LECO

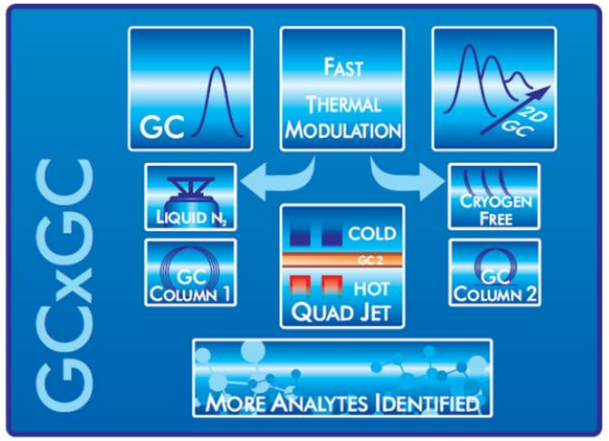
EMPOWERING RESULTS

Exploring PFAS in Consumer Goods Using GCxGC and High-Resolution Mass Spectrometry

David E. Alonso and Joe Binkley

Outline

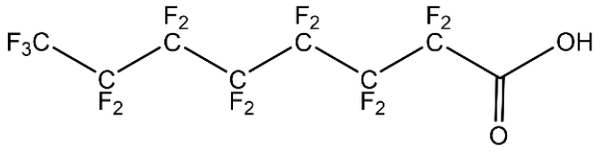
- Background
- Objective
- Experimental
- Results & Discussion
  - *Example A, Anti-Fog Solution – The case for GC-HRTOFMS*
  - *Example B, Chewing Gum – PFAS screening with GCxGC-HRTOFMS*
- Summary



Background: *"Polyfluorinated Alkyl Substances, PFAS"*

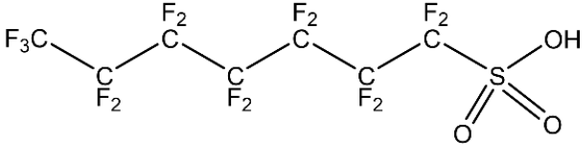
Per- and polyfluorinatedalkyl substances (PFAS) are anthropogenic compounds that are used extensively in industrial and consumer applications due to their unique physicochemical properties (e.g., hydrophobicity)

1



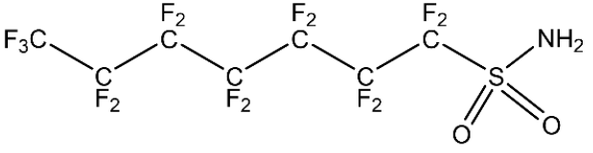
Perfluorooctanoic acid (PFOA)

2



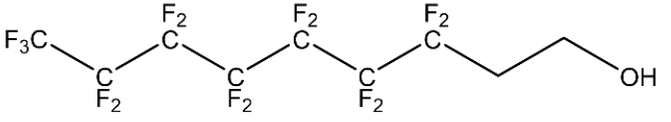
Perfluorooctanesulfonic acid (PFOS)

3



Perfluorooctanesulfoamide (PFOSA)

4



Octylfluorotelomer ethanol (8:2 FTOH)

Objective

To develop methodology for untargeted screening of consumer goods for PFAS & other compounds

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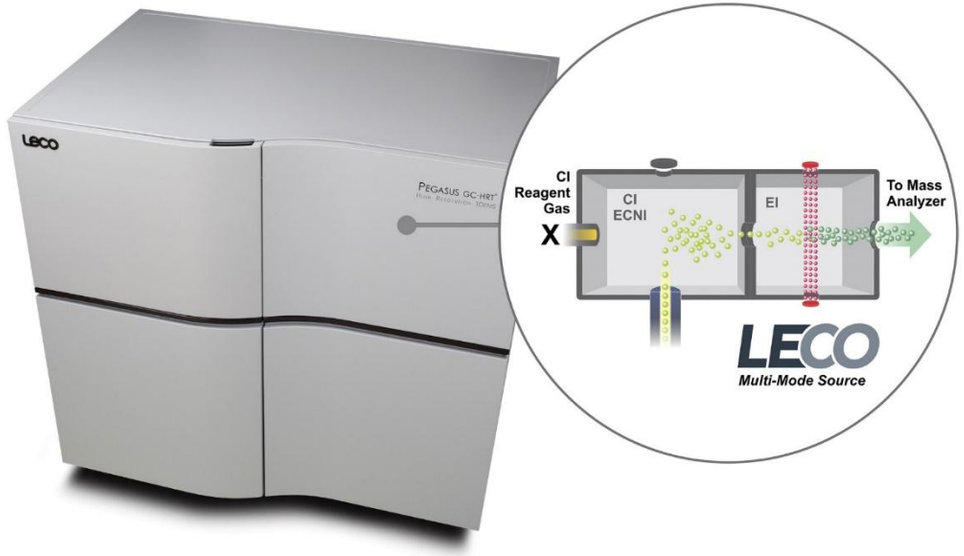
Sample Preparation, Introduction & Analysis

- **Preparation:** Dilute liquid sample in acetone and/or place sample in a microtube and insert into a quartz inlet Liner
- **Introduction:** Thermal desorption and Pyrolysis (GL Sciences Optic-4)
- **Analysis:**
  - GC-TOFMS
  - GC(×GC)-HRTOFMS (w/ MMS source)

LECO Pegasus® BTX 4D



LECO Pegasus® HRT+ 4D

Example A: Anti-fog Solution

- Anti-fog solutions are useful for maintaining clean and clear laboratory, construction, and sports protective eyewear

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Anti-fog Solution

- Anti-fog solutions are useful for maintaining clean and clear laboratory, construction, and sports protective eyewear
- Unfortunately, some anti-fog solutions may contain PFAS

Environmental Science & Technology

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Article

Characterization of Per- and Polyfluorinated Alkyl Substances Present in Commercial Anti-fog Products and Their *In Vitro* Adipogenic Activity

Nicholas J. Herkert, Christopher D. Kassotis, Sharon Zhang, Yuling Han, Vivek Francis Pulikkal, Mei Sun, P. Lee Ferguson, and Heather M. Stapleton*

Cite This: https://doi.org/10.1021/acs.est.1c06990

Read Online

Anti-Fog Sample (GC-TOFMS)

LECO Pegasus® BTX GC-TOFMS

0.9e9
0.8e9
0.7e9
0.6e9
0.5e9
0.4e9
0.3e9
0.2e9
0.1e9
0
Time (s)
500
1000
1500
2000
2500
AIC

AIC= Analytical **I**on **C**hromatogram

Anti-Fog: Peak Find Processing Results

- ✓ Alkanes
- ✓ Alkenes
- ✓ Aromatics
- ✓ Alcohols
- ✓ Aldehydes
- ✓ Ketones
- ✓ Fatty Acids
- ✓ Acid Derivatives
- ✓ Heterocyclic Compounds

Name	*R.T. (s)*	*Similarity*	*Mass Δ*
2-Pentanol, 4-methyl-	110	883	N/A
Toluene	113	952	-0.01
1H,1H-Perfluorooctanol	127	781	N/A
3-Penten-2-one, 4-methyl-	131	921	-0.01
Octane	132	919	-0.02
2-Hexene, 2,5,5-trimethyl-	139	955	-0.02
Hexane, 2,3,5-trimethyl-	142	950	-0.02
4-Hydroxy-2-pentanone	145	850	-0.01
6:2 FTOH	150	955	-0.05
Heptane, 2,6-dimethyl-	153	901	-0.02
Heptane, 2,5-dimethyl-	157	921	-0.02
Diacetone	163	918	N/A
9:1 FTOH	166	745	N/A
Heptane, 3,4-dimethyl-	176	836	-0.02
Octane, 4-methyl-	181	925	-0.02
Octane, 3-methyl-	188	871	-0.02
2-Butanol, 2,3-dimethyl-	212	842	N/A
Nonane	214	948	-0.02
Ethanol, 2-butoxy-	219	740	N/A
8:2 FTOH	246	706	N/A
1-Pentanamine, N-ethyl-	253	880	-0.08
2-Propanol, 1-butoxy-	253	952	N/A
Benzene, 1,2,4-trimethyl-	282	705	-0.02
Decane	317	957	-0.02
1,2,3-Propanetriol	324	923	N/A
10:2 FTOH	355	768	N/A
Compound X	367		
Undecane	427	940	-0.02
Nonanal	431	903	N/A
Hexanoic acid, 2-ethyl-	440	882	N/A
Octanoic acid methyl ester	452	794	-0.02
Octanoic acid	503	818	-0.02
1-Dodecene	526	874	-0.01
N-MeFOSA	531	850	N/A
Dodecane	535	939	-0.02
Dianhydromannitol	542	935	-0.02
Benzothiazole	557	932	-0.01
n-Octanoic acid isopropyl ester	568	905	N/A
Isosorbide	624	932	-0.02
Unknown 6	628		
Tridecane	639	914	-0.02

Name	*R.T. (s)*	*Similarity*	*Mass Δ*
3-Tetradecene, (Z)-	730	818	-0.02
Tetradecane	738	936	-0.02
Hexathiane	829	820	-0.02
Pentadecane	831	935	-0.02
Benzoic acid, 4-ethoxy-, ethyl ester	849	886	-0.02
Unknown 7	851		
2-(Methylthio)benzothiazole	914	859	-0.02
Hexadecane	920	942	-0.02
2(3H)-Benzothiazolone	970	888	-0.02
Heptadecane	1004	933	-0.02
2,6-Diisopropylnaphthalene	1019	777	-0.02
Unknown 8	1053		
Octadecane	1084	956	-0.03
Nonadecane	1160	948	-0.03
Methyl palmitate	1177	716	-0.03
Palmitinic acid	1201	864	-0.03
Eicosane	1233	947	-0.03
Unknown 9	1237		
1,5-Dimethyl-2-piperidone	1247	749	0
Bisphenol AF	1252	883	-0.04
Octathiocane	1255	889	-0.03
Heneicosane	1303	962	-0.03
Methyl stearate	1319	926	-0.03
Octadecanoic acid, ethyl ester	1364	717	-0.03
Docosane	1369	945	-0.04
1,8-Diazacyclotetradecane-2,7-dione	1373	747	-0.02
Unknown 10	1403		
Tricosane	1433	923	-0.04
Tetracosane	1495	952	-0.04
Triphenylene	1519	868	-0.02
N,N-dimethylhexadecanamide	1526	858	N/A
6-(Perfluorophenyl)uracil	1553	922	0.04
Unknown 11	1554		
Hexacosane	1612	950	-0.04
Heptacosane	1678	941	-0.04
Unknown 12	1716		
(13Z)-13-Docosenamide	1731	704	-0.04
Octacosane	1761	920	-0.04
Nonacosane	1866	934	-0.04
Unknown 13	2004		
Unknown 14	2558		

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- ✓ Alkenes
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- ✓ Fatty Acids
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- ✓ **Unknowns***

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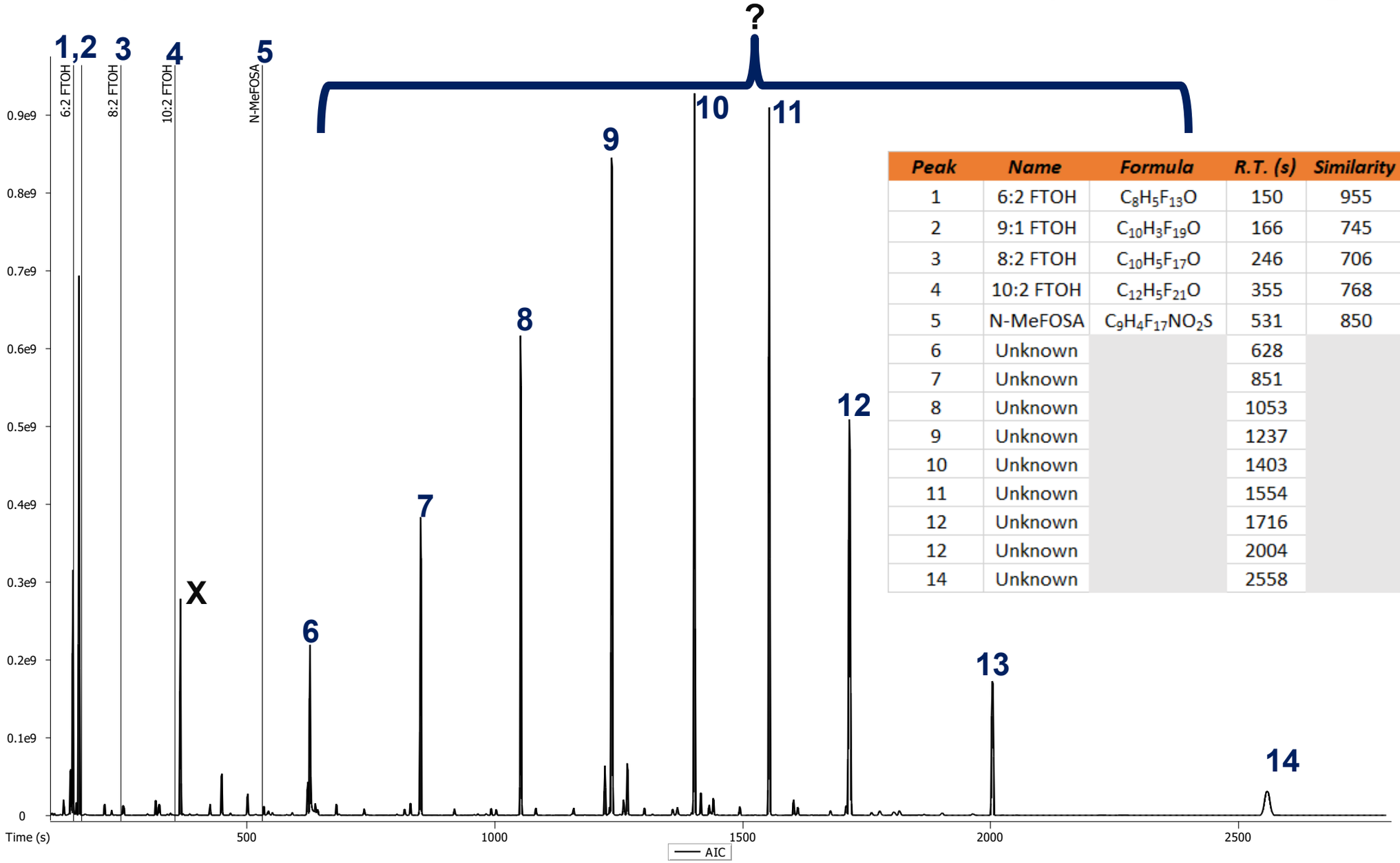
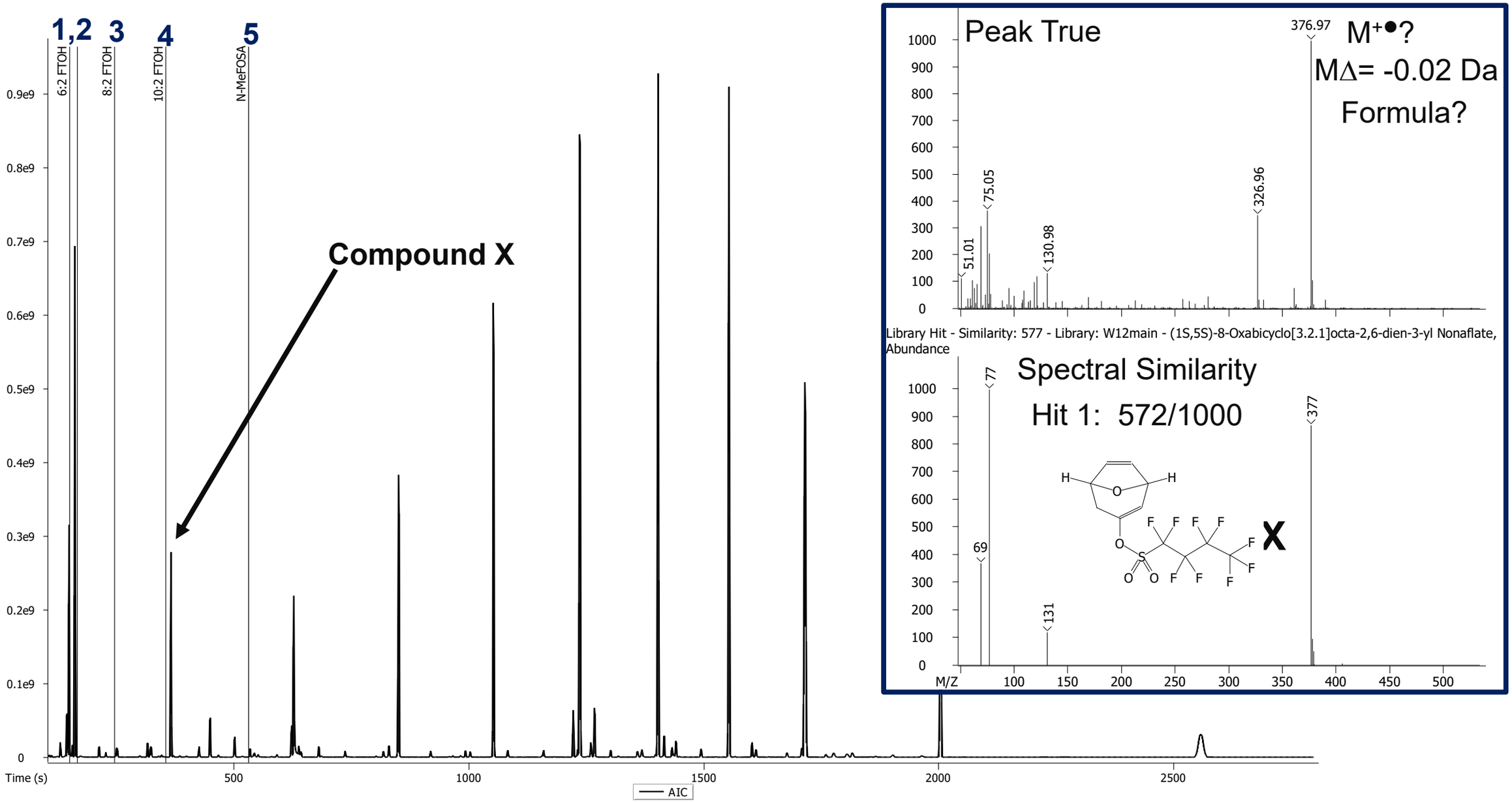
Anti-Fog Sample: Peak Find Processing Results (PFAS)



Peak	Name	Formula	R.T. (s)	Similarity	Obs. RI	Lib. RI
1	6:2 FTOH	$C_8H_5F_{13}O$	150	955	823	822 ± 0(1)
2	9:1 FTOH	$C_{10}H_3F_{19}O$	166	745	842	890 ± 0(1)
3	8:2 FTOH	$C_{10}H_5F_{17}O$	246	706	931	921 ± 0(1)
4	10:2 FTOH	$C_{12}H_5F_{21}O$	355	768	1034	1068 ± 0(1)
5	N-MeFOSA	$C_9H_4F_{17}NO_2S$	531	850	1195	1189 ± 0(1)
6	Unknown		628		1289	
7	Unknown		851		1522	
8	Unknown		1053		1761	
9	Unknown		1237		2005	
10	Unknown		1403		2252	
11	Unknown		1554		2499	
12	Unknown		1716		2745	
12	Unknown		2004		3000	
14	Unknown		2558		3250	

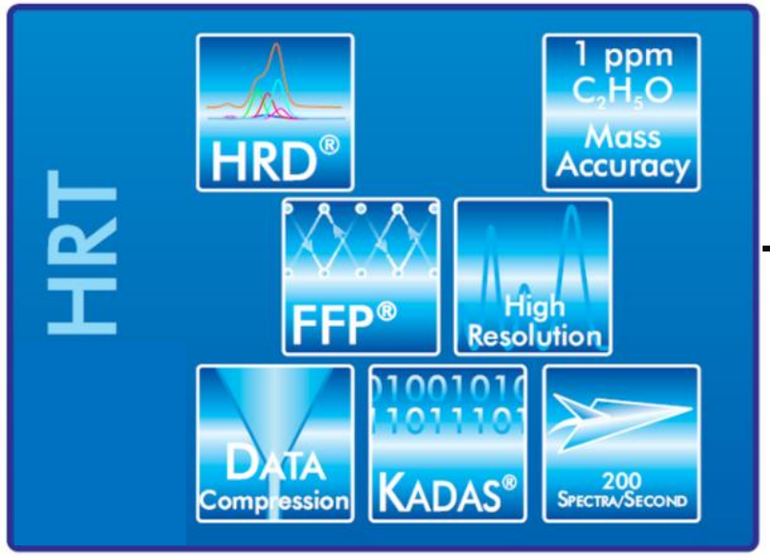
Problem: Unknown X



Solution: GC-HRTOFMS

- Unknown Characterization
- Reduction of matrix interferences through higher mass spectral resolution
- Formula determinations for molecular, adduct and fragment ions for confident compound annotations

