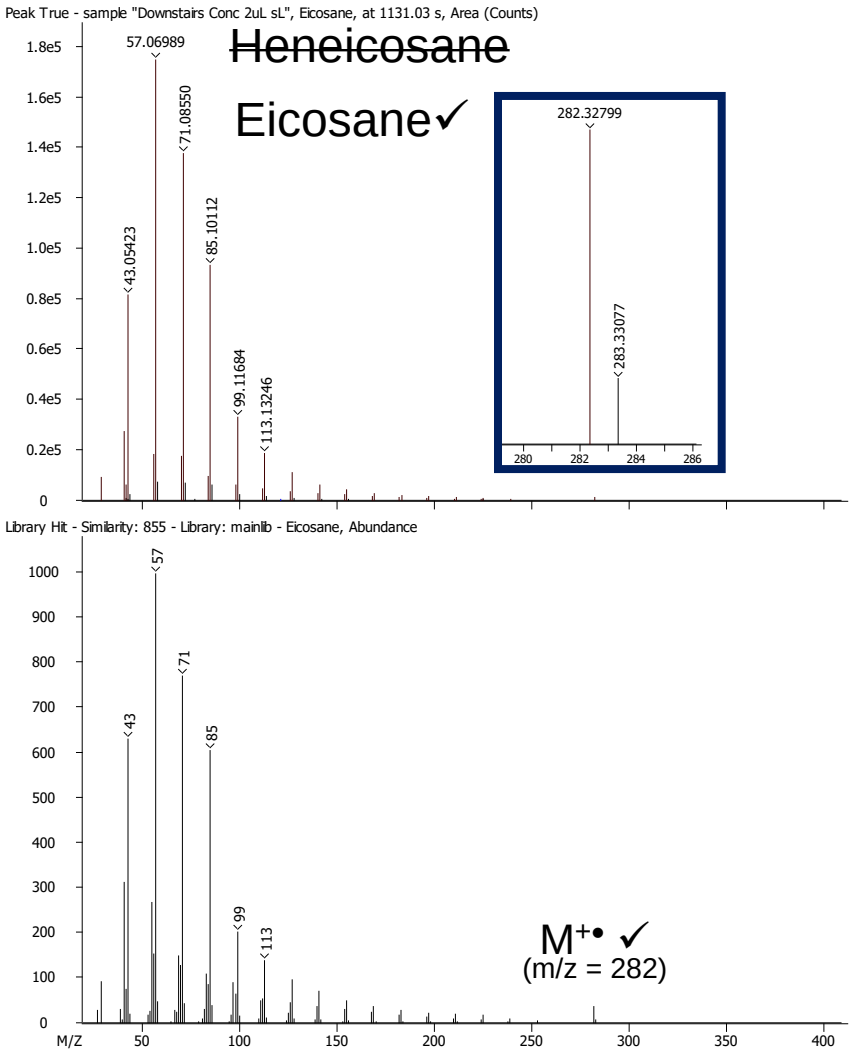








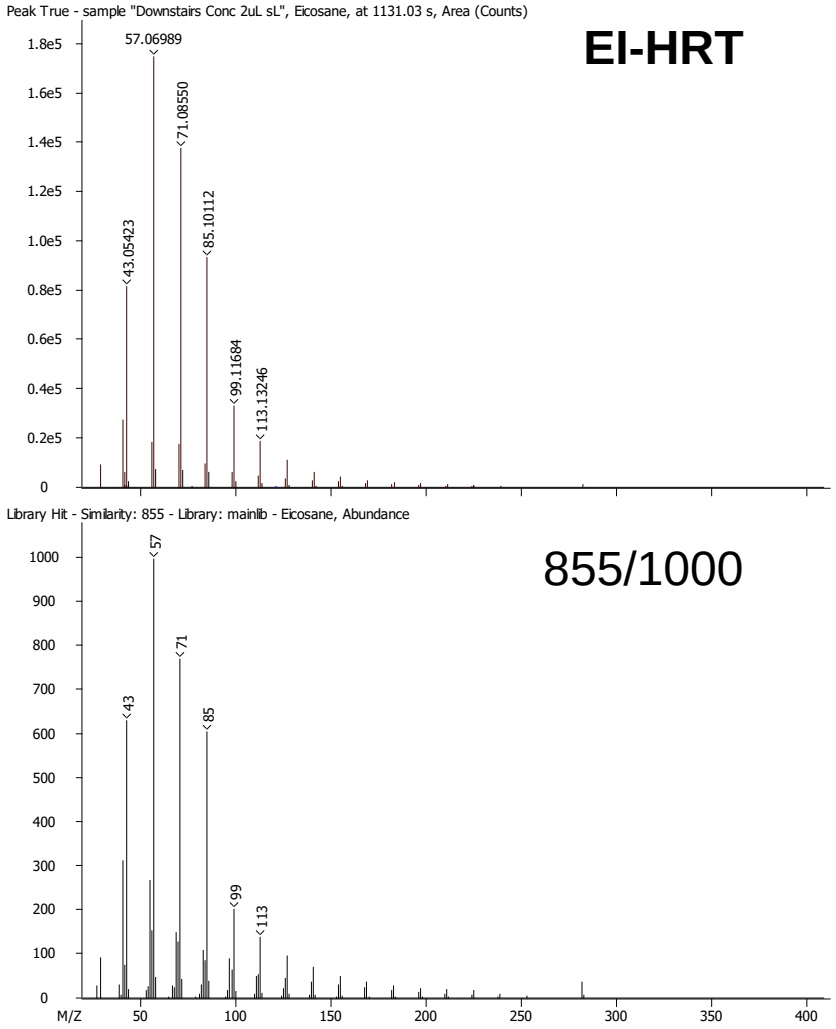
Library Similarity and Mass Accuracy

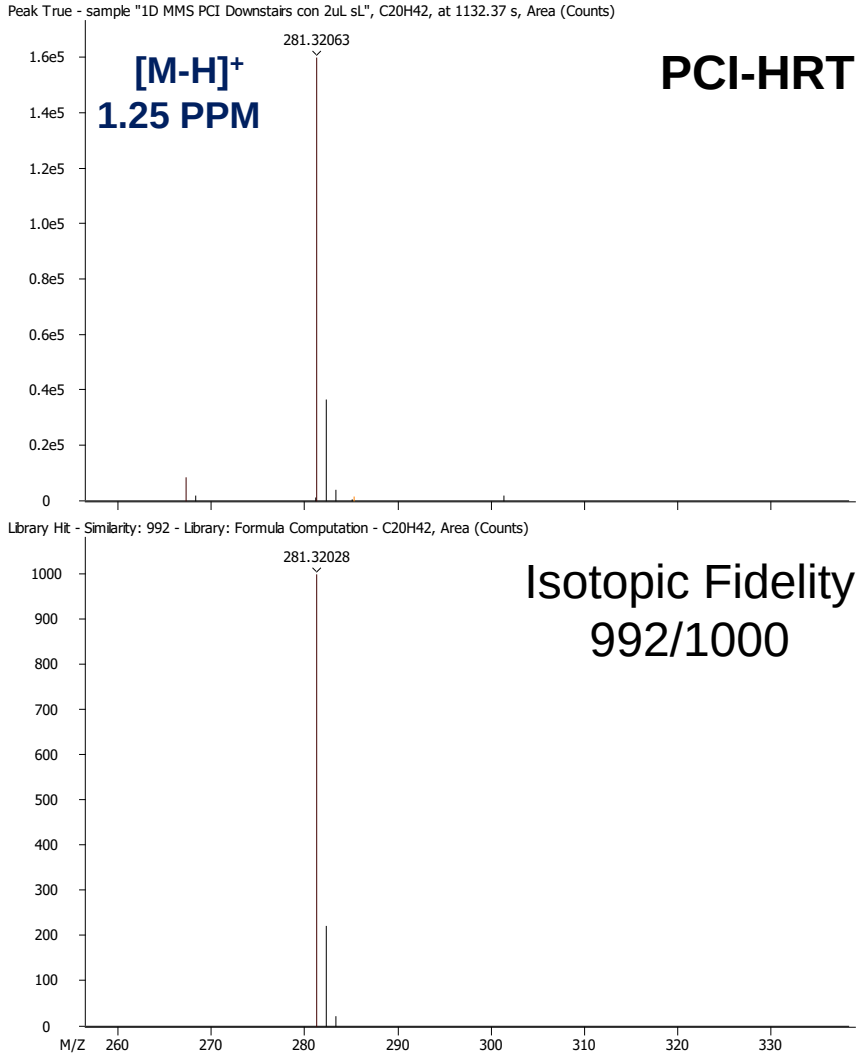


Hit	Name	CAS	Formula	m/z calc	m/z obs	PPM	Similarity
1	Heneicosane	629-94-7	C21H44	296.3438	306.1826	N/A	863
2	Eicosane	112-95-8	C20H42	282.3281	282.328	-0.39	855
