Prachy… necílený screening s využitím GCxGC HRMS instrumentace

Pavel Jiroš, David E. Alonso and Joe Binkley

How Much a Ruble Is Worth

Note: Scale is inverted to show the decline in the ruble's value.

As of 2:30 p.m. ET

Introduction

Pelley J., "*Dust, Unsettled*" ACS Cent. Sci. **2017**, *3*, 5-9.

"…dust can hold a witch's brew of persistent organic pollutants, metals, endocrine disruptors, and more."

- Humans spend a good portion of their time at home (and work)
- Dust is a repository of chemicals and can be used to estimate human exposure to contaminants (e.g., Pesticides, PAHs)

Introduction

Pelley J., "*Dust, Unsettled*" ACS Cent. Sci. **2017**, *3*, 5-9.

Name	*Formula*	*R.T. (s)*	*Similarity*
Methyl salicylate	$C_8H_8O_3$	688, 2.624	822
Salicylic acid	$C_7H_6O_3$	840, 3.440	733
Piperonal	$C_8H_6O_3$	1000, 4.880	919
Nicotine	$C_{10}H_{14}N_2$	1048, 4.085	934
Vanillin	$C_8H_8O_3$	1208, 6.155	913
Myosmine	$C_9H_{10}N_2$	1328, 7.280	909
Lilial	$C_{14}H_{20}O$	1904, 6.620	896
Diethyltoluamide	$C_{12}H_{17}NO$	2216, 4.055	896
Clorprenaline	$C_{11}H_{16}ClNO$	2240, 2.320	781
Ibuprofen	$C_{13}H_{18}O_2$	2328, 2.745	851
N-Methylsaccharin	$C_8H_7NO_3S$	2360, 3.735	812
Acetaminophen	$C_8H_9NO_2$	2488, 3.910	954
Veramoss	$C_{10}H_{12}O_4$	2520, 3.027	898
Cotinine	$C_{10}H_{12}N_2O$	2520, 3.830	895
Tolycaine	$C_{15}H_{22}N_2O_3$	2744, 2.635	798
Caffeine	$C_8H_{10}N_4O_2$	2800, 4.580	903
Tonalid	$C_{18}H_{26}O$	2840, 2.865	842

Name	*Formula*	*R.T. (s)*	*Similarity*
Theobromine	$C_7H_8N_4O_2$	2840, 5.155	910
Benadryl	$C_{17}H_{21}NO$	2896, 3.345	824
Musk ketone	$C_{14}H_{18}N_2O_5$	3088, 3.790	809
Oxybenzone	$C_{14}H_{12}O_3$	3192, 4.625	873
Drometrizole	$C_{13}H_{11}N_3O$	3272, 4.555	859
Octinoxate	$C_{18}H_{26}O_3$	3480, 3.905	883
Etocrylene	$C_{18}H_{15}NO_2$	3528, 5.145	763
Cocaine	$C_{17}H_{21}NO_4$	3688, 5.255	936
Padimate O	$C_{17}H_{27}NO_2$	3744, 4.265	879
Cannabichromene	$C_{21}H_{30}O_2$	4152, 4.500	831
Ketazolam	$C_{20}H_{17}ClN_2O_3$	4320, 7.037	785
Bumetrizole	$C_{17}H_{18}ClN_3O$	4456, 5.135	725
cis-Cinnamoylcocaine	$C_{19}H_{23}NO_4$	4536, 6.305	831
Cannabinol	$C_{21}H_{26}O_2$	4560, 5.332	894
Octocrylene	$C_{24}H_{27}NO_2$	4776, 5.300	849
Octabenzone	$C_{21}H_{26}O_3$	5008, 5.238	835

- Humans spend a good portion of their time at home (and work)
- Dust is a repository of chemicals and can be used to estimate human exposure to contaminants (e.g., Pesticides, PAHs)
- Problem: Dust is complex! Numerous, chemically diverse constituents in a wide concentration range

✓ Aroma
✓ OTC Drugs
✓ Illicit Drugs
✓ Food/Flavor
✓ Tobacco
✓ Cannabinoids

Introduction

Pelley J., "*Dust, Unsettled*" ACS Cent. Sci. **2017**, *3*, 5-9.