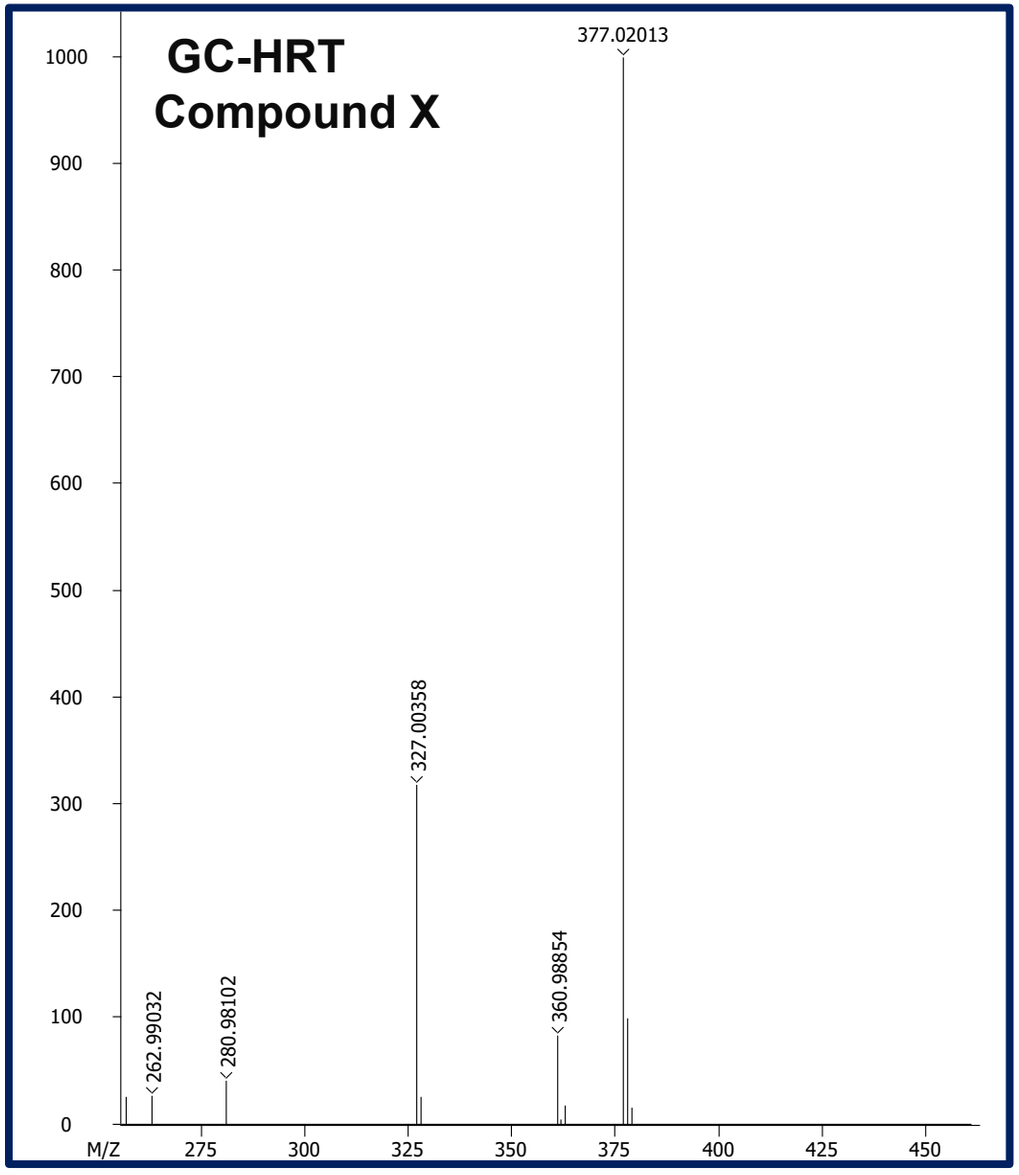
High-Resolution Mass Spectrometry

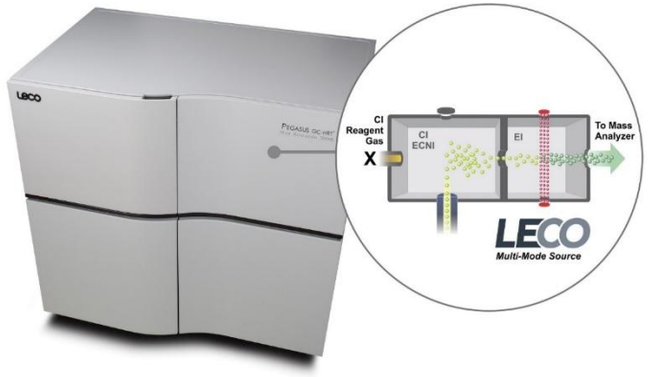


+

Powerful Software

Compound X, HRT Data

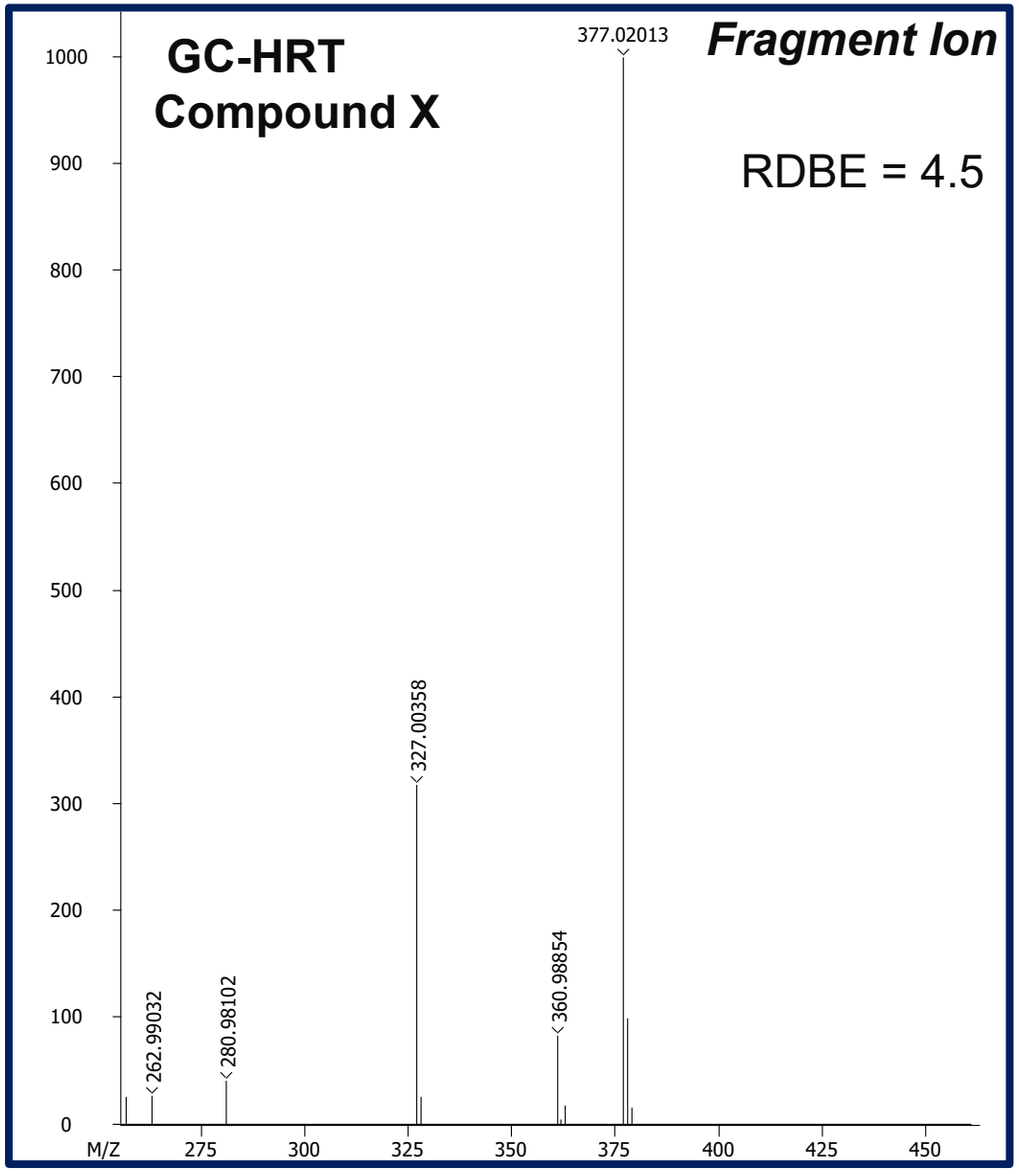




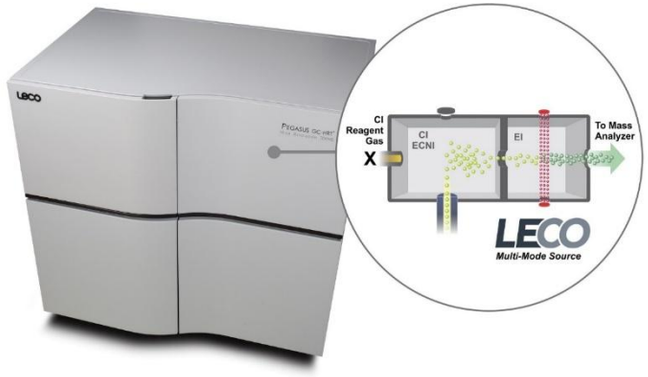
LECO Pegasus® HRT+
And Multi-Mode Source

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

Compound X, HRT Data: RDBE



Ring Double Bond Equivalents
RBDE = C+1-0.5*(X-N)
X = Monovalent Elements



LECO Pegasus® HRT+ And Multi-Mode Source

Mass Accuracy: 1 PPM
Resolution: Up to 50,000
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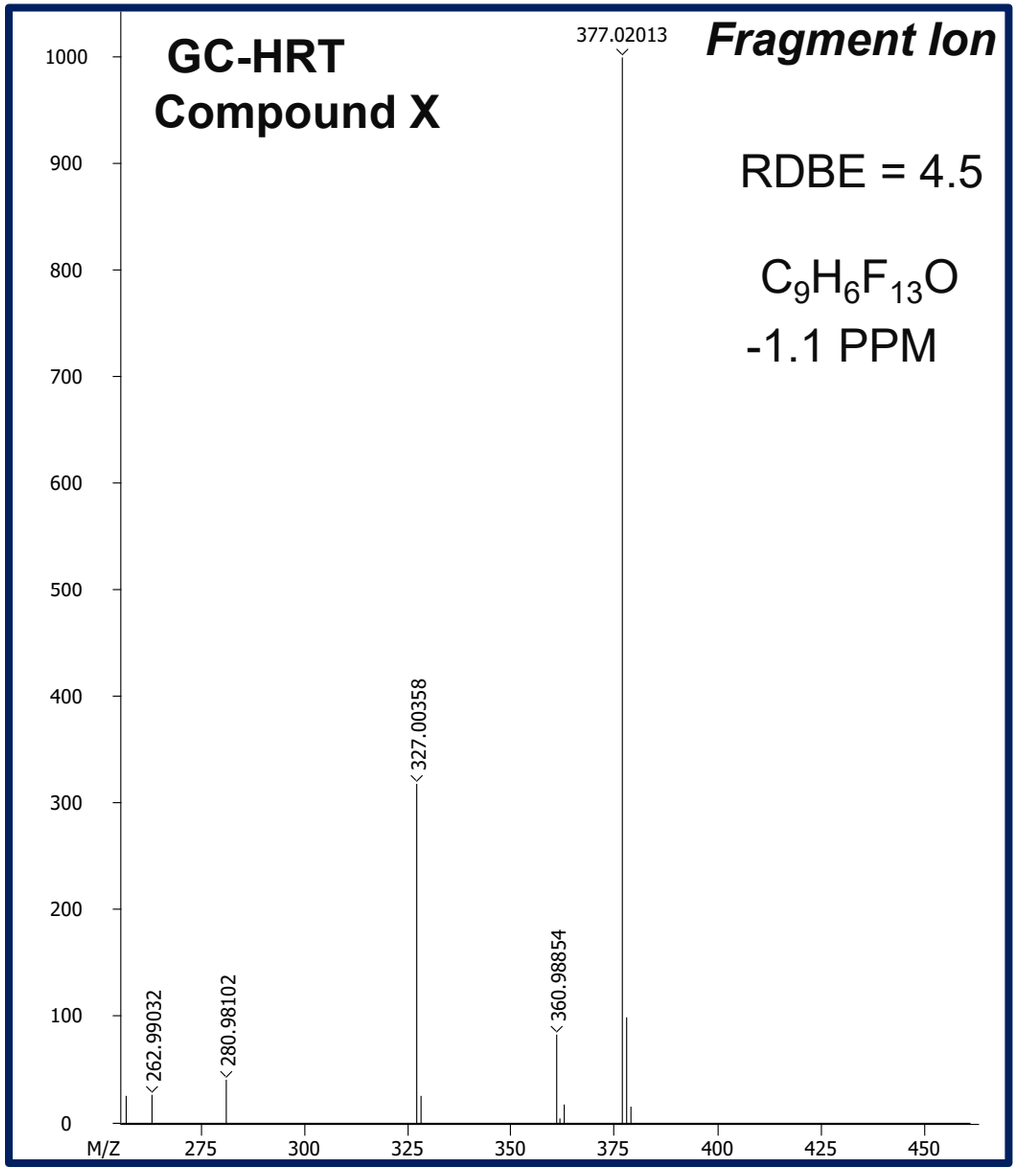
Compound X, HRT Data: Mass Accuracy & RDBE



RDBE = 4.5

$C_9H_6F_{13}O$

-1.1 PPM

Ring Double Bond Equivalents
RBDE = C+1-0.5*(X-N)
X = Monovalent Elements

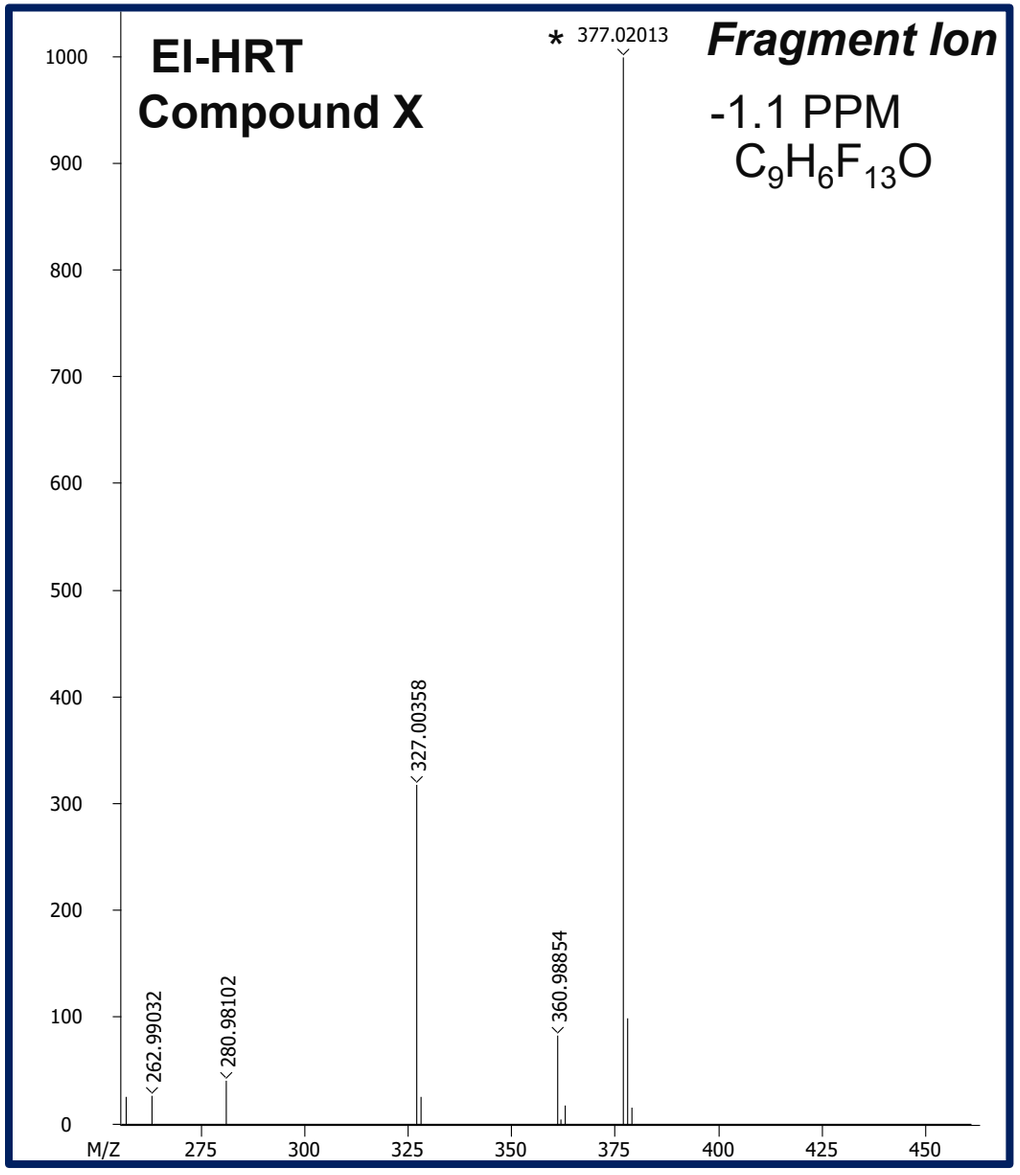
$$\text{Mass Accuracy} = \frac{m/z_{obs} - m/z_{calc}}{m/z_{calc}} \times 10^6$$

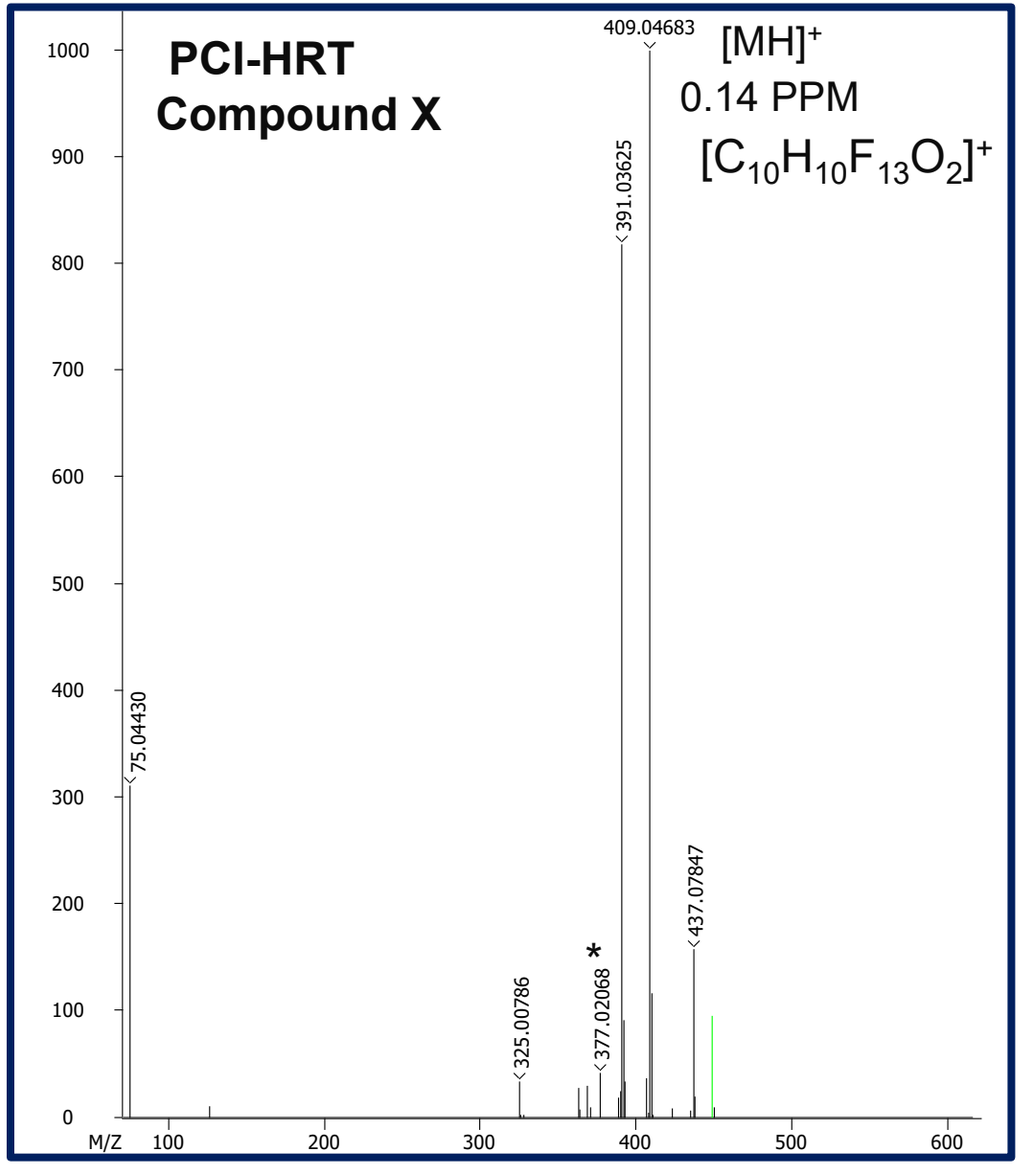
High Resolution Accurate Mass → Formulas

LECO Pegasus® HRT+
And Multi-Mode Source

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

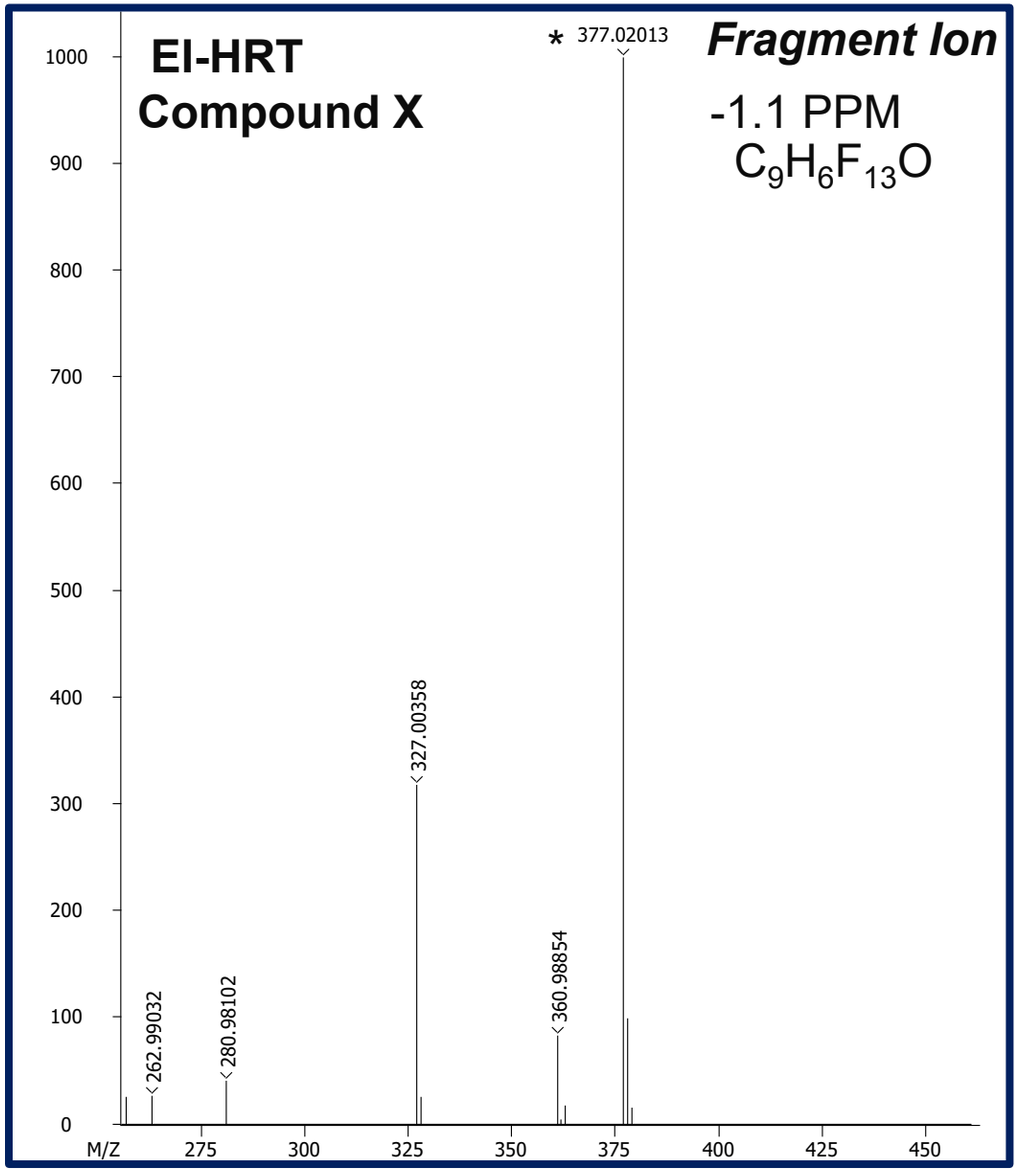
Compound X, Complementary EI & CI-HRT Data