3	Docosane	629-97-0	C22H46	310.3594	306.1826	N/A	845
4	Heneicosane	629-94-7	C21H44	296.3438	306.1826	N/A	844
5	Octadecane	593-45-3	C18H38	254.2968	253.288	N/A	842
6	Octadecane	593-45-3	C18H38	254.2968	253.288	N/A	839
7	Hexadecane	544-76-3	C16H34	226.2655	226.2599	-24.77	835
8	Eicosane	112-95-8	C20H42	282.3281	282.328	-0.39	834
9	Hexadecane	544-76-3	C16H34	226.2655	226.2599	-24.77	833
10	Heptadecane	629-78-7	C17H36	240.2812	240.2767	-18.53	833

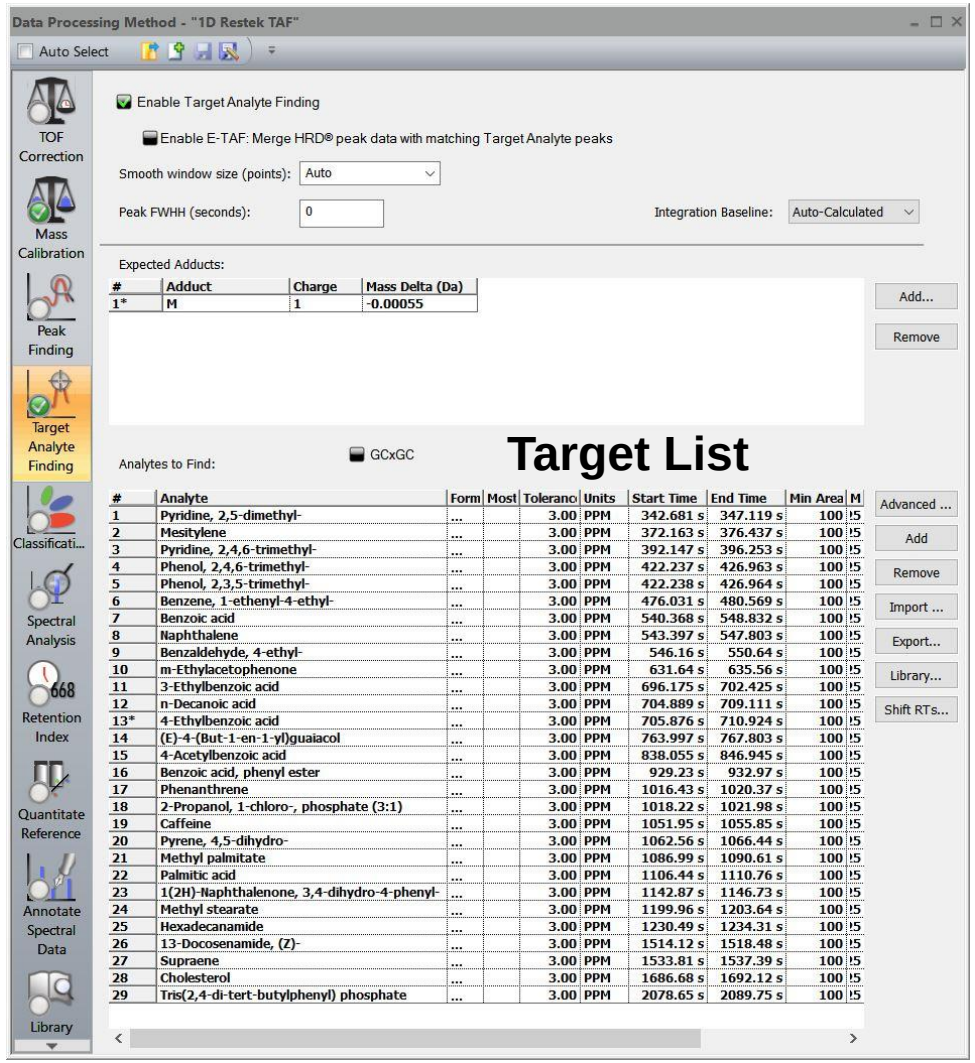
- **Library similarity alone can lead to mis-identifications**
- **Presence of molecular ion and confirmation by mass accuracy improves confidence in matches**