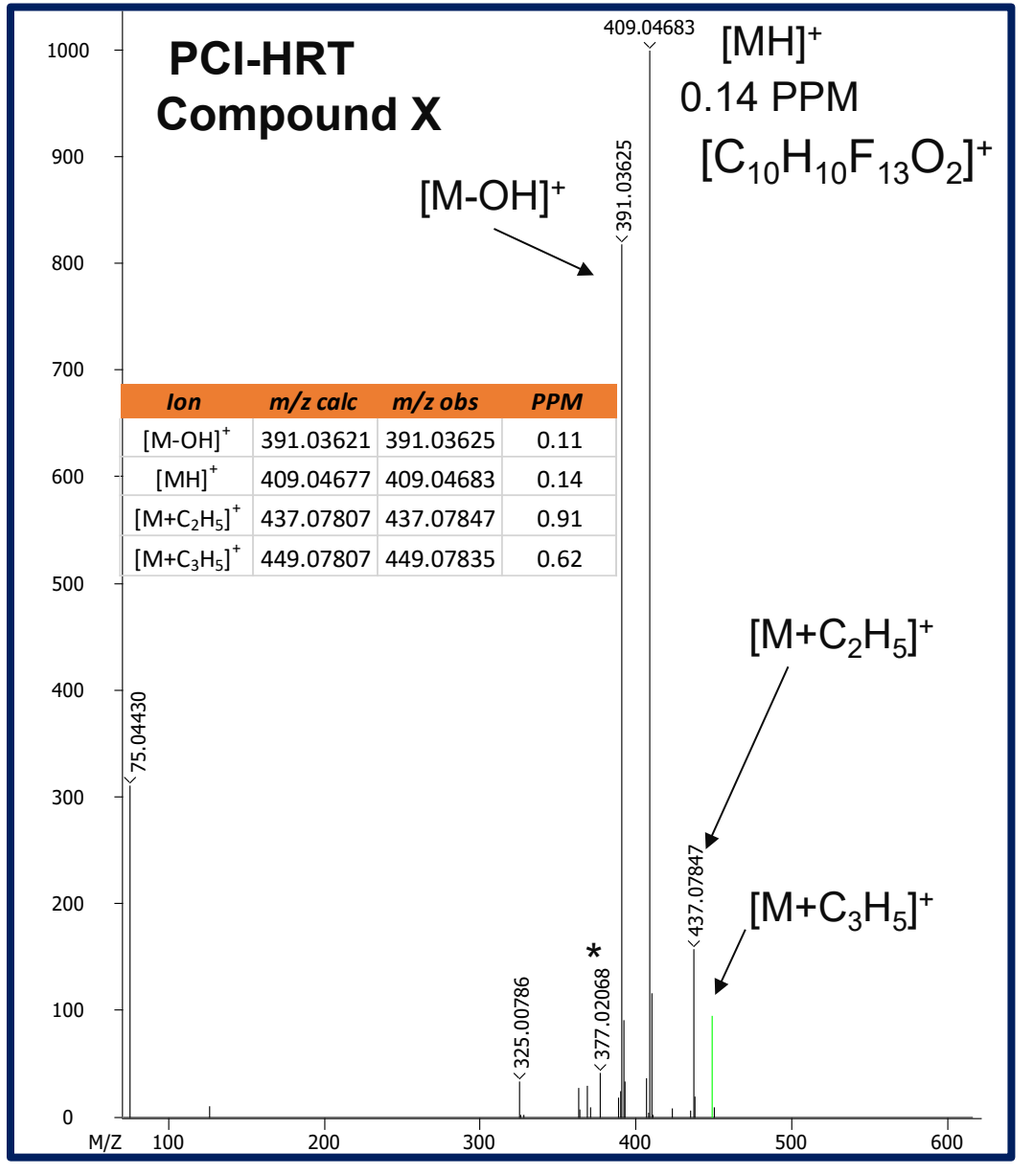




Reagent Gas = Methane

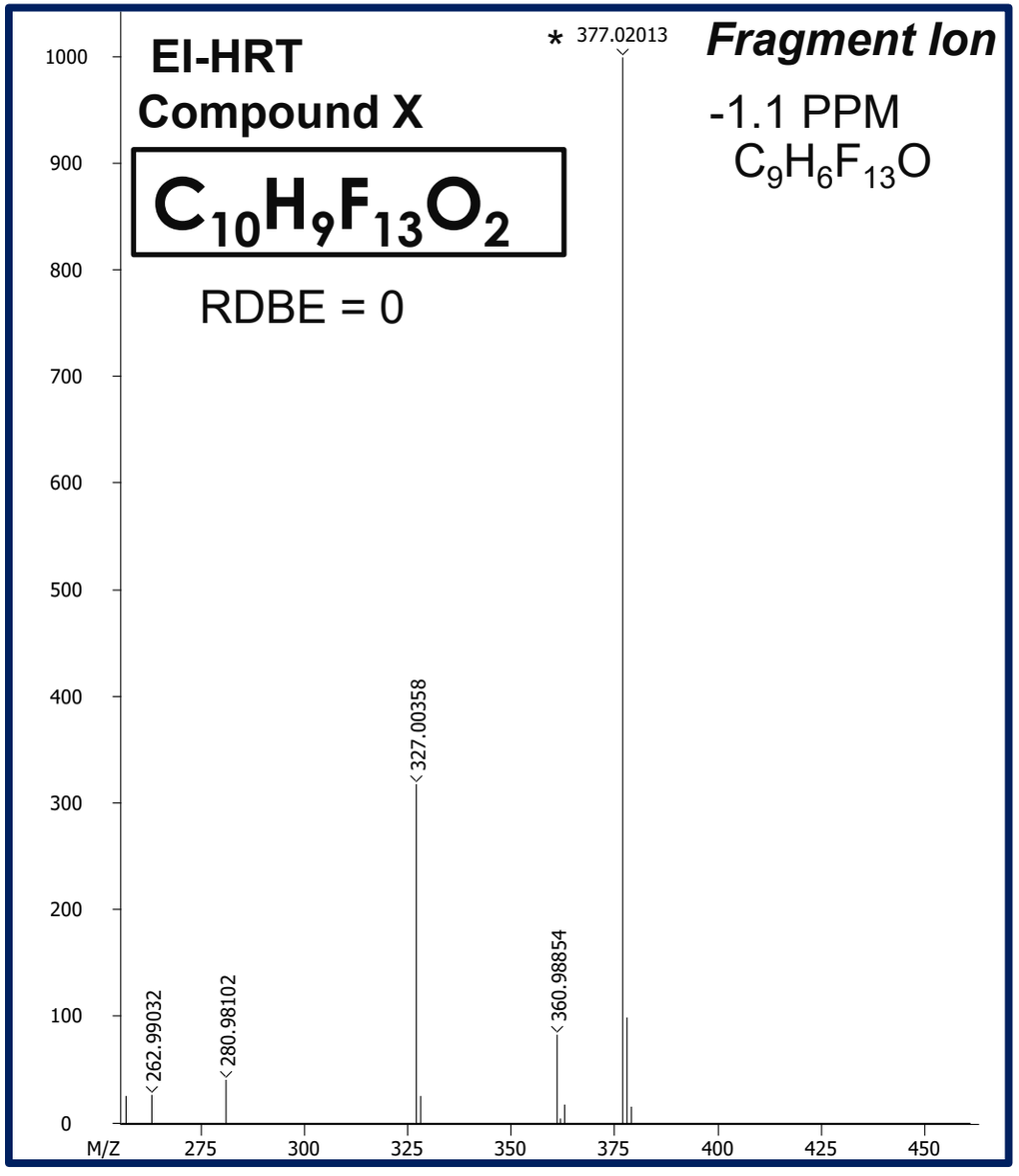
Compound X, Complementary EI & CI-HRT Data

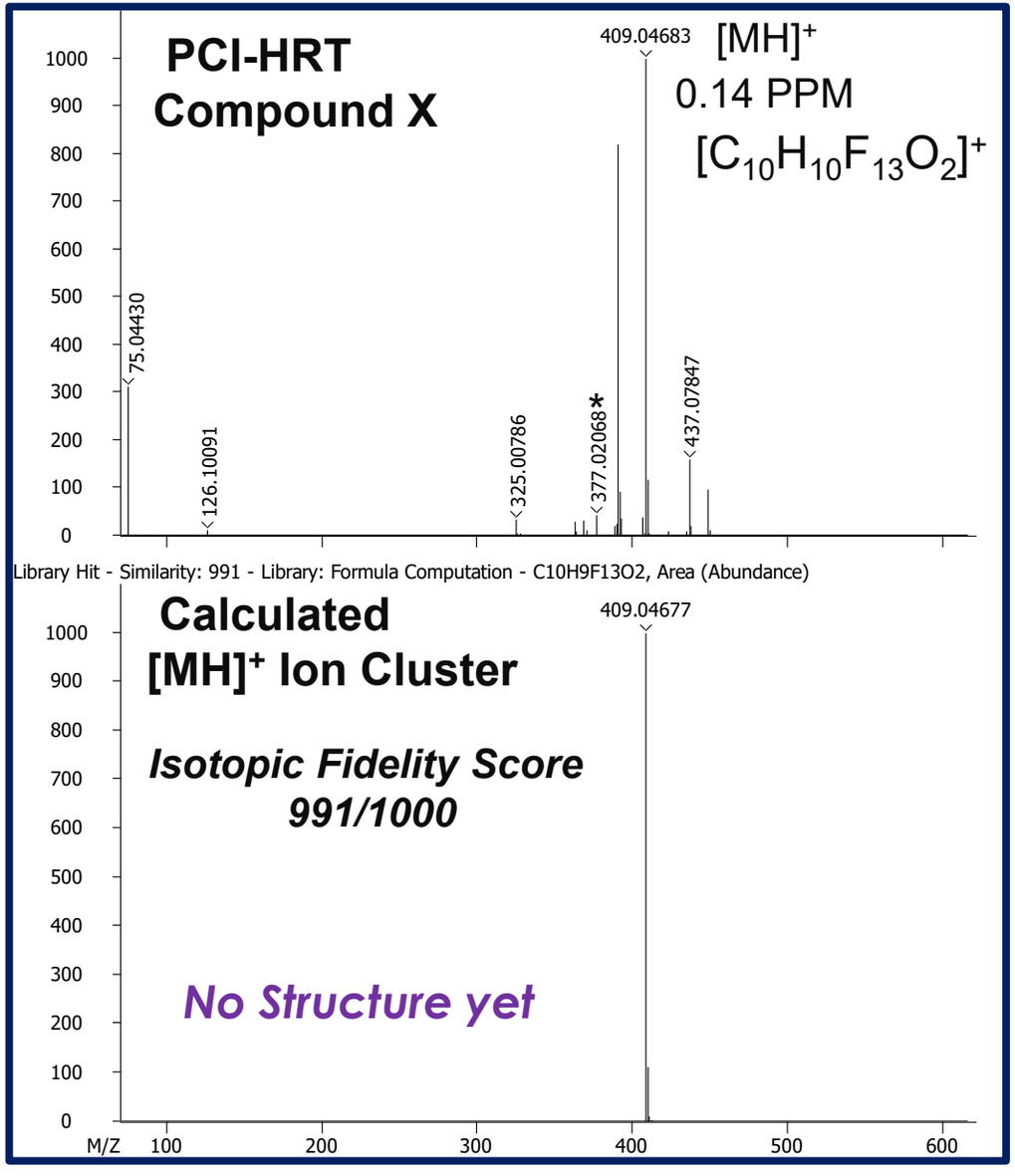




Ion	m/z calc	m/z obs	PPM
$[M-OH]^+$	391.03621	391.03625	0.11
$[MH]^+$	409.04677	409.04683	0.14
$[M+C_2H_5]^+$	437.07807	437.07847	0.91
$[M+C_3H_5]^+$	449.07807	449.07835	0.62

Compound X, EI & CI-HRT Data





$C_{10}H_9F_{13}O_2$ (HRAM) → Search External Databases

ChromaTOF

Hit	Species	Expected Ion m	Observed Ior	Mass Accuracy	RDBE
>1	H Gain	409.04677	409.04683	0.14	0.0
2	C2H5 Gain	437.07807	437.07847	0.91	0.0
3*	C3H5 Gain	449.07807	449.07835	0.62	0.0
4			325.00786	-0.74	1.5
5			377.02068	0.32	0.5
6			391.03625	0.11	0.5

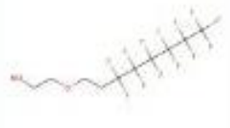
- Select Hit
- Clear Selected Hit
- Delete Hits
- ChemSpider Formula Search
- EPA CompTox Chemicals Formula Search
- View Target
- Copy Selection
- Sort
- Fit Columns

ChemSpider
Search and share chemistry

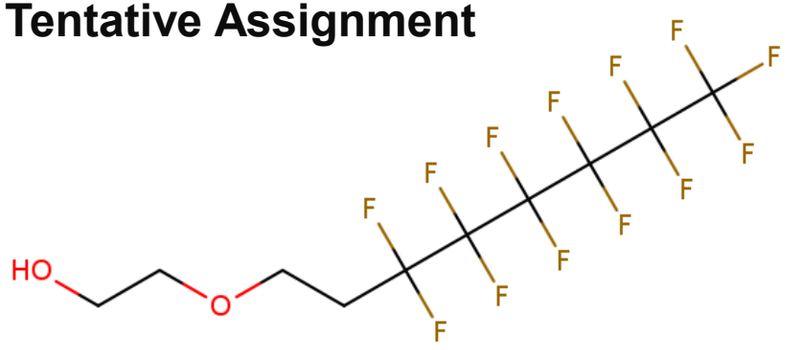
EPA

Software built-in connection to EPA CompTox and Chemspider databases for structure elucidation

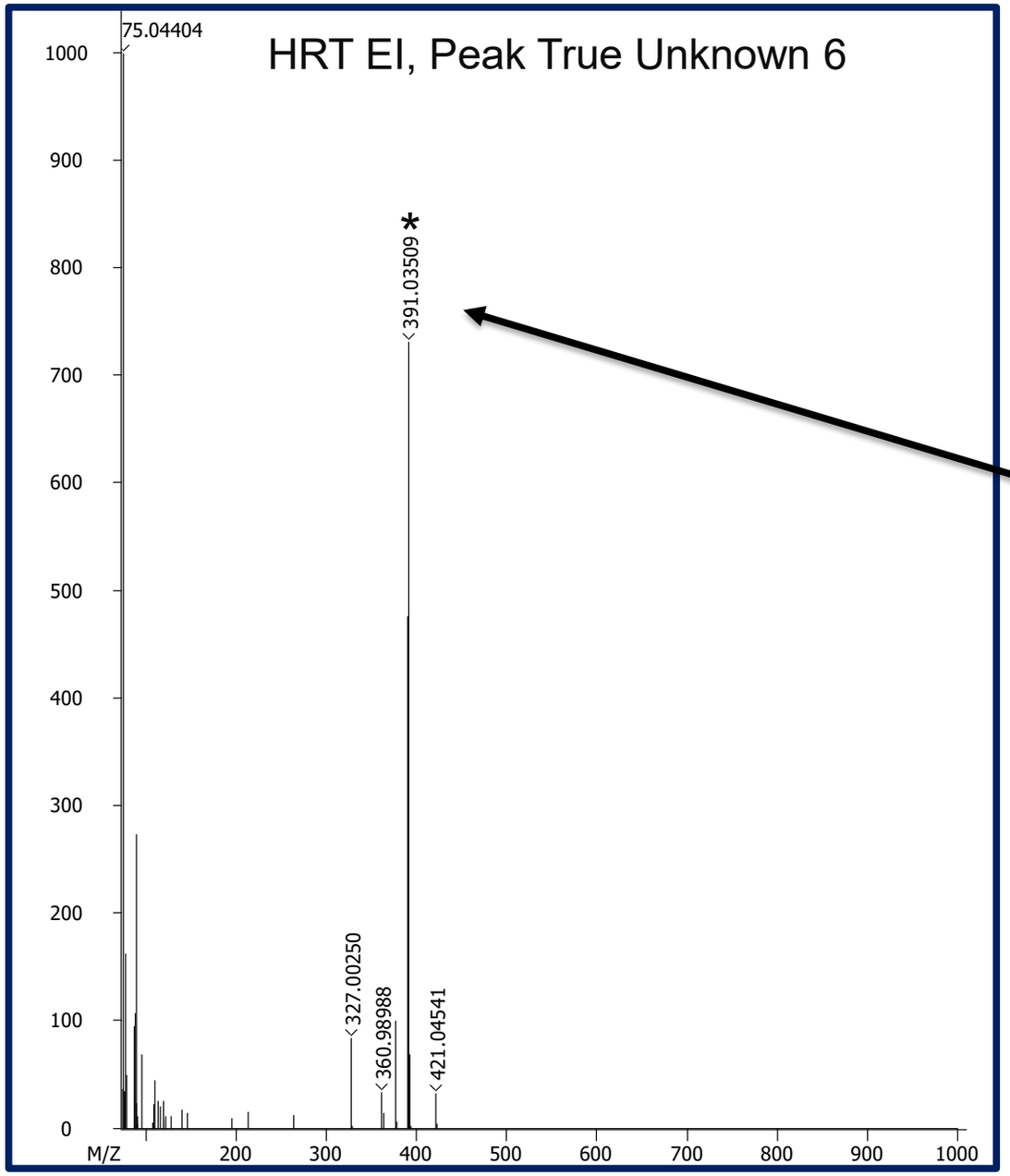
$C_{10}H_9F_{13}O_2$ (HRAM) → EPA CompTox

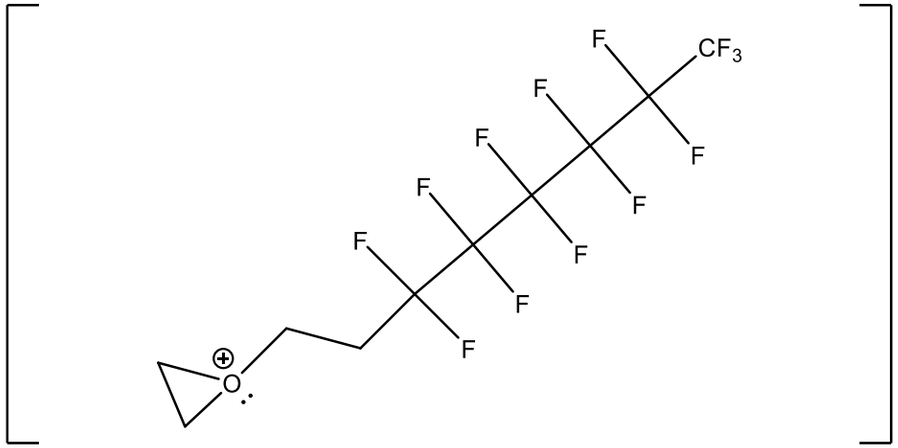
☐		DTXSID10437924	1,2-Decanediol, 5,5,6,6,7,7,8,8,9,9,10,1...	147274-18-8	5
☐		DTXSID20527446	1-Ethoxy-3,3,4,4,5,5,6,6,7,7,8,8,8-tride...	89807-89-6	5
☐		DTXSID30379852	1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8...	142502-76-9	5
☐		DTXSID60560190	2-((Perfluorohexyl)ethoxy)ethanol	55427-50-4	2

Tentative Assignment



HRT Anti-Fog, EI Unknown 6



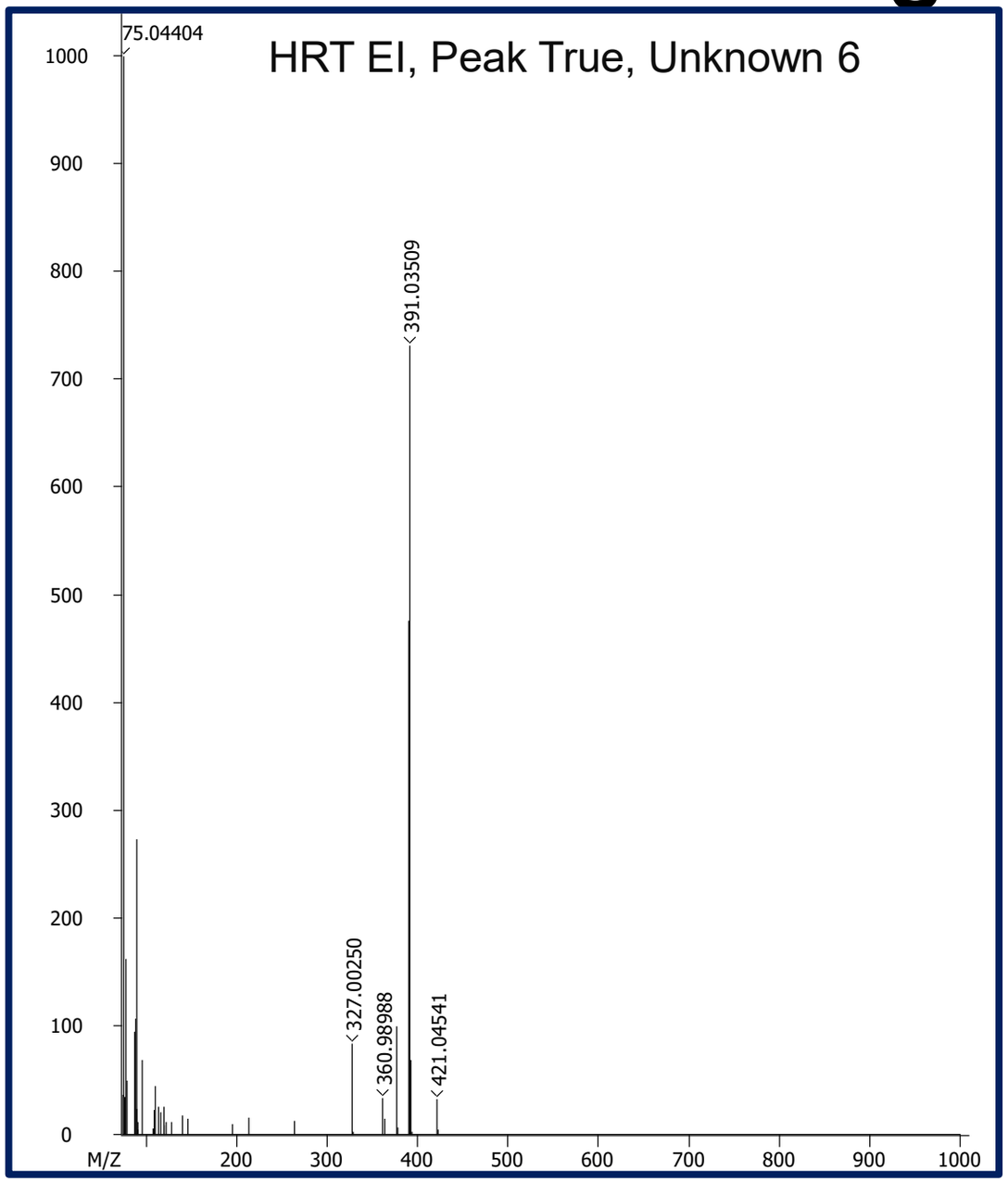


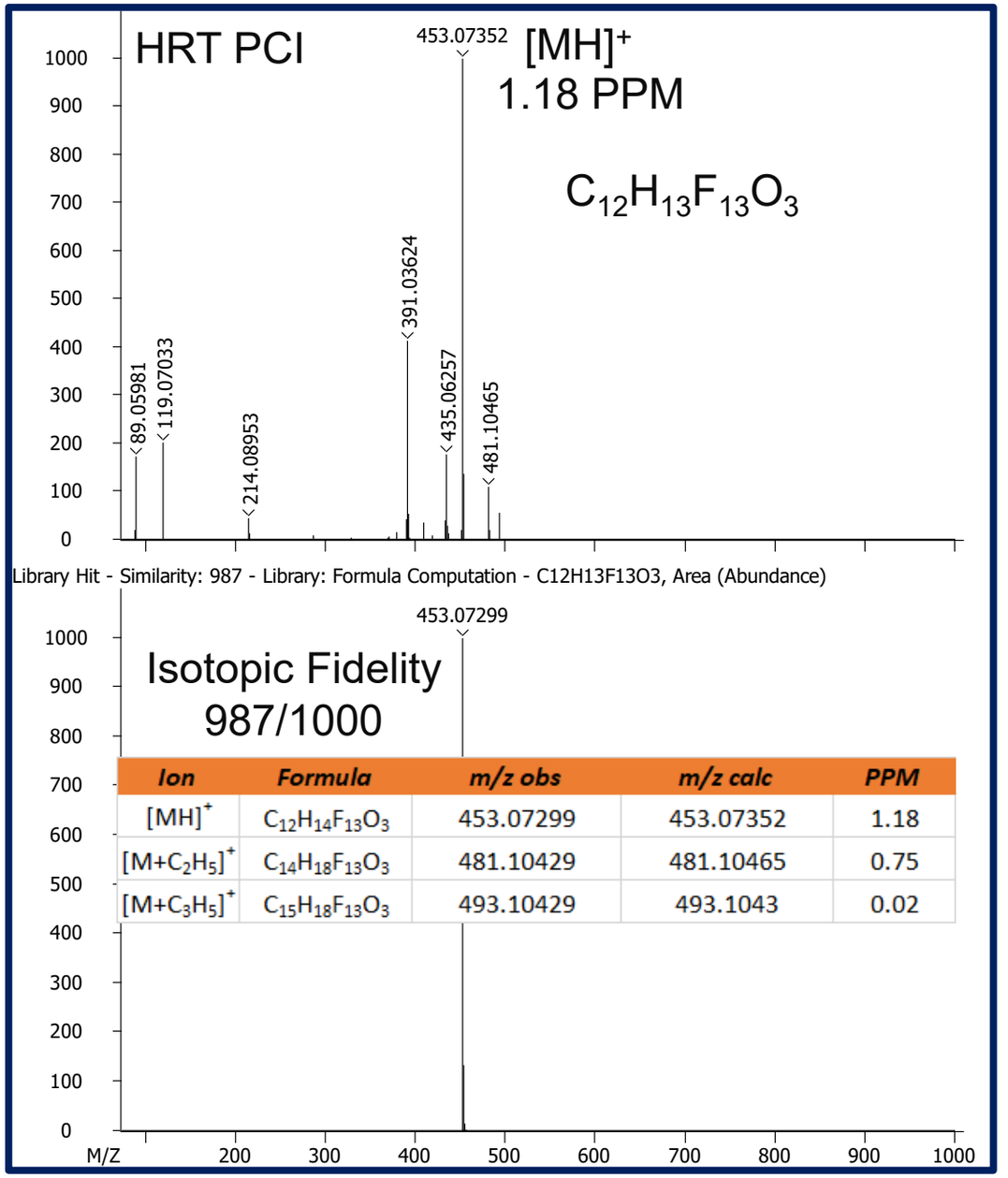
Fragment Ion*

$C_{10}H_8F_{13}O$

-1.9 ppm

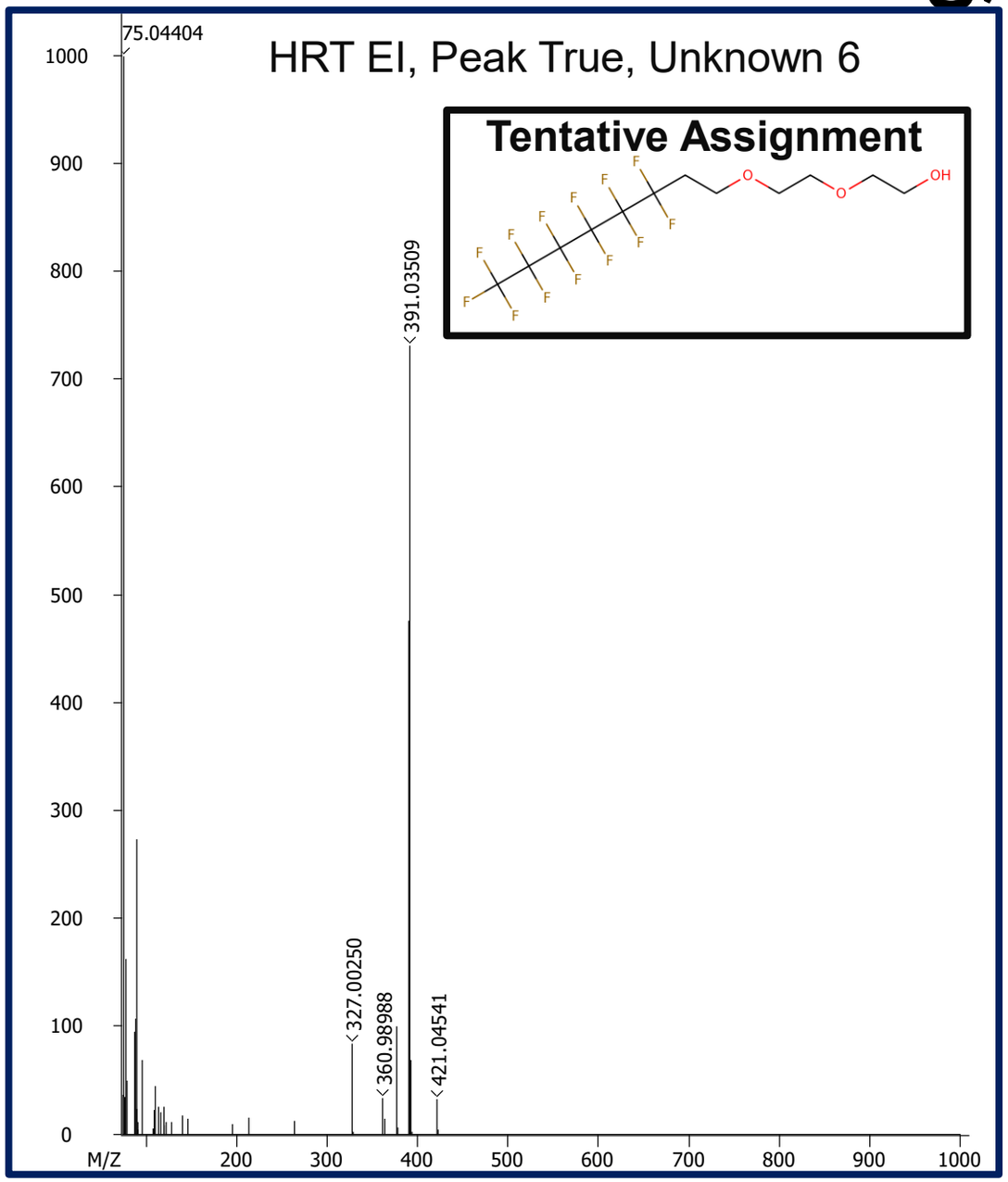
HRT Anti-Fog 3, EI & PCI Unknown 6

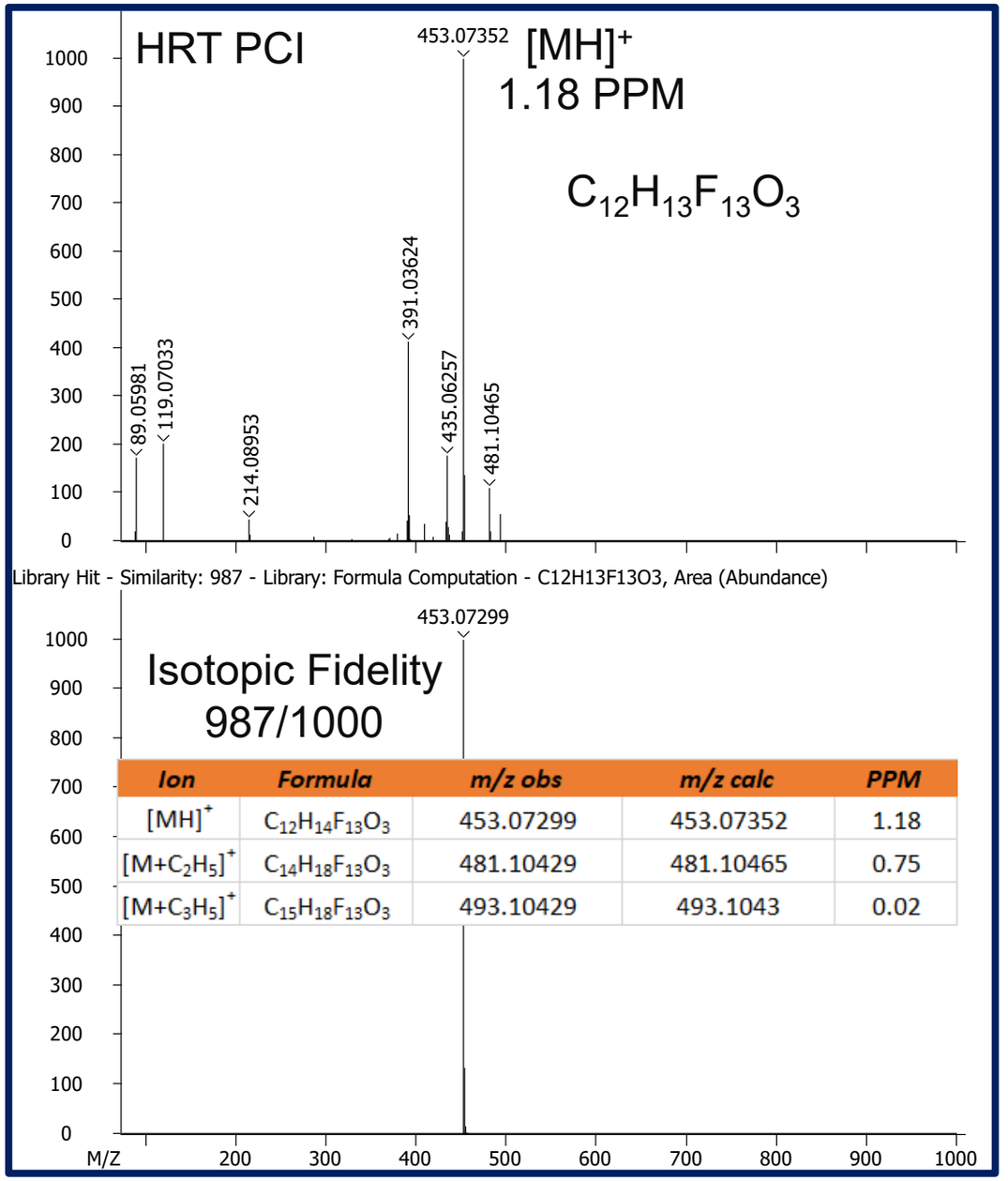




Ion	Formula	m/z obs	m/z calc	PPM
$[MH]^+$	$C_{12}H_{14}F_{13}O_3$	453.07299	453.07352	1.18
$[M+C_2H_5]^+$	$C_{14}H_{18}F_{13}O_3$	481.10429	481.10465	0.75
$[M+C_3H_5]^+$	$C_{15}H_{18}F_{13}O_3$	493.10429	493.1043	0.02

HRT Anti-Fog, EI & PCI Unknown 6





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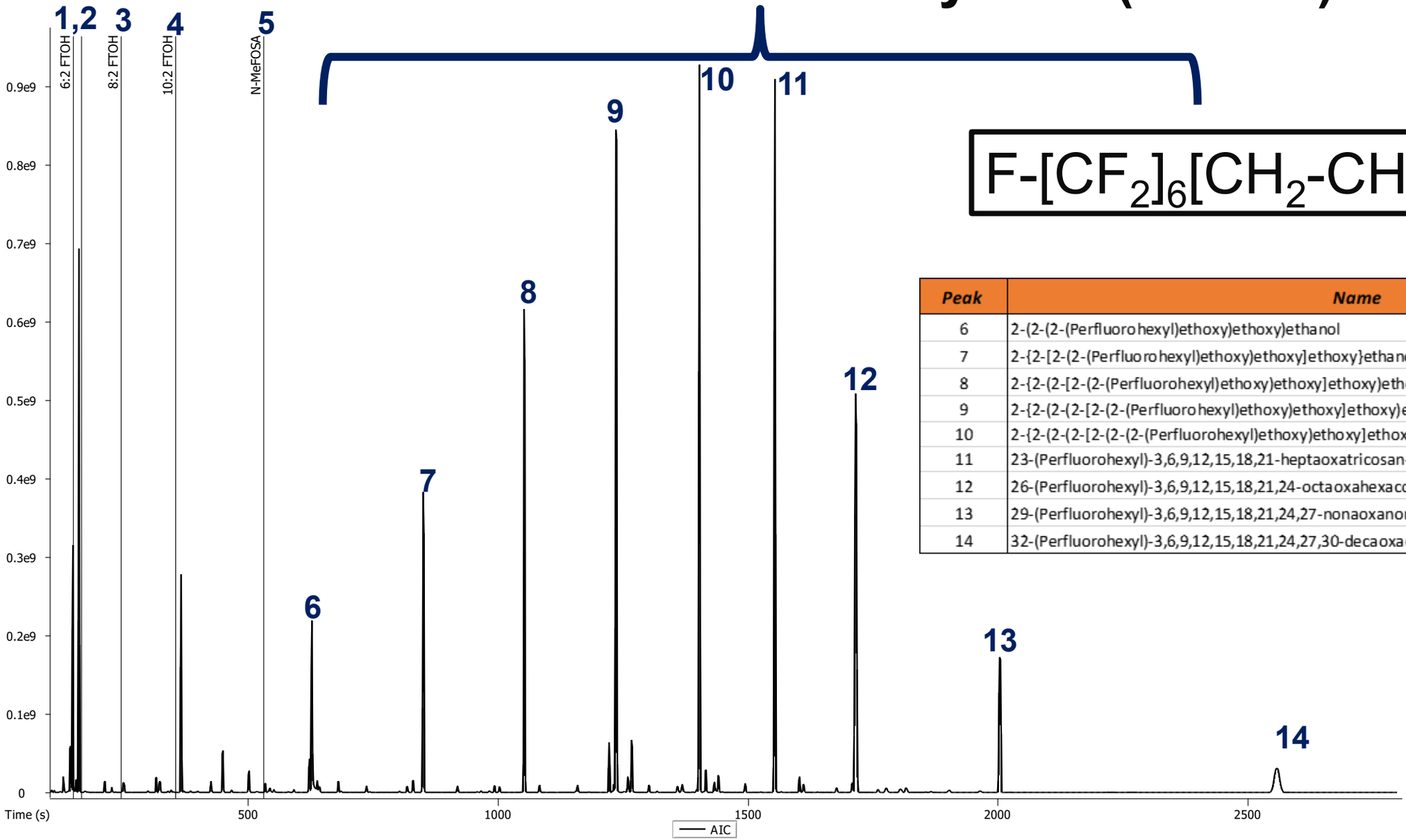
Anti-Fog

Fluorotelomer Ethoxylates (FTEOs)

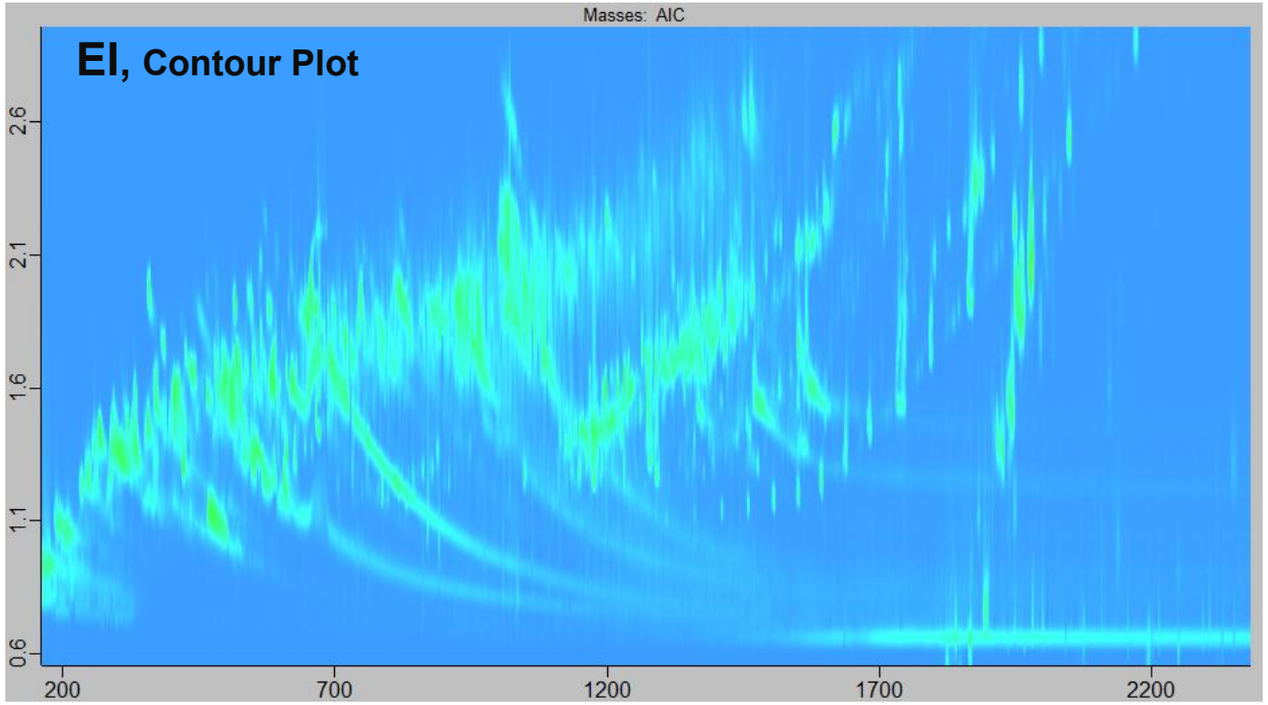


$$F\text{-}[CF_2]_6[CH_2\text{-}CH_2O]_n\text{-}H$$

Peak	Name
6	2-(2-(2-(Perfluorohexyl)ethoxy)ethoxy)ethanol
7	2-{2-[2-(2-(Perfluorohexyl)ethoxy)ethoxy]ethoxy}ethanol
8	2-{2-(2-[2-(2-(Perfluorohexyl)ethoxy)ethoxy]ethoxy)ethoxy}ethanol
9	2-{2-(2-(2-[2-(2-(Perfluorohexyl)ethoxy)ethoxy]ethoxy)ethoxy)ethoxy}ethanol
10	2-{2-(2-(2-[2-(2-(2-(Perfluorohexyl)ethoxy)ethoxy]ethoxy)ethoxy)ethoxy)ethoxy}ethanol
11	23-(Perfluorohexyl)-3,6,9,12,15,18,21-heptaoxatricosan-1-ol
12	26-(Perfluorohexyl)-3,6,9,12,15,18,21,24-octaoxahexacosan-1-ol
13	29-(Perfluorohexyl)-3,6,9,12,15,18,21,24,27-nonaoxanonacosan-1-ol
14	32-(Perfluorohexyl)-3,6,9,12,15,18,21,24,27,30-decaoxadotriacontan-1-ol

Example B: Chewing Gum

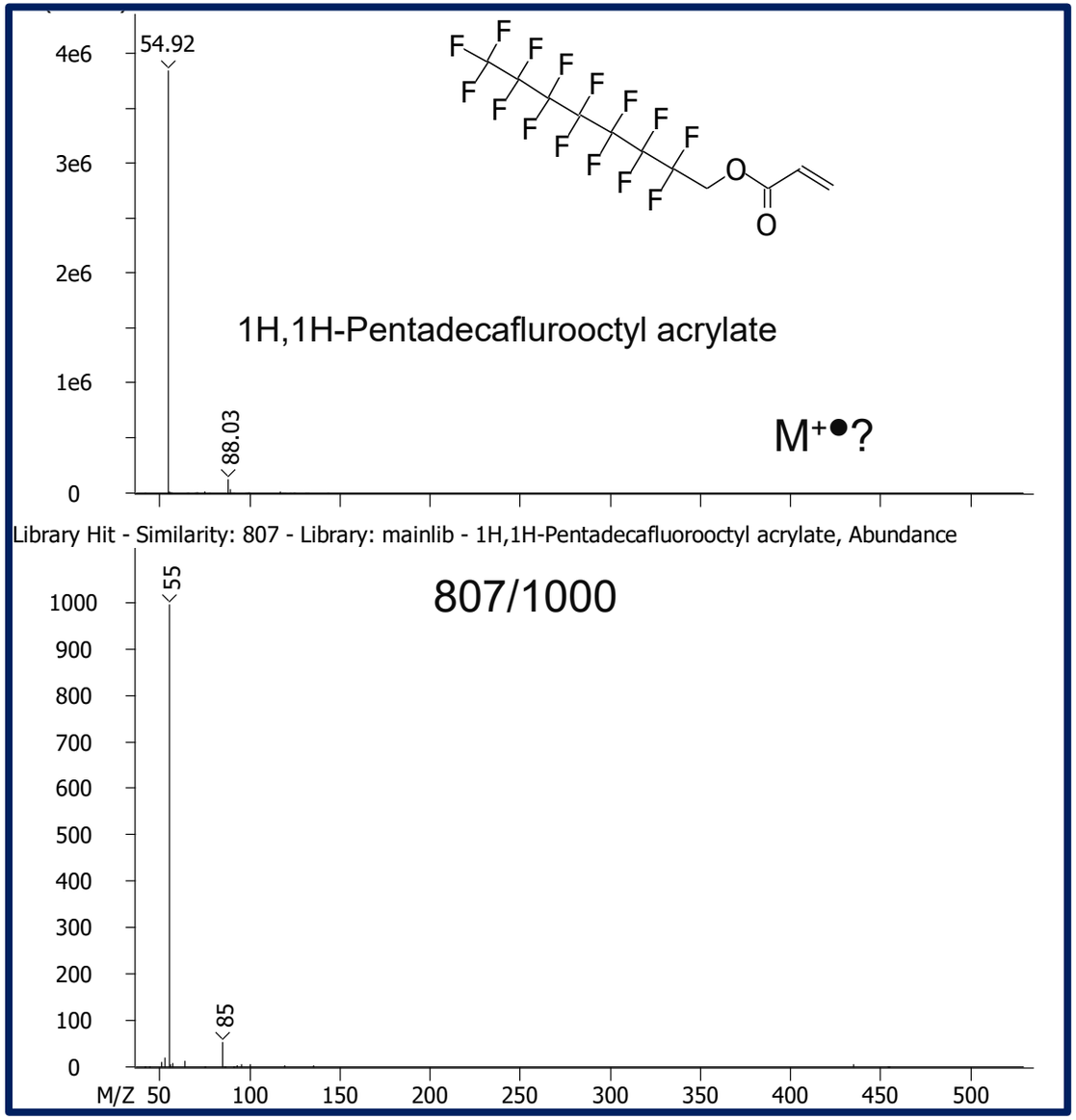
Screening for PFAS in Chewing Gum



Challenges

- High degree of complexity of gum
  - Large numbers of sample constituents
  - Varying physiochemical properties
  - Wide concentration range

Screening for PFAS in Chewing Gum



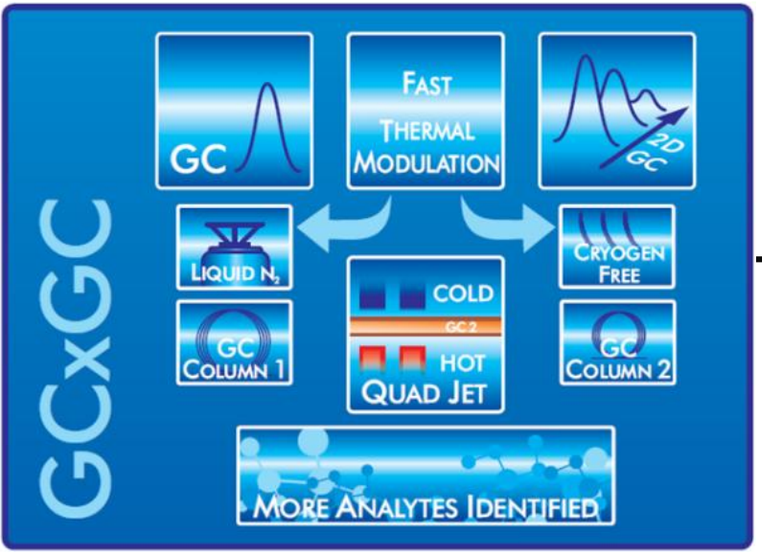
Challenges

- High degree of complexity of gum
  - Large numbers of sample constituents
  - Varying physiochemical properties
  - Wide concentration range
- Some classes of PFAS produce non-descript spectra
- PFAS are often trace constituents in complex samples