Complementary EI and CI Data





Target Analyte Finding



Input Masses For Target Analyte Finding

Analyte: 4-Ethylbenzoic acid

#	Formula	Isotope	M/Z	Tolerance	Units	Required
1*			105.06989	3.00	PPM	☒
2			135.04400	3.00	PPM	☐
3	$C_9H_{10}O_2$	150.06808		3.00	PPM	☒

- In addition to library search, a targeted search can be done
- Based on retention time HRAM target ions, and mass accuracy

Library and Target Search Results

Name	Formula	R.T. (s)	Similarity	PPM
3-Penten-2-one, 4-methyl-	C6H10O	237	867	-0.23
2,5-Hexanedione	C6H10O2	336	851	-0.81
Benzene, 1-ethyl-4-methyl-	C9H12	373	806	-1.46
Pyridine, 2,4,6-trimethyl-	C8H11N	393	907	-1.52
Phenol, 2,4,6-trimethyl-	C9H12O	424	805	-1.14
Benzene, 1-ethenyl-3-ethyl-	C10H12	478	885	-0.99
1,3-Benzenediol, 4-ethyl-	C8H10O2	483	801	-1.18
Benzene, 1-ethenyl-4-ethyl-	C10H12	485	739	-0.81
3-Hexen-2-one	C6H10O	531	710	-0.52
Benzene, 1-methyl-4-(1-propynyl)-	C10H10	538	805	-1.92
Naphthalene	C10H8	545	808	-1.06
Benzoic acid	C7H6O2	548	944	-1.37
Ethanone, 1-(4-ethylphenyl)-	C10H12O	633	877	-0.85
Ethanone, 1-(2,4,5-trimethylphenyl)-	C11H14O	667	708	-1.82
3-Ethylbenzoic acid	C9H10O2	700	858	-1.23
4-Ethylbenzoic acid	C9H10O2	709	830	-1.39
1-Tetracosene	C24H48	1008	774	N/A
Octadecane	C18H38	1012	911	-1.82
Phenanthrene	C14H10	1019	859	-1.32
Naphthalene, 1,2-dihydro-4-phenyl-	C16H14	1024	901	-1.62
Pyrene, 4,5-dihydro-	C16H12	1065	858	-1.97
4,4'-Diisopropylbiphenyl	C18H22	1085	745	-0.88
Methyl palmitate	C17H34O2	1089	846	-1.02
n-Hexadecanoic acid	C16H32O2	1109	907	-1.27
1-Hexacosene	C26H52	1128	872	N/A
1(2H)-Naphthalenone, 3,4-dihydro-4-phenyl-	C16H14O	1145	860	-1.48
Octadecanenitrile	C18H35N	1193	710	N/A
Methyl stearate	C19H38O2	1202	800	-1.52
Docosane	C22H46	1240	741	-0.53
1,2-Benzenediol, o-(4-ethylbenzoyl)-	C15H14O3	1302	866	N/A
Tris(1,3-dichloroisopropyl)phosphate	C9H15Cl6O4P	1320	810	N/A
9-Octadecenamide, (Z)-	C18H35NO	1327	906	-1.91
Cyclohexane, 1,3,5-triphenyl-	C24H24	1378	848	-0.99
Palmitoleamide	C16H31NO	1425	786	N/A
13-Docosenamide, (Z)-	C22H43NO	1516	747	-1.82
Supraene	C30H50	1536	828	-0.47
Tris(2,4-di-tert-butylphenyl) phosphate	C42H63O4P	2085	861	N/A