GC×GC-HRTOFMS

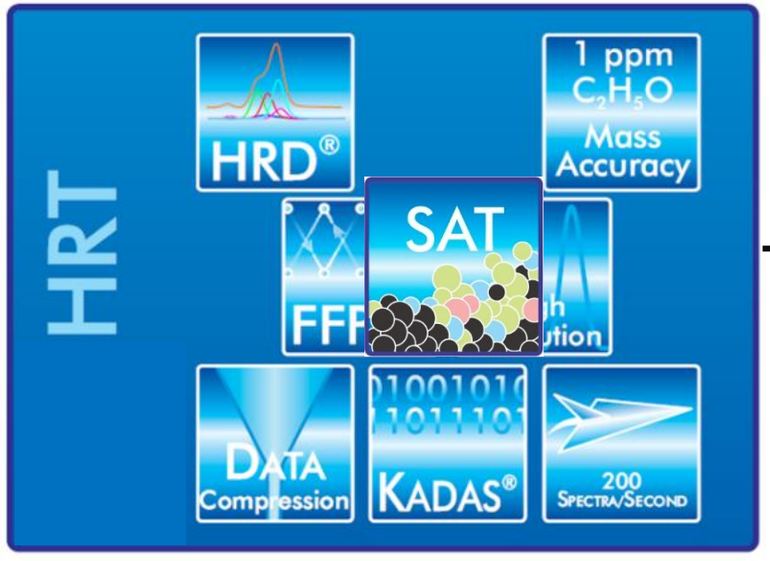
- Increased spectral and chromatographic resolution for difficult samples
- Fewer interferences → Cleaner spectra→ Improved database comparisons
- Formular determinations→Confident annotations
- Additional Software Tools

Enhanced Chromatography



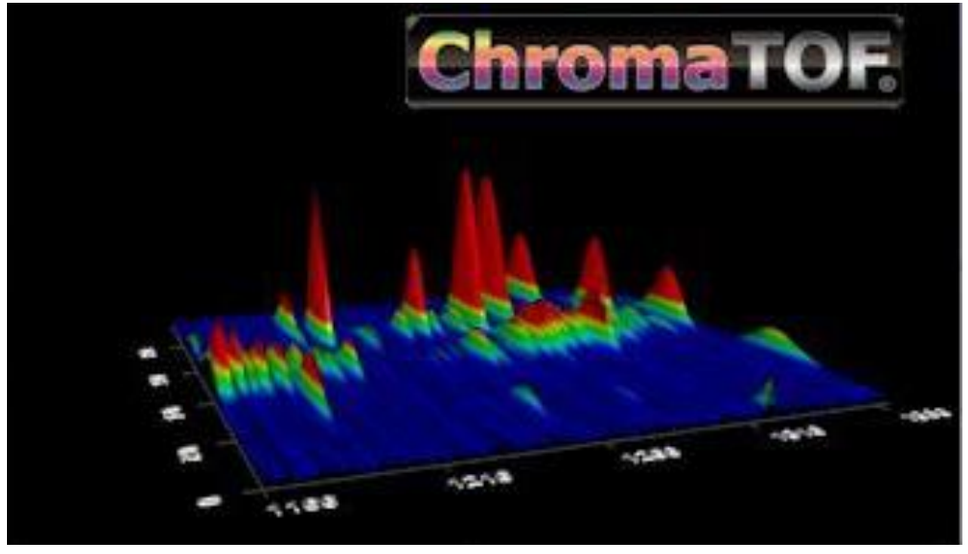
+

High-Resolution Mass Spectrometry

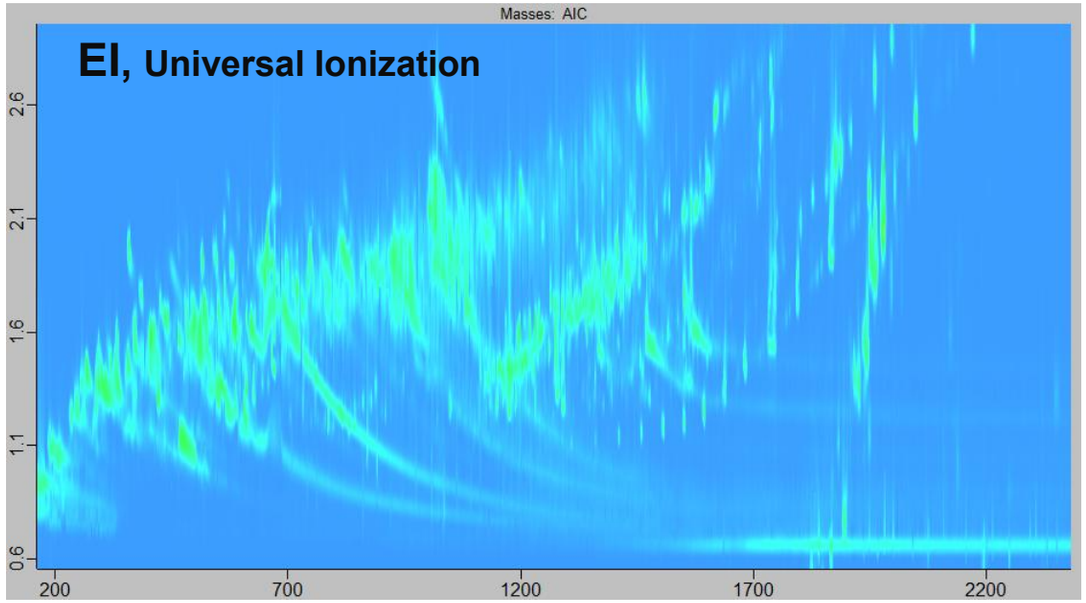


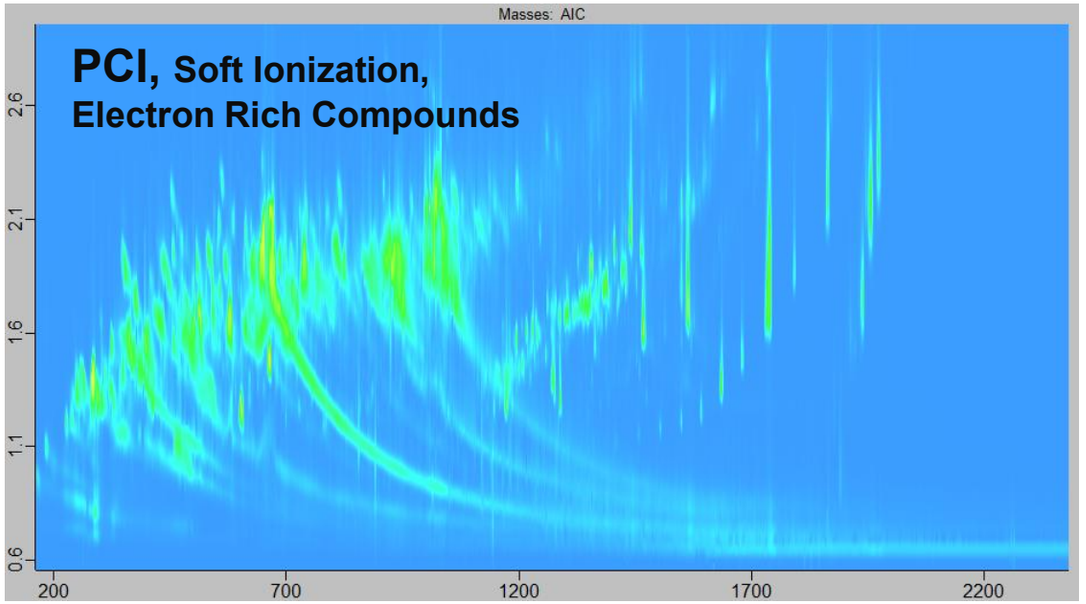
+

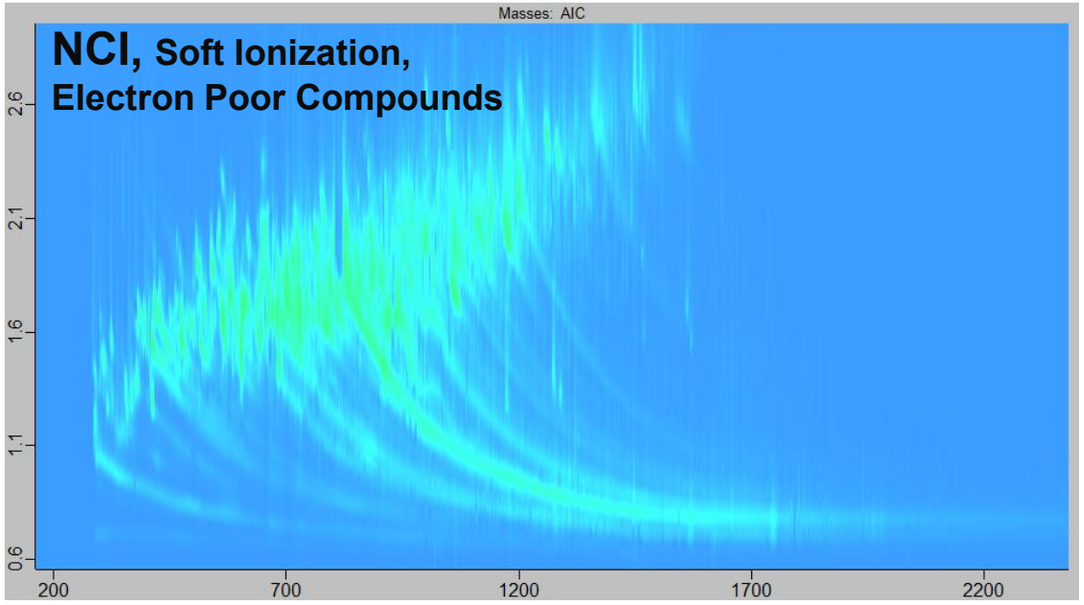
Powerful Software



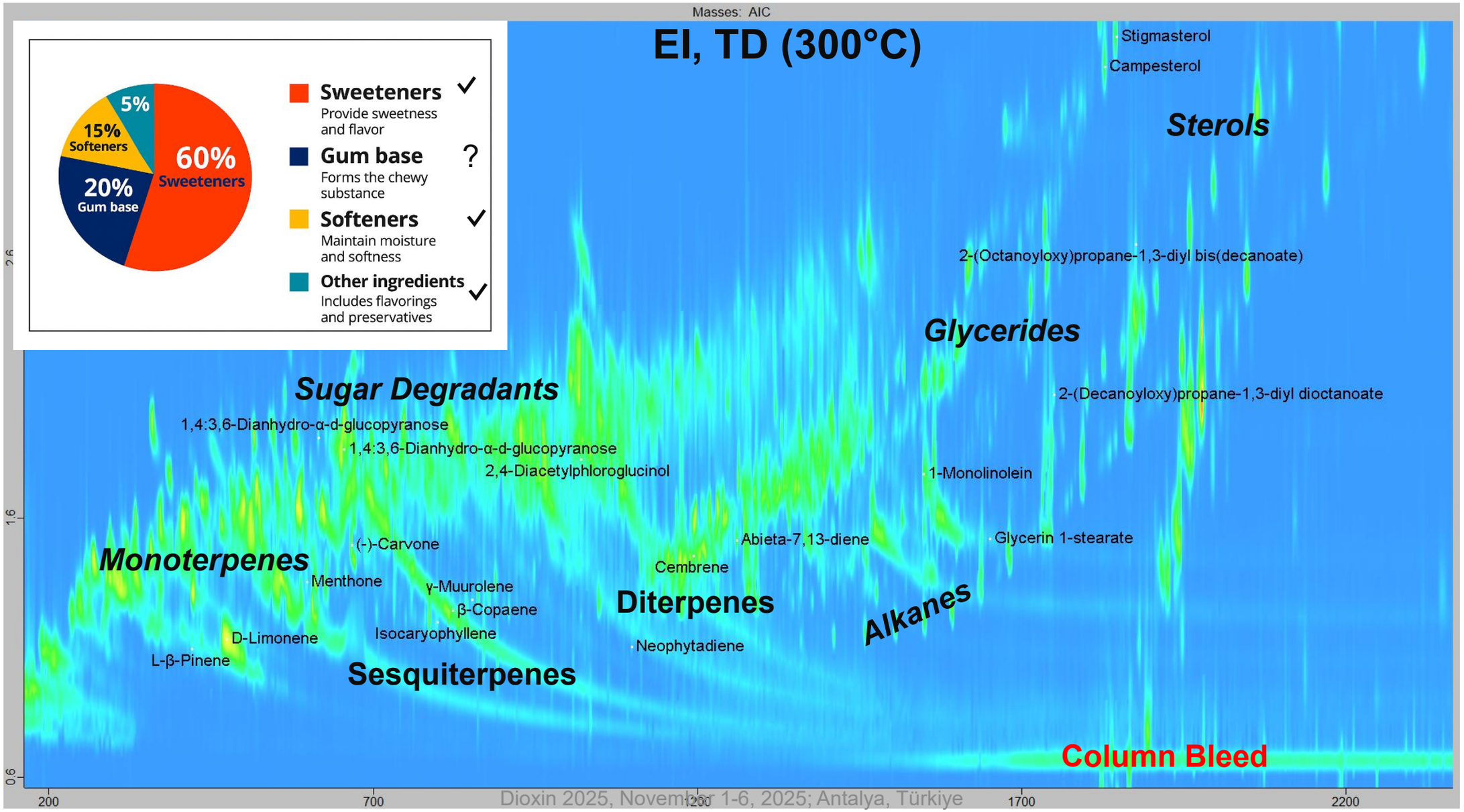
Chewing Gum Plots, Thermal Desorption (TD)



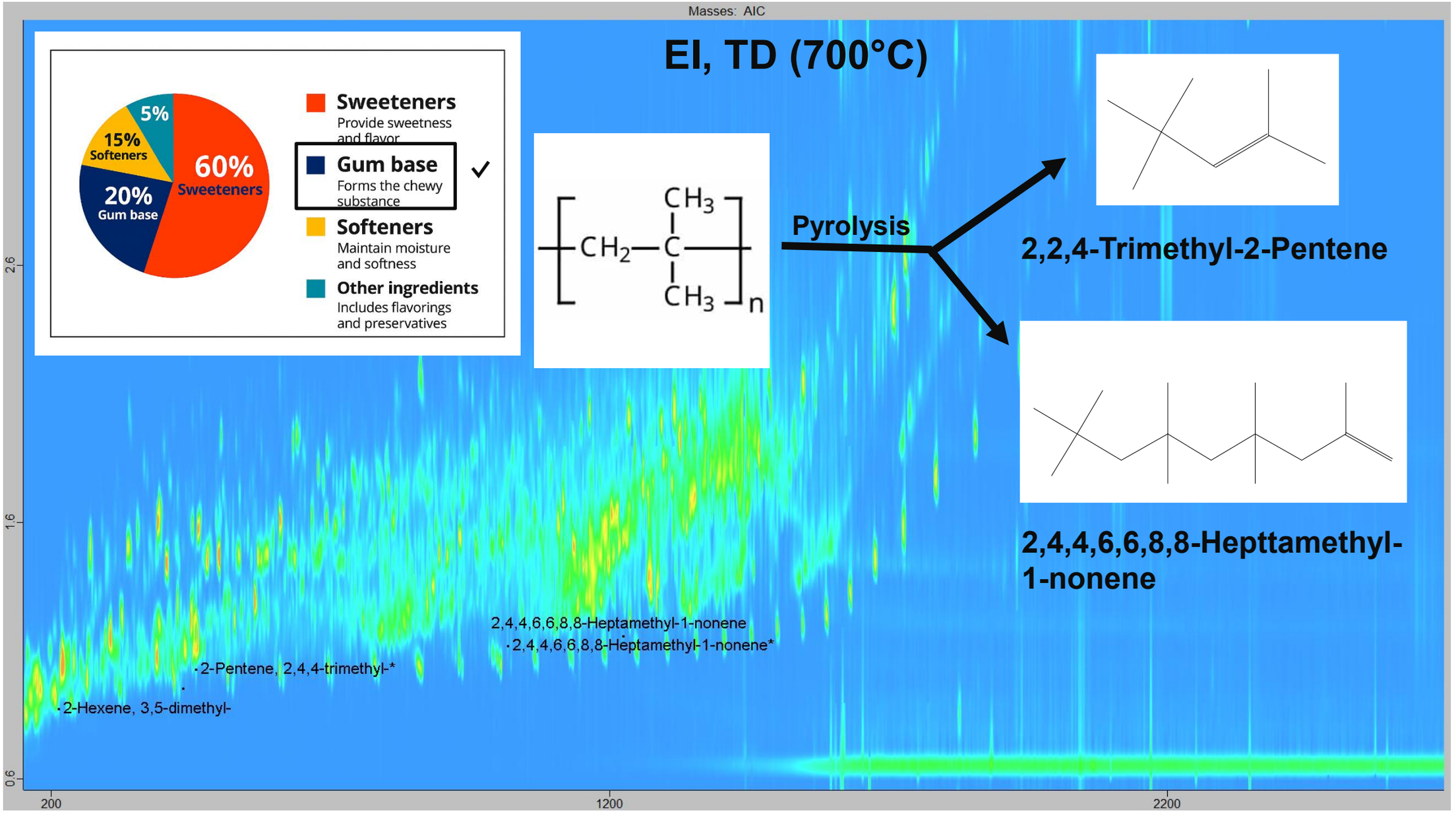




Chewing Gum, Thermal Desorption (TD/EI-HRT)



Chewing Gum, Pyrolysis (Pyr/EI-HRT)

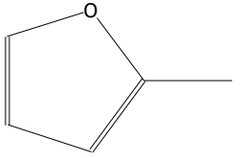


Representative Compounds (TD)

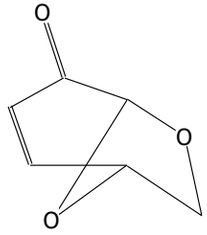
Name	R.T. (s)	Formula	Similarity	PPM
2-Propenal	150, 2.400	C_3H_4O	845	0.6
Acetaldehyde, hydroxy-	159, 1.064	$C_2H_4O_2$	873	-0.66
Acetic acid	201, 0.915	$C_2H_4O_2$	807	-1.02
Pyrazine	225, 1.220	$C_4H_4N_2$	862	-1.11
Furan, 2-methyl-	237, 1.150	C_5H_6O	874	-1.39
Acetic acid, methyl ester	249, 1.265	$C_3H_6O_2$	878	-1.44
3(2H)-furanone	270, 1.435	$C_4H_4O_2$	928	0.88
2,5-Furandione	309, 1.715	$C_4H_2O_3$	929	-1.54
Furfuryl formate	351, 1.350	$C_6H_6O_3$	823	-1.34
β-Ocimene	378, 1.026	$C_{10}H_{16}$	858	0.14
2(5H)-Furanone, 5-methyl-	381, 1.790	$C_5H_6O_2$	919	-0.88
Pentanal, 4-oxo-	414, 1.615	$C_5H_8O_2$	844	0.18
α-Methyl-γ-crotonolactone	417, 1.850	$C_5H_6O_2$	894	-0.35
L-β-Pinene	420, 1.095	$C_{10}H_{16}$	833	-0.79
Propanoic acid, 3-hydroxy-	426, 1.314	$C_3H_6O_3$	752	-0.07
4H-Pyran-4-one	426, 1.860	$C_5H_4O_2$	827	-0.71
1H-Pyrrole-2,5-dione	447, 1.680	$C_4H_3NO_2$	742	-1.3
2-Hydroxy-gamma-butyrolactone	456, 1.854	$C_4H_6O_3$	866	-1.55
Methyl pyruvate	462, 0.890	$C_4H_6O_3$	856	-0.56
p-Cymene	465, 1.185	$C_{10}H_{14}$	810	-1.39
2-Propanone, 1-hydroxy-	471, 0.885	$C_3H_6O_2$	913	-1.14
2-[(1S)-1-methylpropyl]furan	483, 1.374	$C_8H_{12}O$	761	-1.4
o-Cymene	489, 1.140	$C_{10}H_{14}$	735	-1.56
Propanal, 2-oxo-	492, 0.727	$C_3H_4O_2$	820	-1.25
2(3H)-Furanone, dihydro-3-methyl-	495, 2.010	$C_5H_8O_2$	923	-0.91
trans-4-Thujanol	510, 1.185	$C_{10}H_{18}O$	904	-1.45
Furaneol	510, 1.570	$C_6H_8O_3$	944	-0.56
Methanamine, N,N-dimethyl-	519, 0.701	C_3H_9N	935	0
Benzofuran, 2-methyl-	546, 1.455	C_9H_8O	852	-1.63
Levoglucosenone	546, 1.930	$C_6H_6O_3$	833	N/A
Menthone	588, 1.325	$C_{10}H_{18}O$	914	-1.39
Pyranone	594, 1.565	$C_6H_8O_4$	841	-1.04
5-Hydroxymaltol	621, 1.655	$C_6H_6O_4$	843	0.27
8-p-Menthen-2-ol	627, 1.320	$C_{10}H_{18}O$	762	-0.24

Name	R.T. (s)	Formula	Similarity	PPM
p-Menth-8-en-2-one	627, 1.410	$C_{10}H_{16}O$	852	-0.95
cis-Carveol	645, 1.380	$C_{10}H_{16}O$	887	-1.3
1,4:3,6-Dianhydro-α-d-glucopyranose	654, 1.864	$C_6H_8O_4$	731	-0.41
(-)-Carvone	672, 1.580	$C_{10}H_{14}O$	832	-0.21
Piperitone	678, 1.475	$C_{10}H_{16}O$	747	-1.63
5-Acetoxymethyl-2-furaldehyde	717, 1.805	$C_8H_8O_4$	898	-0.68
2-Vinylguaicol	723, 1.612	$C_9H_{10}O_2$	850	-0.73
5-Acetyl-2-furanmethanol	723, 1.779	$C_7H_8O_3$	817	-1.57
5-Hydroxymethyl-2-furaldehyde	726, 1.533	$C_6H_6O_3$	917	-1.3
Dihydrocarveol acetate	732, 1.290	$C_{12}H_{20}O_2$	701	0.47
Carhydrine	732, 1.295	$C_{12}H_{20}O_2$	878	0.47
5-Hydroxymethylfurfural	738, 1.481	$C_6H_6O_3$	916	-1.31
2-t-Butyl-5-methylphenol	762, 1.425	$C_{11}H_{16}O$	926	-0.89
Longicyclene	780, 1.222	$C_{15}H_{24}$	923	-0.74
Tetradecane	789, 1.028	$C_{14}H_{30}$	813	0.13
Jasmone	792, 1.560	$C_{11}H_{16}O$	883	-1.02
Isocaryophyllene	798, 1.200	$C_{15}H_{24}$	803	-0.6
Di(2-furyl)ketone	804, 1.925	$C_9H_6O_3$	926	-0.4
β-Copaene	822, 1.245	$C_{15}H_{24}$	876	-1.57
(E)-β-Farnesene	831, 1.180	$C_{15}H_{24}$	901	N/A
(-)-Isogermacrene D	834, 1.265	$C_{15}H_{24}$	864	0.19
γ-Muurolene	852, 1.283	$C_{15}H_{24}$	876	-1.09
8-isopropyl-1-methyl-tetralin	852, 1.415	$C_{14}H_{20}$	744	-1.46
(-)-Germacrene D	861, 1.295	$C_{15}H_{24}$	939	-0.12
Eremophilene	873, 1.295	$C_{15}H_{24}$	820	-1.56
Valerena-4,7(11)-diene	888, 1.364	$C_{15}H_{24}$	878	-0.48
Lauric acid	909, 1.247	$C_{12}H_{24}O_2$	880	-1.36
Eudalene	936, 1.555	$C_{14}H_{16}$	757	-1.05
Epiglobulol	948, 1.400	$C_{15}H_{26}O$	852	-1.71
Furfural	1011, 0.732	$C_5H_4O_2$	875	-1.27
Pentadecanal-	1020, 1.225	$C_{15}H_{30}O$	910	N/A
2,4-Diacetylphloroglucinol	1020, 1.825	$C_{10}H_{10}O_5$	766	-1.01
Myristic Acid	1047, 1.265	$C_{14}H_{28}O_2$	927	-1.33
2,6-Diisopropylnaphthalene	1047, 1.630	$C_{16}H_{20}$	735	0.17

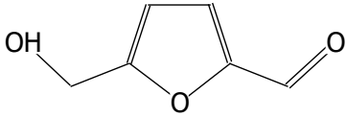
Sweeteners
Provide sweetness and flavor



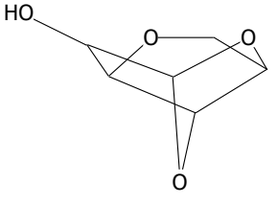
Furan, 2-methyl-



Levoglucosenone



5-Hydroxymethyl-2-furaldehyde



1,4:3,6-Dianhydro-α-d-glucopyranose

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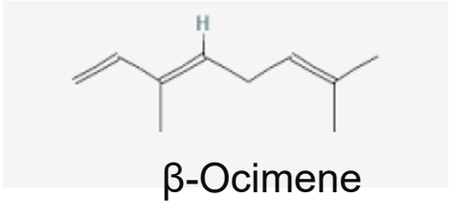
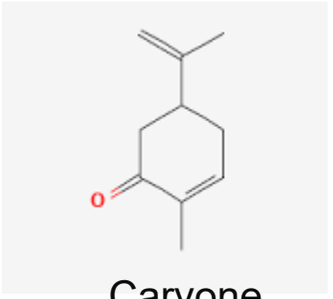
Carhydrine	732, 1.295	$C_{12}H_{20}O_2$	878	0.47
5-Hydroxymethylfurfural	738, 1.481	$C_6H_6O_3$	916	-1.31
2-t-Butyl-5-methylphenol	762, 1.425	$C_{11}H_{16}O$	926	-0.89
Longicyclene	780, 1.222	$C_{15}H_{24}$	923	-0.74
Tetradecane	789, 1.028	$C_{14}H_{30}$	813	0.13
Jasmone	792, 1.560	$C_{11}H_{16}O$	883	-1.02
Isocaryophyllene	798, 1.200	$C_{15}H_{24}$	803	-0.6
Di(2-furyl)ketone	804, 1.925	$C_9H_6O_3$	926	-0.4
β-Copaene	822, 1.245	$C_{15}H_{24}$	876	-1.57
(E)-β-Farnesene	831, 1.180	$C_{15}H_{24}$	901	N/A
(-)-Isogermacrene D	834, 1.265	$C_{15}H_{24}$	864	0.19
γ-Muurolene	852, 1.283	$C_{15}H_{24}$	876	-1.09
8-isopropyl-1-methyl-tetralin	852, 1.415	$C_{14}H_{20}$	744	-1.46
(-)-Germacrene D	861, 1.295	$C_{15}H_{24}$	939	-0.12
Eremophilene	873, 1.295	$C_{15}H_{24}$	820	-1.56
Valerena-4,7(11)-diene	888, 1.364	$C_{15}H_{24}$	878	-0.48
Lauric acid	909, 1.247	$C_{12}H_{24}O_2$	880	-1.36
Eudalene	936, 1.555	$C_{14}H_{16}$	757	-1.05
Epiglobulol	948, 1.400	$C_{15}H_{26}O$	852	-1.71
Furfural	1011, 0.732	$C_5H_4O_2$	875	-1.27
Pentadecanal-	1020, 1.225	$C_{15}H_{30}O$	910	N/A
2,4-Diacetylphloroglucinol	1020, 1.825	$C_{10}H_{10}O_5$	766	-1.01
Myristic Acid	1047, 1.265	$C_{14}H_{28}O_2$	927	-1.33
2,6-Diisopropylnaphthalene	1047, 1.630	$C_{16}H_{20}$	735	0.17

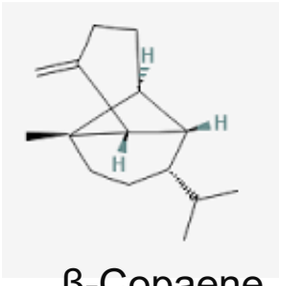
Misc. Ingredients Flavorings, preservatives, …



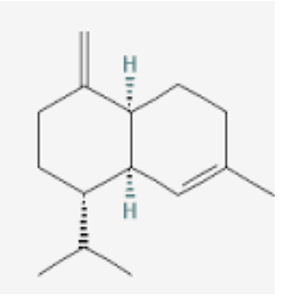
β-Ocimene



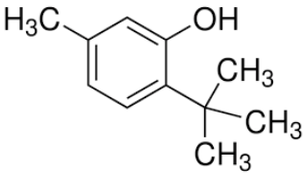
Carvone



β-Copaene



γ-Muurolene



2-*t*-Butyl-5-methylphenol

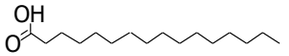
Representative Compounds (TD)

Name	R.T. (s)	Formula	Similarity	PPM
Palmitic acid	1176, 1.250	$C_{16}H_{32}O_2$	876	0.16
Proline anhydride	1188, 2.480	$C_{10}H_{14}N_2O_2$	881	-0.79
Cirsiumaldehyde	1200, 2.246	$C_{12}H_{10}O_5$	865	-0.24
18-Norabieta-8,11,13-triene	1218, 1.602	$C_{19}H_{28}$	814	0.82
Margaric acid	1230, 1.293	$C_{17}H_{34}O_2$	850	-0.1
Simonellite	1239, 1.703	$C_{19}H_{24}$	770	-1.71
Linoleic Acid methyl ester	1251, 1.320	$C_{19}H_{34}O_2$	799	-1.06
Abieta-7,13-diene	1260, 1.515	$C_{20}H_{32}$	875	-1.1
4,4'-Diisopropylbiphenyl	1263, 1.745	$C_{18}H_{22}$	828	0.2
Methyl stearate	1269, 1.236	$C_{19}H_{38}O_2$	809	-1.52
Linoleic Acid	1272, 1.475	$C_{18}H_{32}O_2$	878	0.73
Oleic Acid	1278, 1.325	$C_{18}H_{34}O_2$	896	0.21
Stearic acid	1290, 1.435	$C_{18}H_{36}O_2$	794	0.36
Butyl citrate	1299, 1.500	$C_{18}H_{32}O_7$	862	N/A
Sandaracopimaral	1308, 1.650	$C_{20}H_{30}O$	823	-1.17
Retene	1329, 1.940	$C_{18}H_{18}$	871	0.49
Isopimarol	1335, 1.720	$C_{20}H_{32}O$	845	-0.46
Glycidyl palmitate	1359, 1.402	$C_{19}H_{36}O_3$	880	N/A
Dehydroabietal	1359, 1.895	$C_{20}H_{28}O$	878	-0.95
1-Monomyristin	1365, 1.533	$C_{17}H_{34}O_4$	901	N/A
Henicosanal	1377, 1.279	$C_{21}H_{42}O$	904	N/A
Dehydroabietinol	1377, 1.925	$C_{20}H_{30}O$	800	0.19
Pimaric acid	1392, 1.845	$C_{20}H_{30}O_2$	810	1.04
Eicosanoic acid	1395, 1.325	$C_{20}H_{40}O_2$	849	-0.05
Isodextropimaric acid	1401, 1.817	$C_{20}H_{30}O_2$	883	-0.55
Octadecanamide	1410, 1.545	$C_{18}H_{37}NO$	822	-0.63
Neoabietal	1410, 1.935	$C_{20}H_{30}O$	724	0.02
Methyl isopimarate	1413, 1.715	$C_{21}H_{32}O_2$	768	-0.24
Methyl abietate	1416, 1.760	$C_{21}H_{32}O_2$	850	-1.09
Methyl podocarpate	1437, 2.230	$C_{18}H_{24}O_3$	799	0.89
Abietic acid	1467, 1.962	$C_{20}H_{30}O_2$	889	0.3
Behenic acid	1491, 1.365	$C_{22}H_{44}O_2$	777	-1.65
Neoabietic acid	1491, 2.065	$C_{20}H_{30}O_2$	882	-0.18
1-Monolinolein	1548, 1.771	$C_{21}H_{38}O_4$	880	-0.64

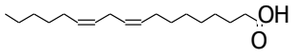
Name	R.T. (s)	Formula	Similarity	PPM
2-Monopalmitin	1560, 1.355	$C_{19}H_{38}O_4$	802	N/A
Lignoceric acid	1581, 1.423	$C_{24}H_{48}O_2$	735	1.19
Octacosanol	1590, 1.260	$C_{28}H_{58}O$	933	N/A
2-Monostearin	1623, 1.534	$C_{21}H_{42}O_4$	863	N/A
Glycerin 1-stearate	1650, 1.520	$C_{21}H_{42}O_4$	884	N/A
Glycerol tricaprylate	1650, 1.702	$C_{27}H_{50}O_6$	881	N/A
Eicosanal-	1704, 1.740	$C_{20}H_{40}O$	842	N/A
Germanicol	1713, 2.450	$C_{30}H_{50}O$	843	N/A
(R)-δ-Tocotrienol	1716, 2.742	$C_{27}H_{40}O_2$	816	1.16
Tetratetracontane	1719, 1.534	$C_{44}H_{90}$	796	N/A
Stigmasta-3,5-diene	1740, 2.580	$C_{29}H_{48}$	869	0.36
2-(Decanoyloxy)propane-1,3-diyl dioctanoate	1749, 2.075	$C_{29}H_{54}O_6$	852	N/A
Vitamin E	1758, 2.555	$C_{29}H_{50}O_2$	913	-0.34
Cholesterol	1758, 2.859	$C_{27}H_{46}O$	840	-0.52
γ-Tocotrienol	1779, 3.230	$C_{28}H_{42}O_2$	873	-0.67
1-Dodecanol, 2-octyl-	1782, 1.771	$C_{20}H_{42}O$	875	N/A
Campesterol	1827, 3.340	$C_{28}H_{48}O$	915	-0.09
Stigmasterol	1845, 3.455	$C_{29}H_{48}O$	937	1.48
Octacosanol	1875, 2.345	$C_{28}H_{58}O$	883	N/A
2-(Octanoyloxy)propane-1,3-diyl bis(decanoate)	1875, 2.655	$C_{31}H_{58}O_6$	877	N/A
Methyl melissate	1890, 2.420	$C_{31}H_{62}O_2$	770	1.03
γ-Sitosterol	1893, 0.780	$C_{29}H_{50}O$	926	-1.67
Germanicol	1926, 1.370	$C_{30}H_{50}O$	884	0.78
Melissic acid	1929, 2.742	$C_{30}H_{60}O_2$	758	1.32
Lup-20(29)-en-3-one	1947, 1.967	$C_{30}H_{48}O$	915	0.13
3-Epilupeol	1956, 1.846	$C_{30}H_{50}O$	921	1.42
Lupeol	1980, 2.095	$C_{30}H_{50}O$	934	-0.64
Dotriacontanal	1995, 2.880	$C_{32}H_{64}O$	892	1
Epilupeol acetate	2001, 2.240	$C_{32}H_{52}O_2$	822	N/A
γ-Sitostenone	2004, 2.040	$C_{29}H_{48}O$	790	0.06
3-Acetyllupeol	2052, 2.315	$C_{32}H_{52}O_2$	840	1.23
Heptatriacontane	2316, 3.360	$C_{37}H_{76}$	910	-0.14
1-Hentetracontanol	2346, 1.318	$C_{41}H_{84}O$	855	N/A

Similarity Ave. 852/1000

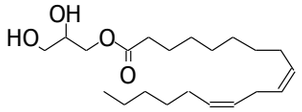
Softeners
Maintain moisture and softness



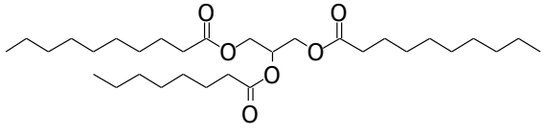
Palmitic acid



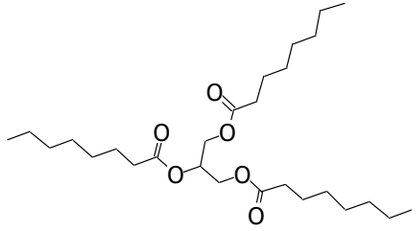
Linoleic Acid



1-Monolinolein



Glycerol tricaprylate



2-(Octanoyloxy)propane-
1,3-diyl bis(decanoate)

Are there PFAS in the Chewing Gum Sample?

Are there PFAS in the Chewing Gum Sample?

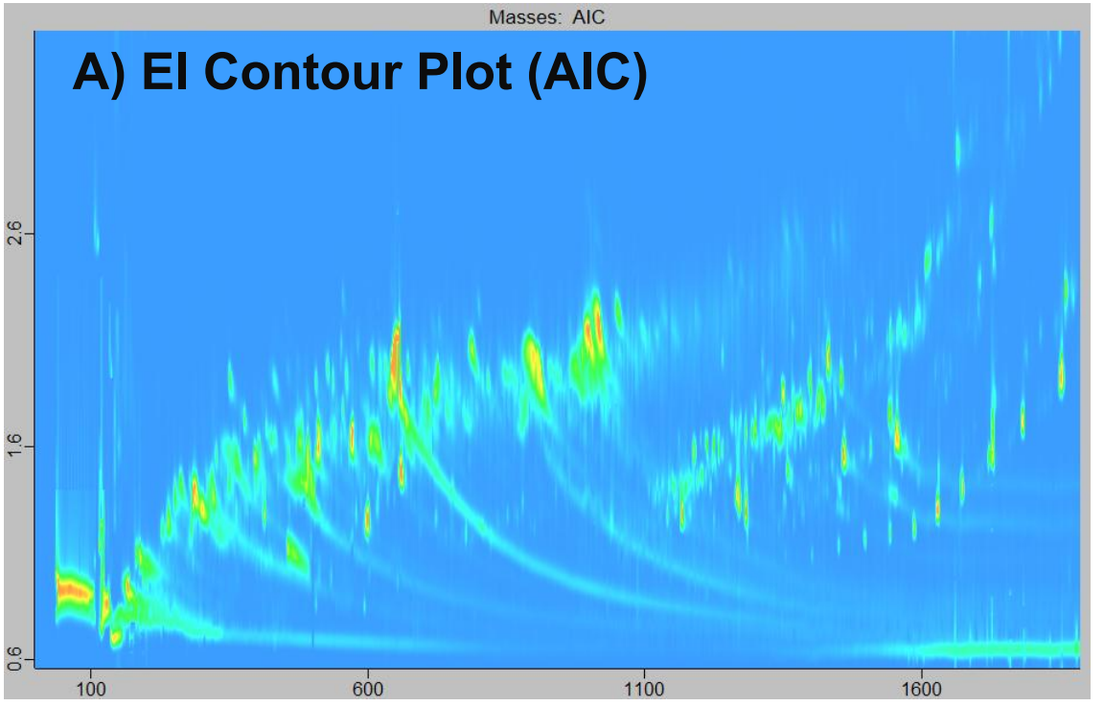
No!

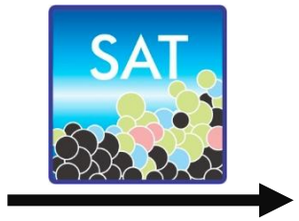
- Not in the gum
- Not in the wrapping paper
- Not in the box

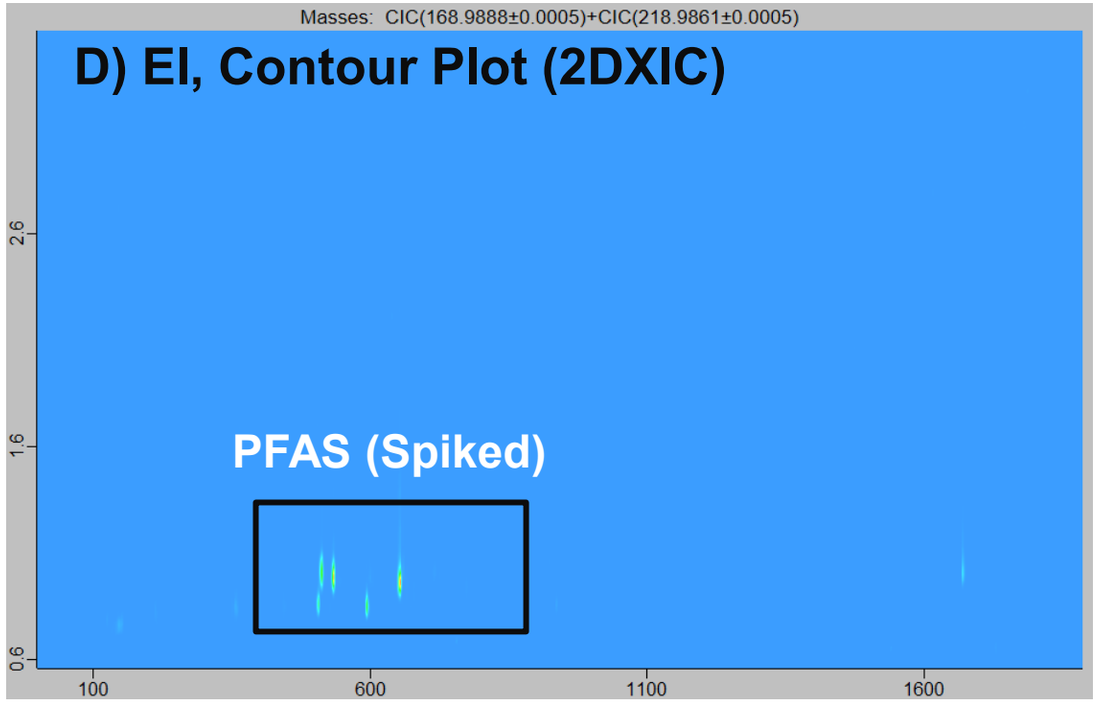
PFAS Screening: Spectral Analysis Tools (SAT)

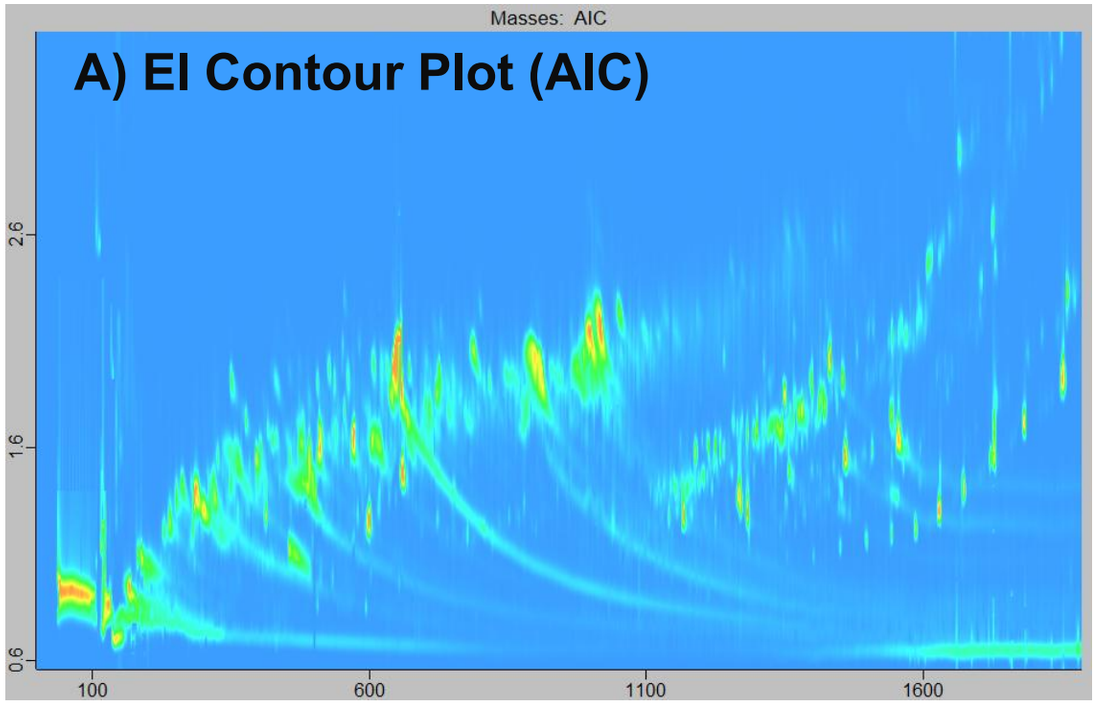
Analytical Workflow

1. Sum all contour plot ions to produce a mass defect plot
2. Use SAT to scale and filter the mass defect plot for PFAS
3. Display PFAS on the simplified contour plot (XIC)
4. Characterize PFAS using complementary EI, CI-HRTOFMS