Name	R.T. (s)	Lab 1	Lab 2	Upstairs	Downstairs	Outside	Basement	Blank
Pyridine, 2,5-dimethyl-	345	152949	16654			7217	370398	
Mesitylene	374	850291	104510	2996001	786923	430791	7996627	49229
Pyridine, 2,4,6-trimethyl-	394	10250356		42859146	4227280	373437	88331	1561
Phenol, 2,4,6-trimethyl-	425	806941	141350	2812204	672453	132962	183903	143247
Phenol, 2,3,5-trimethyl-	425	806941	141350	2812204	672453	132962	47723	143247
Benzene, 1-ethenyl-4-ethyl-	478	382052	26405	293687	1355856	44611	1037596	14995
Benzoic acid	545	12117211	5320053	21778833	28381572	4042177	31377717	4515978
Naphthalene	546	178096	5711	124945	1194741	8659	443537	3677
Benzaldehyde, 4-ethyl-	548	257890	35837	196560	356496	48843	234340	59949
m-Ethylacetophenone	634	505941	128638	602296	560632	241158	4056399	230196
3-Ethylbenzoic acid	699	1805288	404727	2709814	4429110	217204	2822753	323275
n-Decanoic acid	707	1012552	265392	1634600	758017	489958	865613	43746
4-Ethylbenzoic acid	708	2226809		3840128	4752473		3613152	
(E)-4-(But-1-en-1-yl)guaiacol	766	1441133	5053	778220	3831205	4510	1262971	5541
4-Acetylbenzoic acid	843	422298	53772	1303643	844192			9881
Benzoic acid, phenyl ester	931	555034	16255	314132	1642299	16429	433918	14146
Phenanthrene	1018	244292	12300	515466	167733	40478	4108111	7313
2-Propanol, 1-chloro-, phosphate (3:1)	1020	66447	26159	143475	59798	41356	31687	13018
Caffeine	1054	27276	28565	55134	36719	18786	20575	3951
Pyrene, 4,5-dihydro-	1065	235908	2227	91788	298062	3424	183903	
Methyl palmitate	1089	2789689	3538808	4667398	3383883	18094834	243214	1413054
Palmitic acid	1109	2840142	1018703	13345980	4553202	536493	602303	48421
1(2H)-Naphthalenone, 3,4-dihydro-4-phenyl-	1145	149901	5283	77243	529167	8144	371440	5759
Methyl stearate	1202	1747912	2322300	2786688	2324708	8582380	5186465	4669389
Hexadecanamide	1232	3175375	4568609	11102206	8127365	5603988	135611	9672632
13-Docosenamide, (Z)-	1516	7988159	7452341	21331950	13134242	11127936	3644943	4269155
Supraene	1536	428097	5456202	32728565	12283024	5595007	19823	441696
Cholesterol	1689	205753	306701	1554775	507339	320107	375233	19106
Tris(2,4-di-tert-butylphenyl) phosphate	2084	3551668	2527640	7352729	4158788	3289682	6097256	6137507

- **Despite all these powerful tools, no untargeted PFAS detected**

Final Results – No Detectable PFAS

- **Many studies of indoor PFAS exposure point to dust as a major contributor**
  - Samplers were in out of the way places that may not generate airborne dust
- **Other studies show that volatile FTOH can be present in air at low or sub ng/m^3**
  - Larger sampling volumes or more sensitive instrumentation may be needed to properly identify and quantify PFAS in indoor air

Conclusions

- Lab-based testing shows small volume SDVB resin samplers can be used for a wide variety PFAS, including FTOH
- GC-MS can be used for volatile PFAS analysis, and GC-HRTOFMS can facilitate non-target characterization
- Real-world samples taken from a home show collection of many VOCs, but no presence of PFAS compounds
- Further work to increase sensitivity is needed to reach PFAS levels seen in some studies

Questions?

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