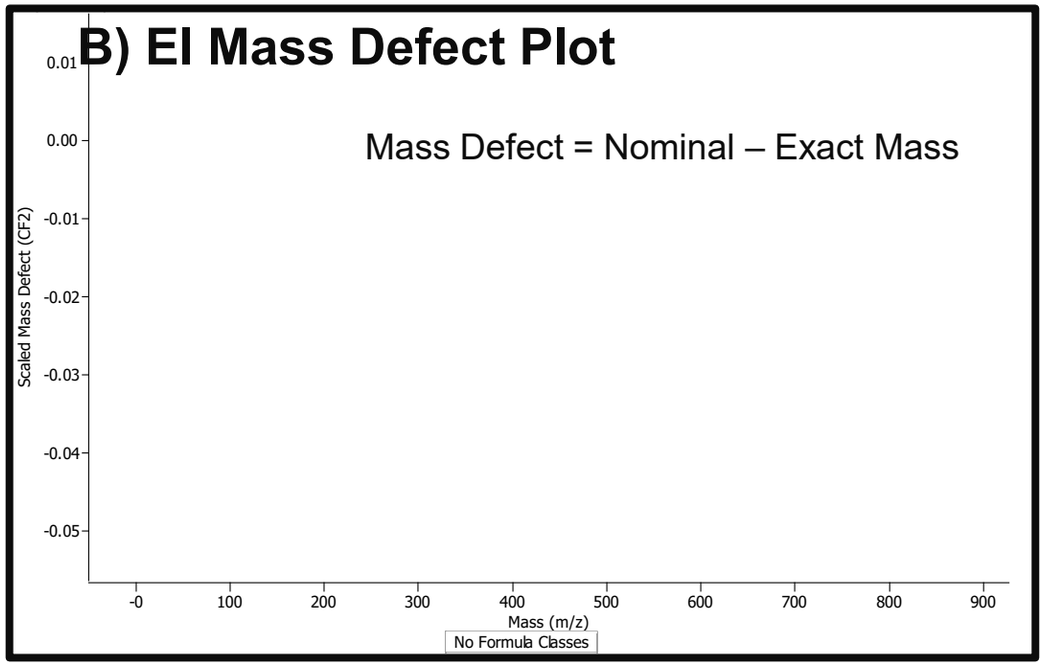


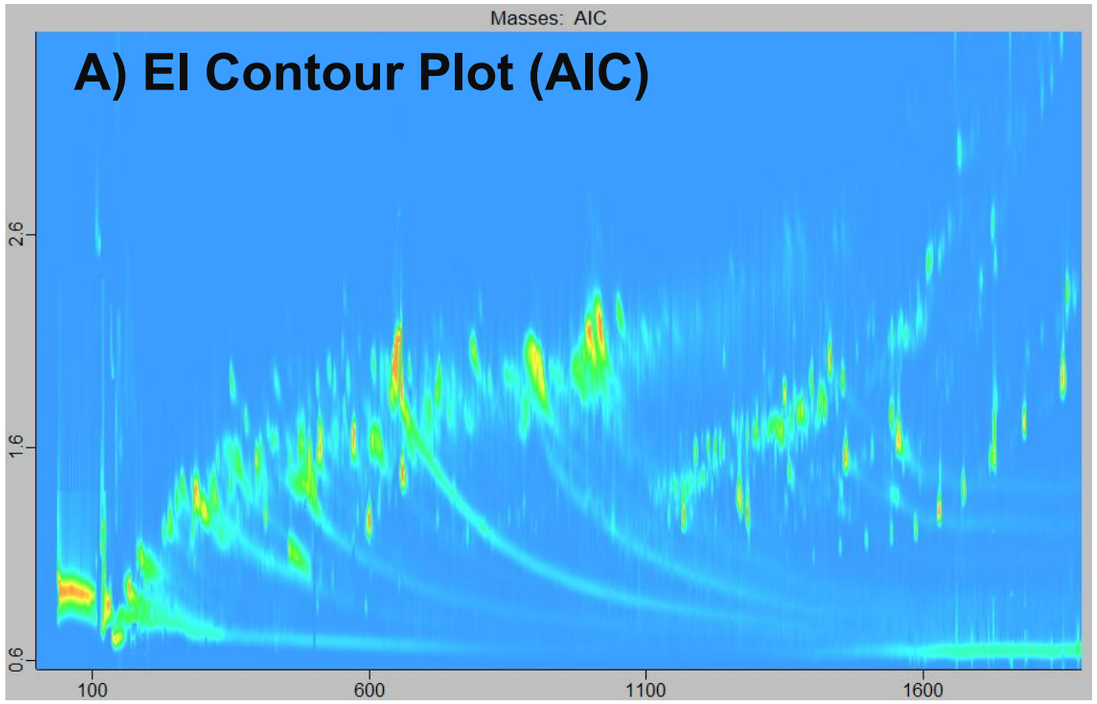




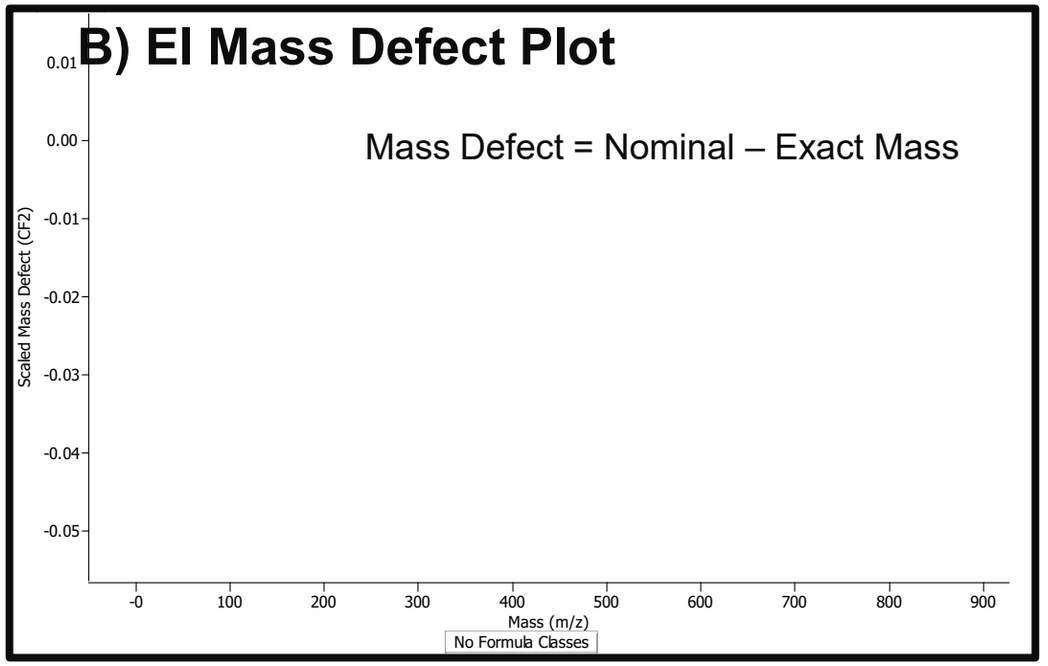

Masses: AIC
A) EI Contour Plot (AIC)
2.6
1.6
0.6
100
600
1100
1600

1


B) EI Mass Defect Plot
Mass Defect = Nominal – Exact Mass
Scaled Mass Defect (CF2)
0.01
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
-0
100
200
300
400
500
600
700
800
900
Mass (m/z)
No Formula Classes



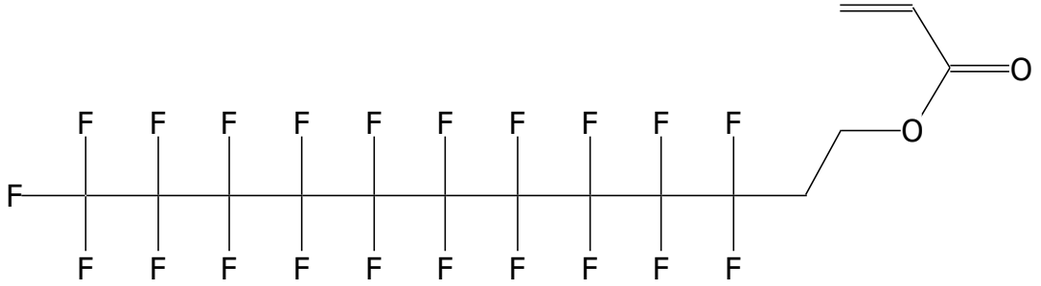
1



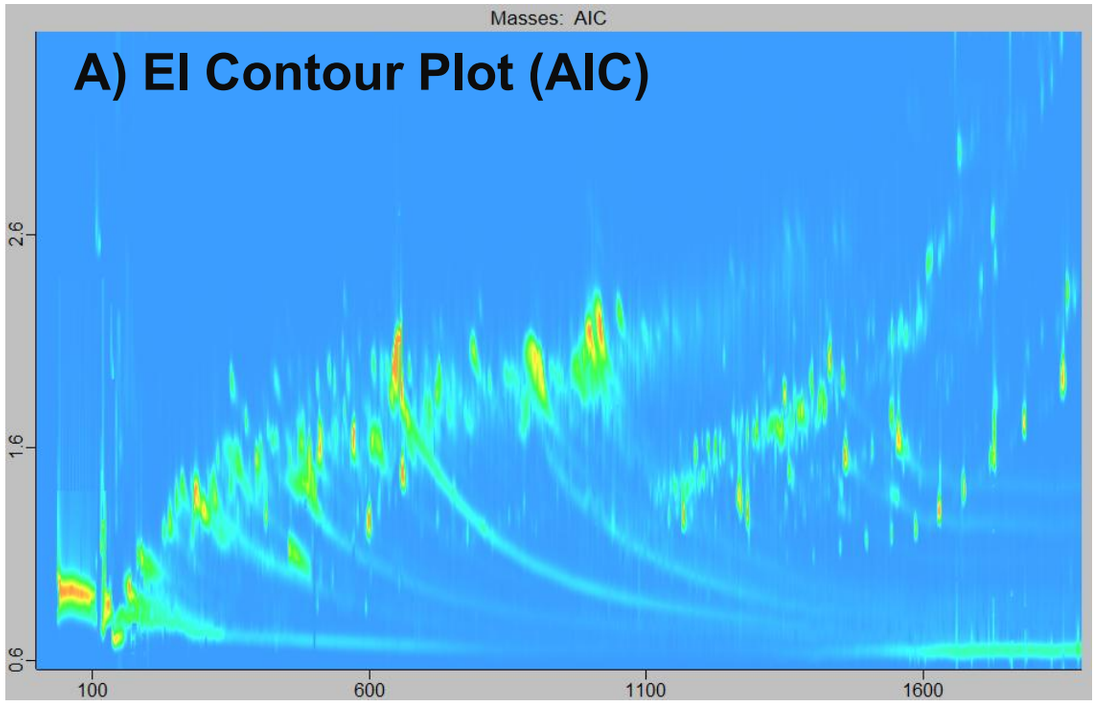
Mass Defect Series - "PFAS"

Auto Select

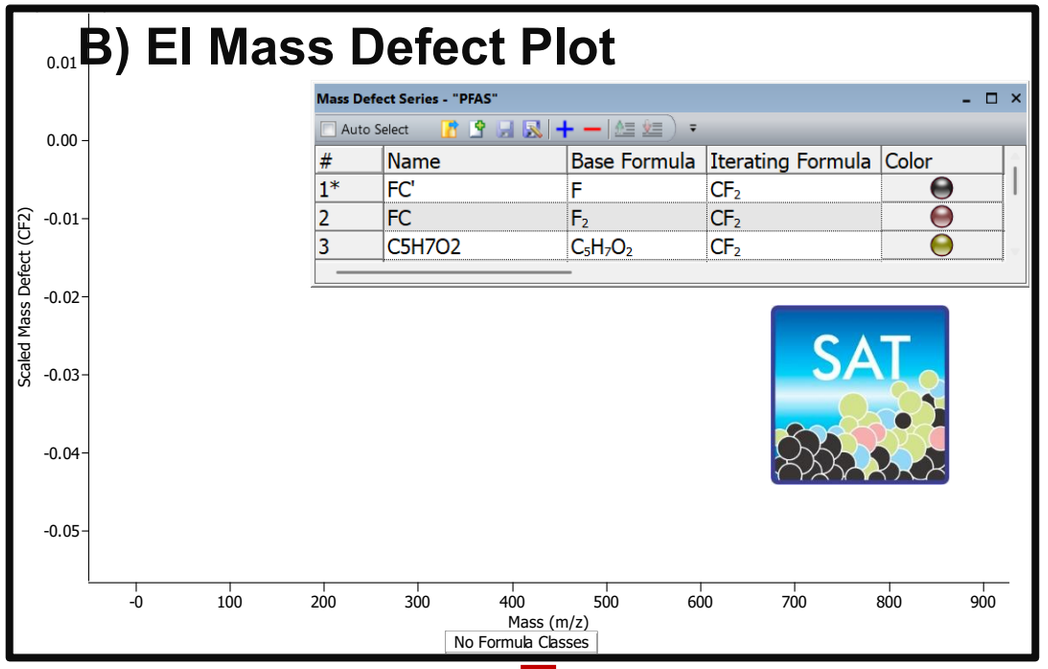
#	Name	Base Formula	Iterating Formula	Color
1*	FC'	F	CF_2	
2	FC	F_2	CF_2	
3	C5H7O2	$C_5H_7O_2$	CF_2	



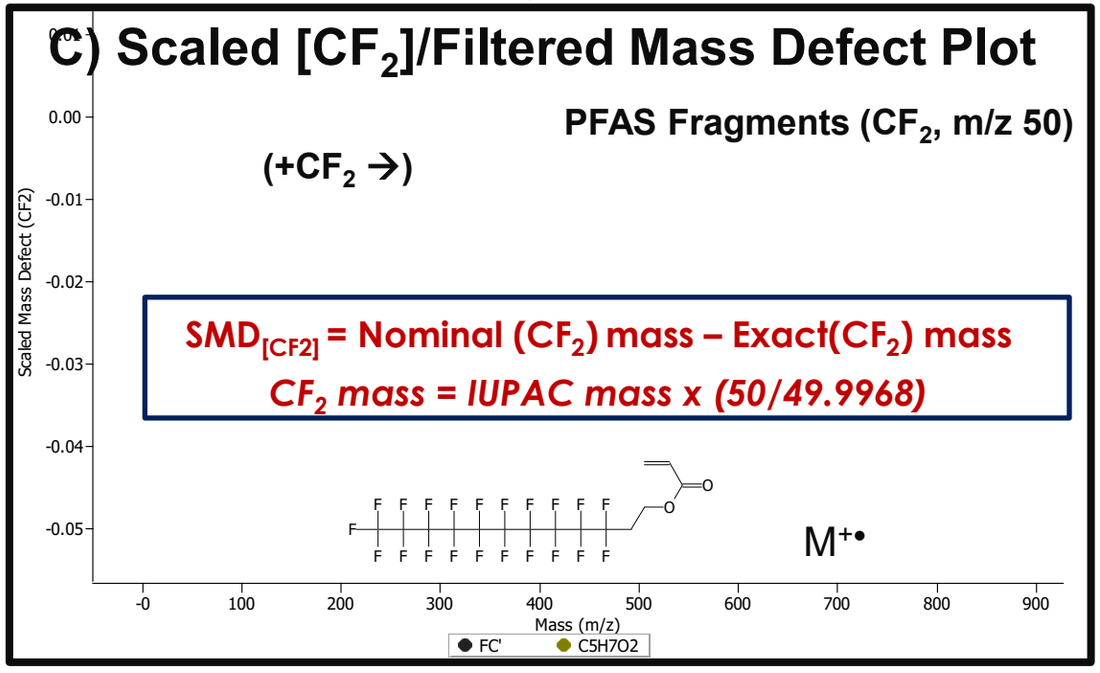
Tail **Head**

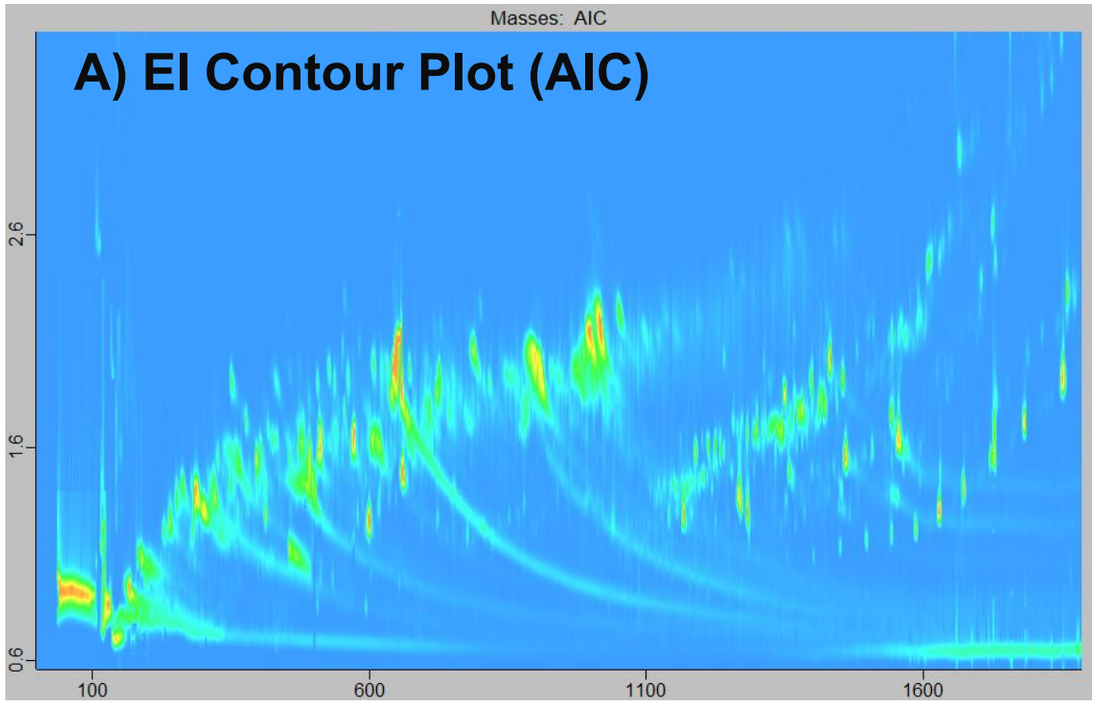

Masses: AIC
A) EI Contour Plot (AIC)
2.6
1.6
0.6
100
600
1100
1600

1

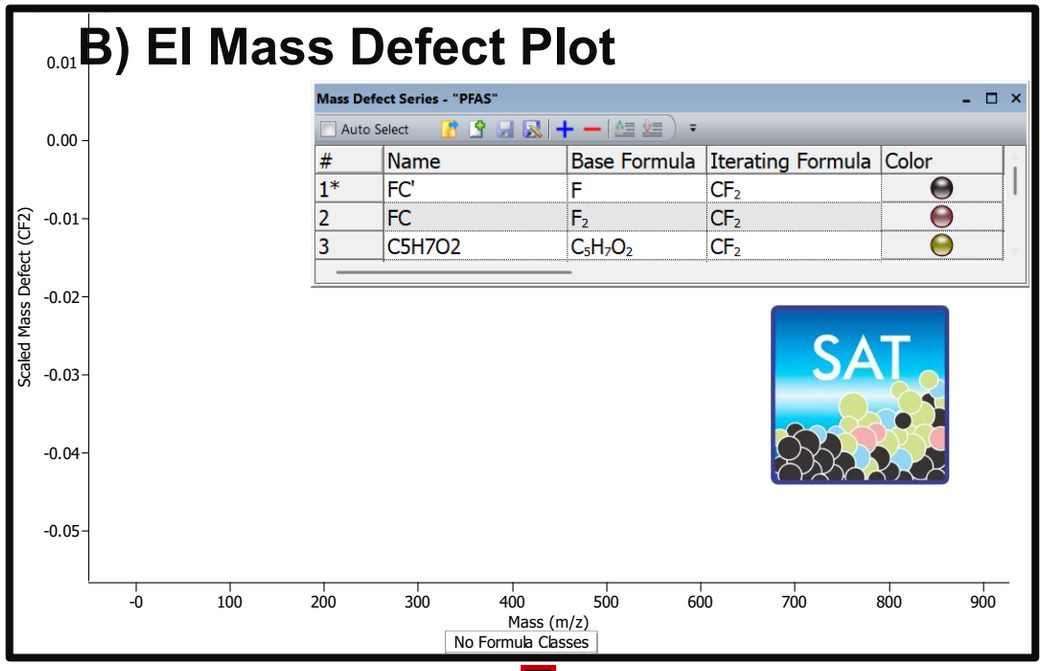

B) EI Mass Defect Plot
Mass Defect Series - "PFAS"
Auto Select
| Name | Base Formula | Iterating Formula | Color
1* | FC' | F | CF2
2 | FC | F2 | CF2
3 | C5H7O2 | C5H7O2 | CF2
SAT
Scaled Mass Defect (CF2)
0.01
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
-0
100
200
300
400
500
600
700
800
900
Mass (m/z)
No Formula Classes

2

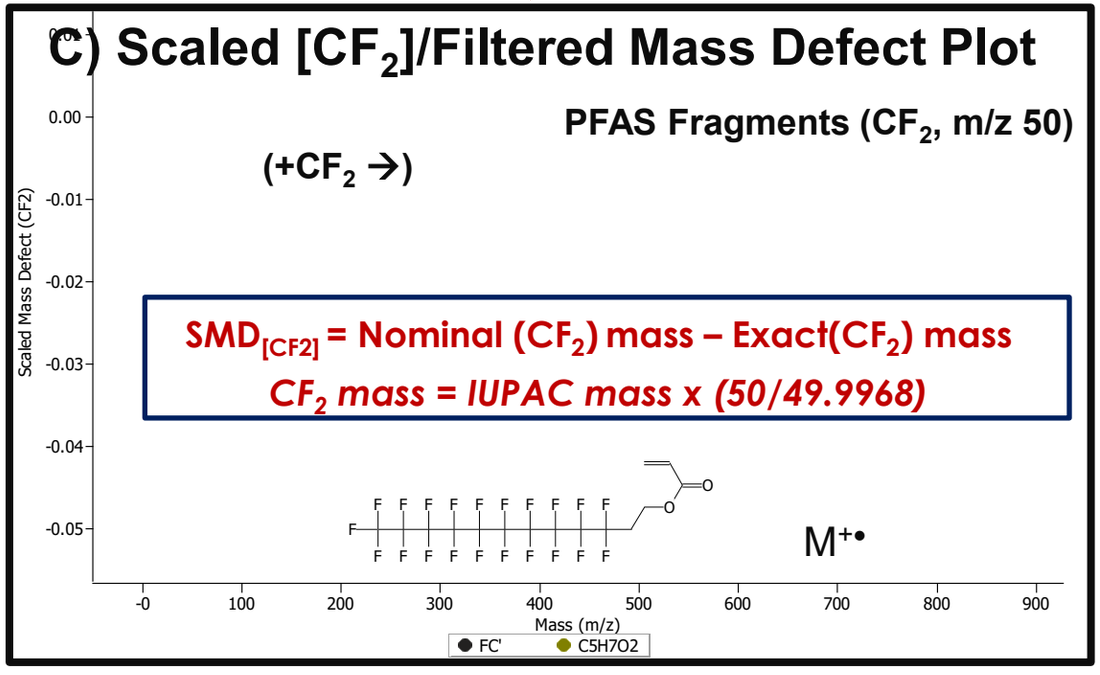

C) Scaled [CF2]/Filtered Mass Defect Plot
PFAS Fragments (CF2, m/z 50)
(+CF2 →)
SMD[CF2] = Nominal (CF2) mass – Exact(CF2) mass
CF2 mass = IUPAC mass x (50/49.9968)
M+•
Scaled Mass Defect (CF2)
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
-0
100
200
300
400
500
600
700
800
900
Mass (m/z)
FC'
C5H7O2


Masses: AIC
A) EI Contour Plot (AIC)
2.6
1.6
0.6
100
600
1100
1600

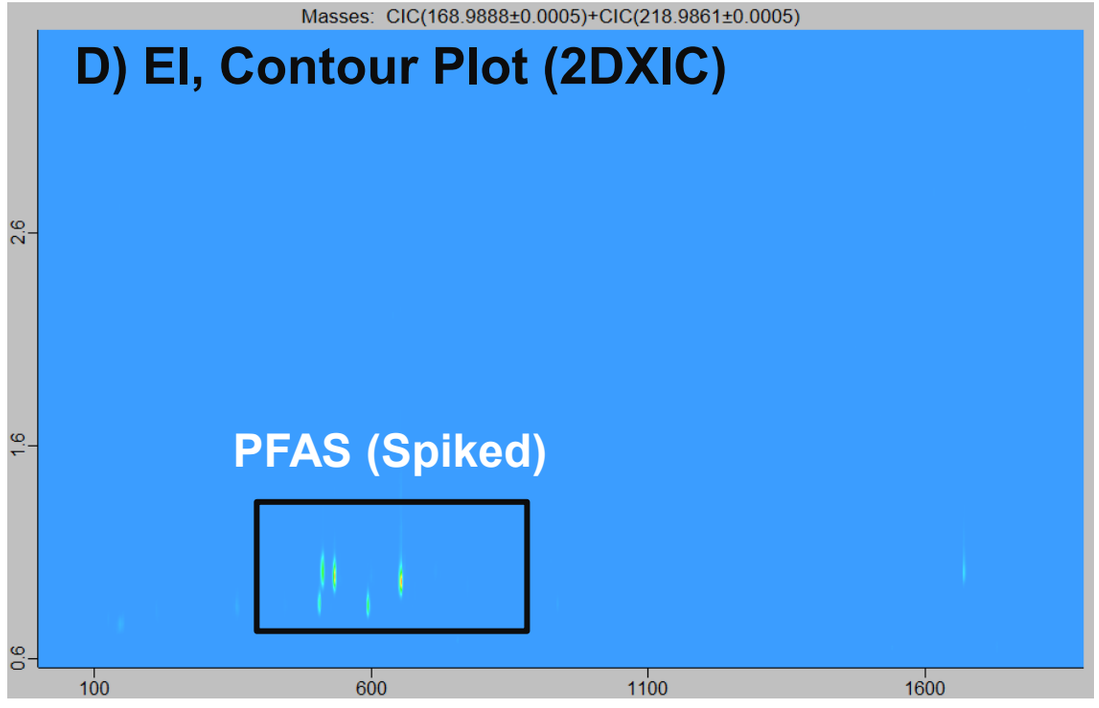
1


B) EI Mass Defect Plot
Mass Defect Series - "PFAS"
Auto Select
| Name | Base Formula | Iterating Formula | Color
1* | FC' | F | CF2
2 | FC | F2 | CF2
3 | C5H7O2 | C5H7O2 | CF2
SAT
0.01
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
Scaled Mass Defect (CF2)
-0
100
200
300
400
500
600
700
800
900
Mass (m/z)
No Formula Classes

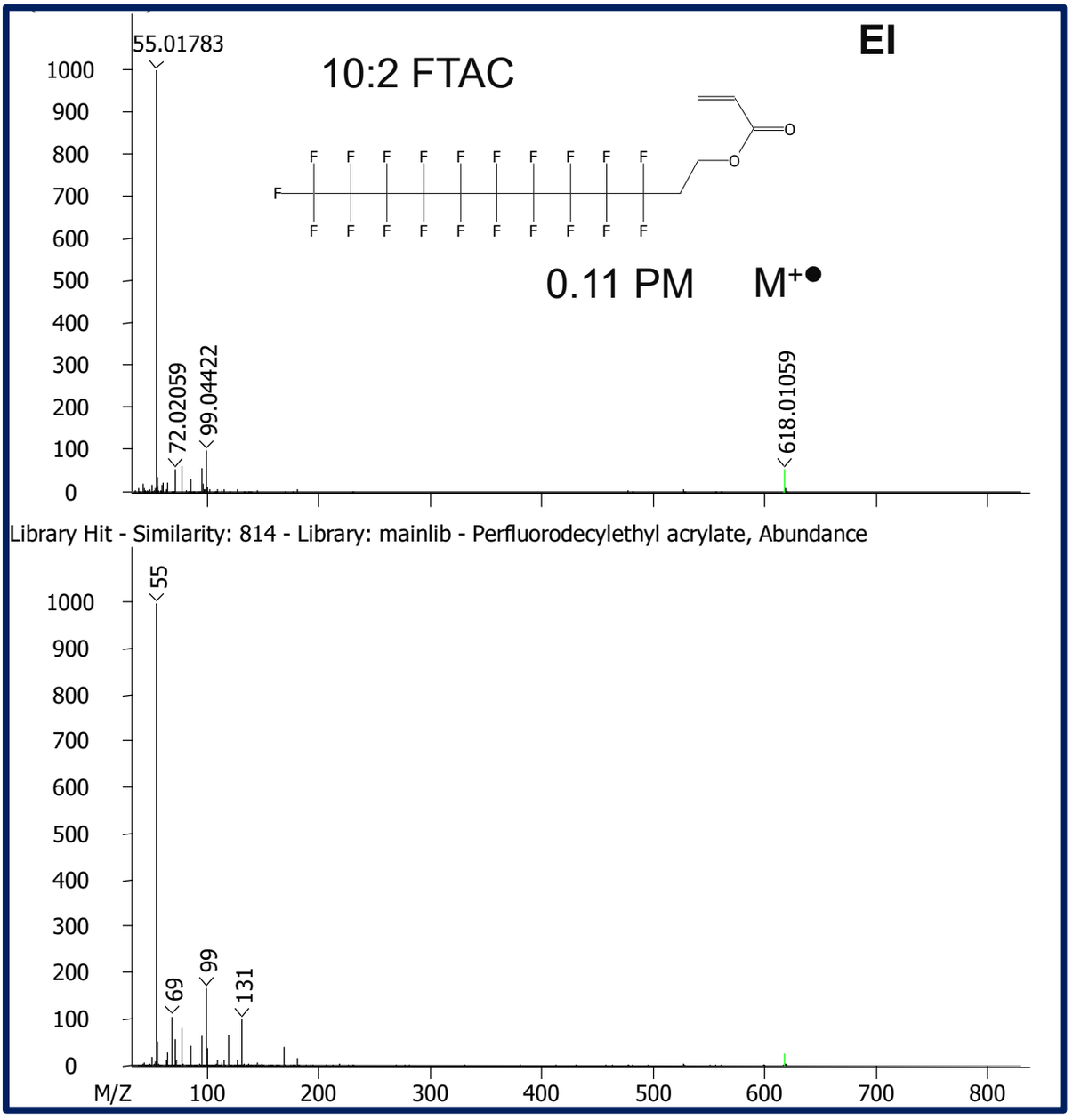
2


C) Scaled [CF2]/Filtered Mass Defect Plot
PFAS Fragments (CF2, m/z 50)
(+CF2 →)
SMD[CF2] = Nominal (CF2) mass – Exact(CF2) mass
CF2 mass = IUPAC mass x (50/49.9968)
M+•
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
Scaled Mass Defect (CF2)
-0
100
200
300
400
500
600
700
800
900
Mass (m/z)
FC'
C5H7O2

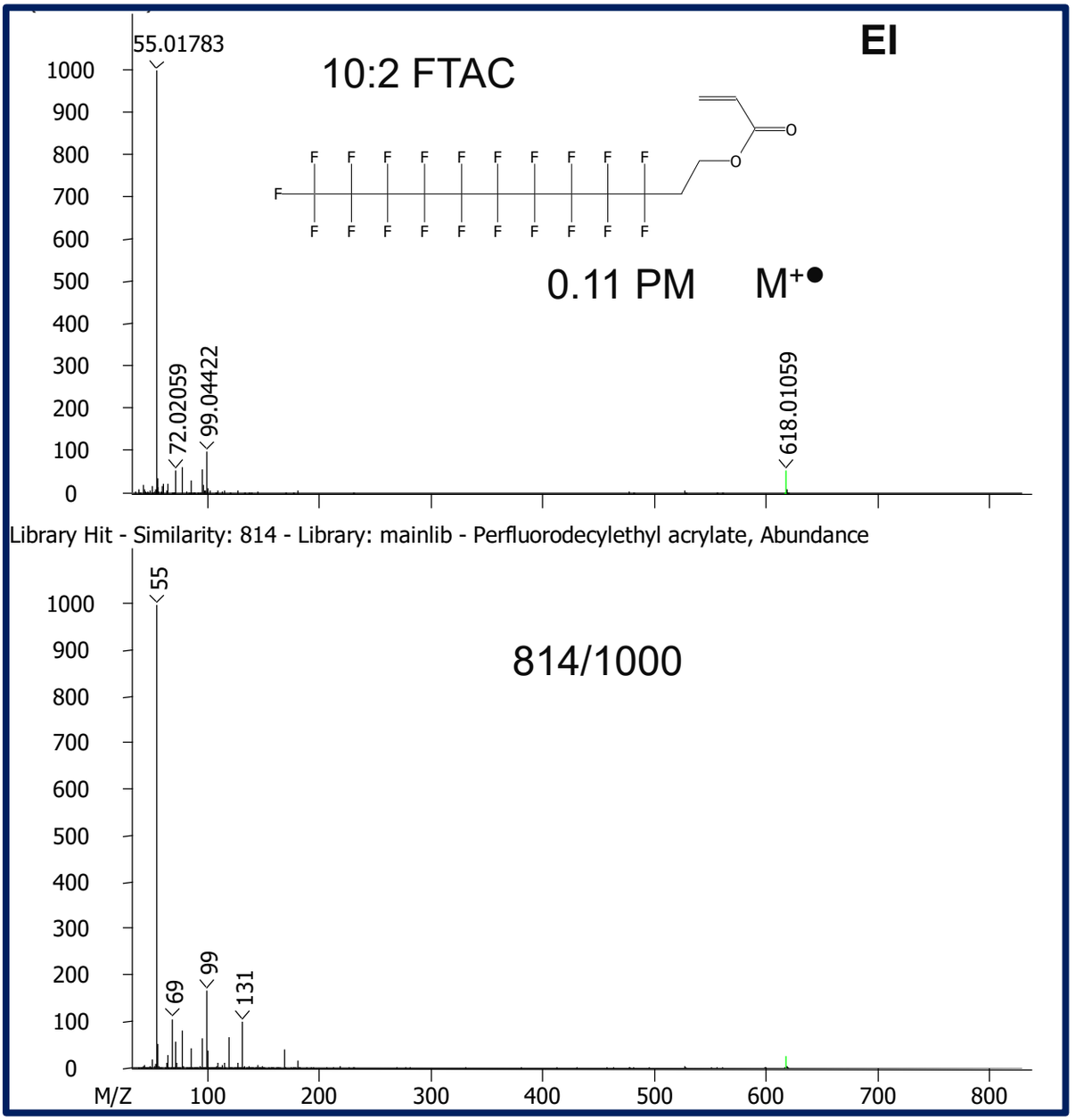
3

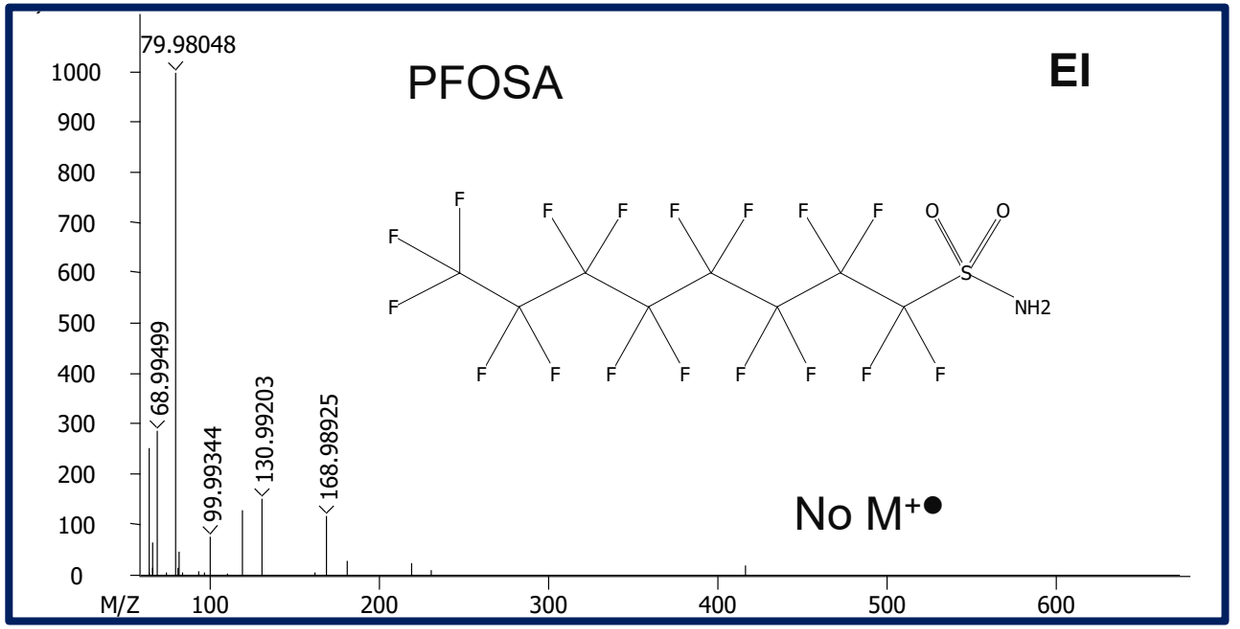

Masses: CIC(168.9888±0.0005)+CIC(218.9861±0.0005)
D) EI, Contour Plot (2DXIC)
PFAS (Spiked)
2.6
1.6
0.6
100
600
1100
1600

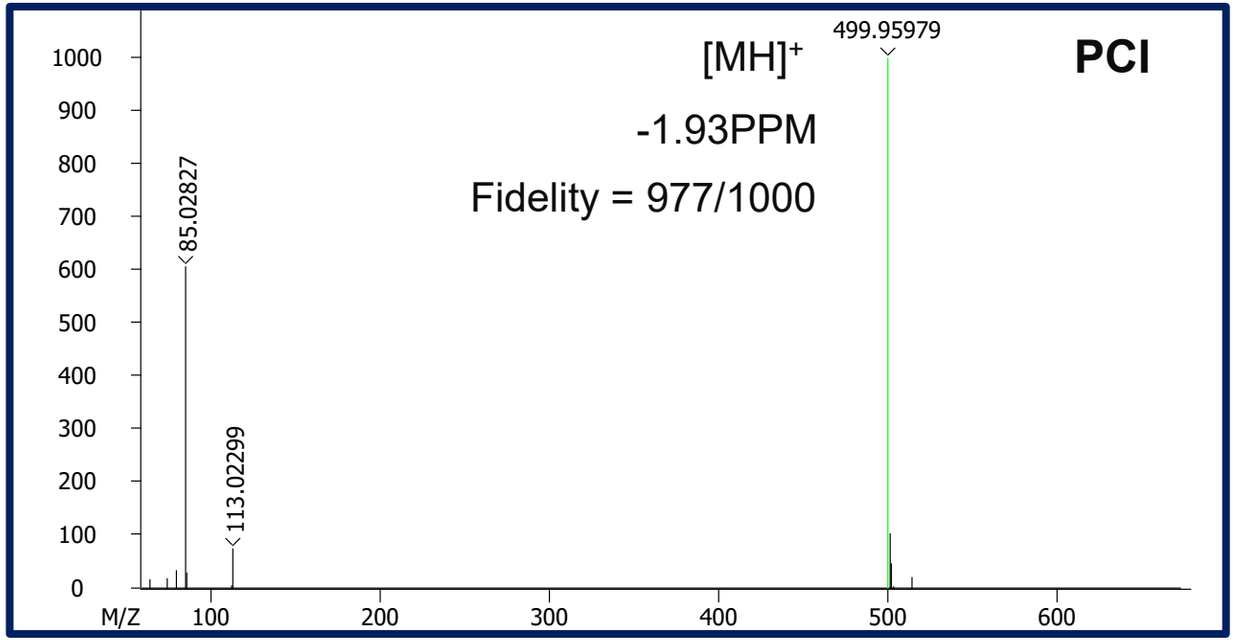
EI-HRTOFMS Characterization



EI/CI-HRTOFMS Characterization

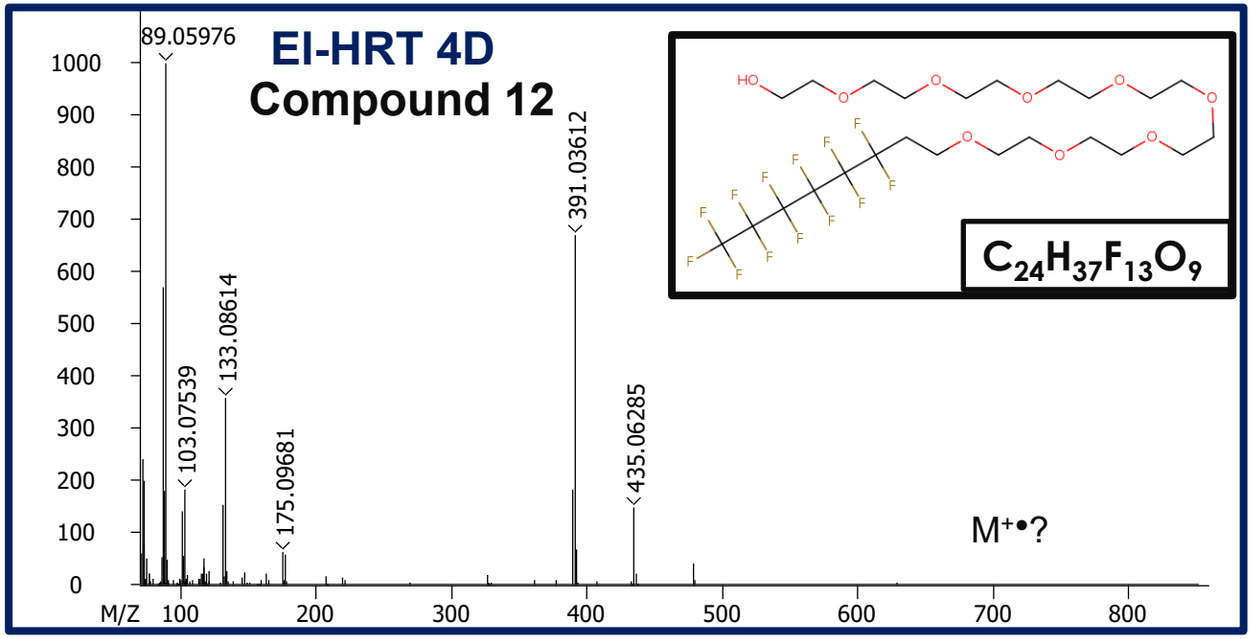


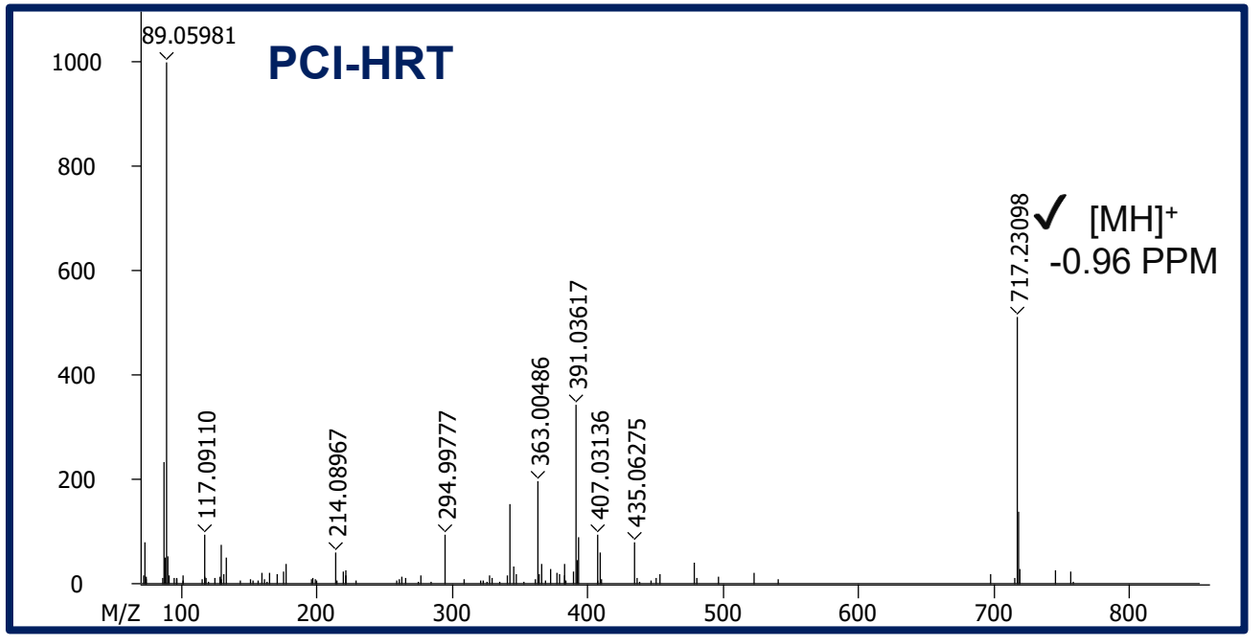




Summary

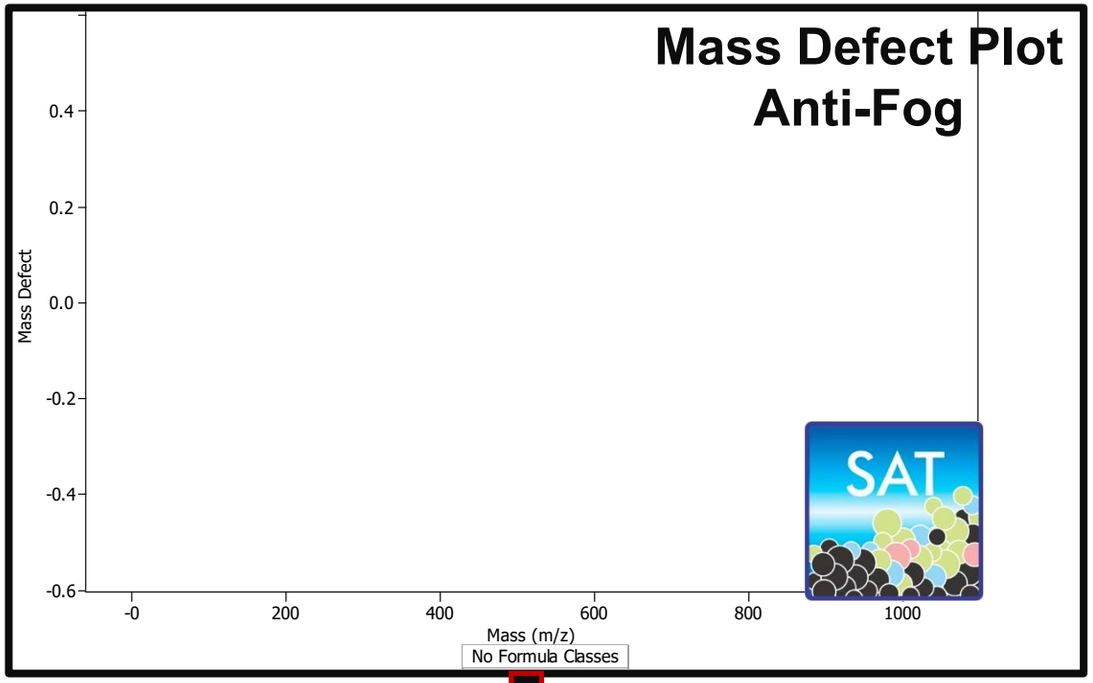
- GC (×GC)-TOFMS are excellent tools for non-targeted screening
- HR-TOFMS is important for molecules not present in commercial databases (or no standards available)
- Positive and Negative ionization modes (i.e.. PCI/NCI) are essential for better compound annotations





Summary

- GC (×GC)-TOFMS are excellent tools for non-targeted screening
- HR-TOFMS is important for molecules not present in commercial databases (or no standards available)
- Positive and Negative ionization modes (i.e.. PCI/NCI) are essential for better compound annotations
- Mass defect plots & Mass defect series reduce the complexity of rich chromatograms and effectively screen for PFAS



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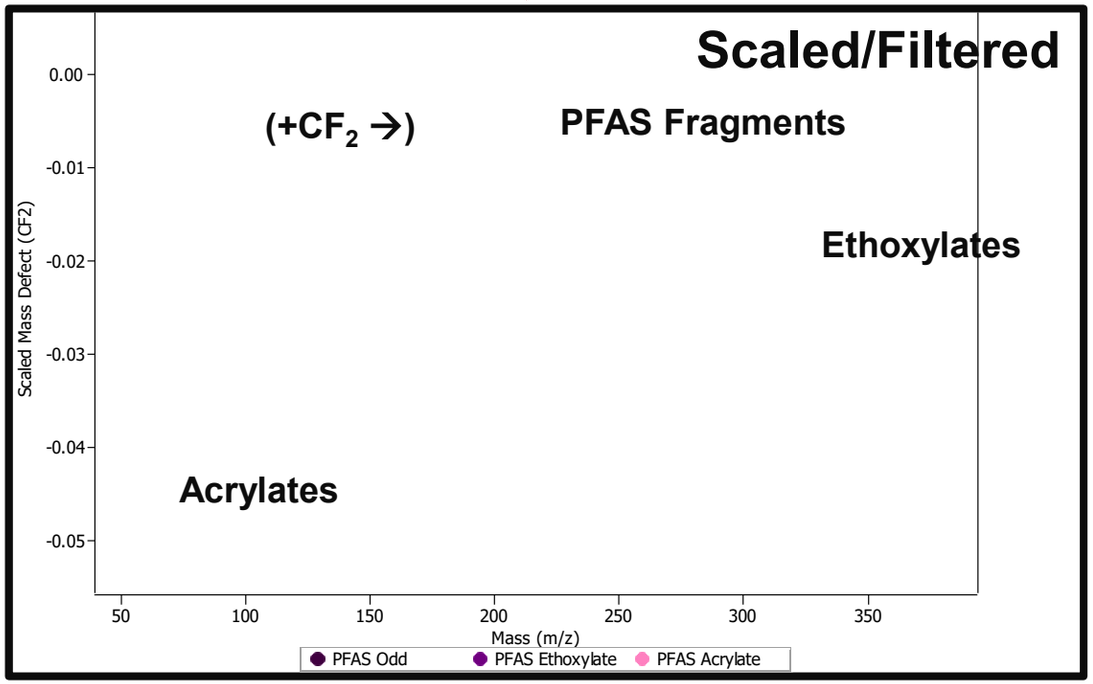

THANKS

Email: info@leco.com
www.leco.com