Analytical and Bioanalytical Chemistry
https://doi.org/10.1007/s00216-019-01615-6

PAPER IN FOREFRONT

Check for updates

The strength in numbers: comprehensive characterization of house dust using complementary mass spectrometric techniques

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Received: 6 November 2018 / Revised: 20 December 2018 / Accepted: 15 January 2019

- Humans spend a good portion of their time at home (and work)
- Dust is a repository of chemicals and can be used to estimate human exposure to contaminants (e.g., Pesticides, PAHs)
- Problem: Dust is complex! Numerous, chemically diverse constituents in a wide concentration range
- Analysis of dust has primarily been conducted using targeted methods and a variety of instrumental techniques

Objectives

1) *To use a novel multimode source with high resolution time-of-flight mass spectrometry for the non-targeted analysis of dust*

Multi-Faceted Tool

=

Objectives

1) *To use a novel multimode source with high resolution time-of-flight mass spectrometry for the non-targeted analysis of dust*
2) *To conduct retrospective analysis of the comprehensive data*

Multi-Faceted Tool

=

Objectives

1) *To use a novel multimode source with high resolution time-of-flight mass spectrometry for the non-targeted analysis of dust*
2) *To conduct retrospective analysis of the comprehensive data*
3) *To perform quantitative analysis of Polychlorinated Paraffins (PCPs) in dust*

Multi-Faceted Tool

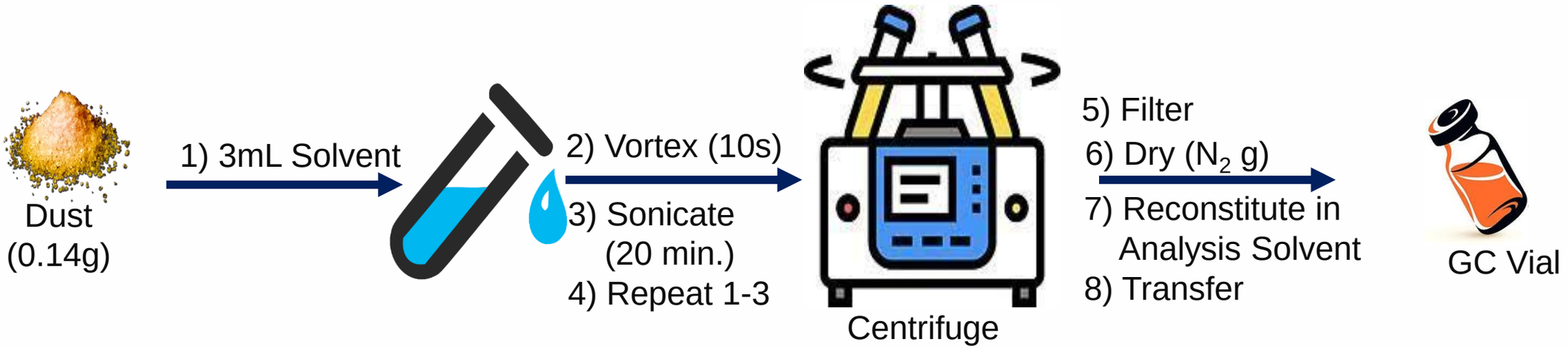
=

Experimental: Standard &Samples

1) NIST SRM 2585
2) Household Dust
3) Office Dust

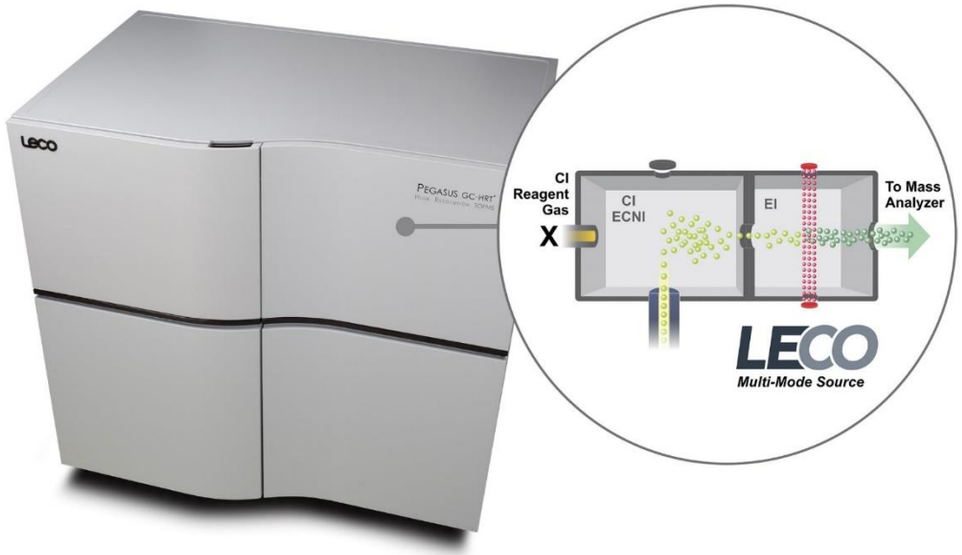
Experimental: Compound Extraction

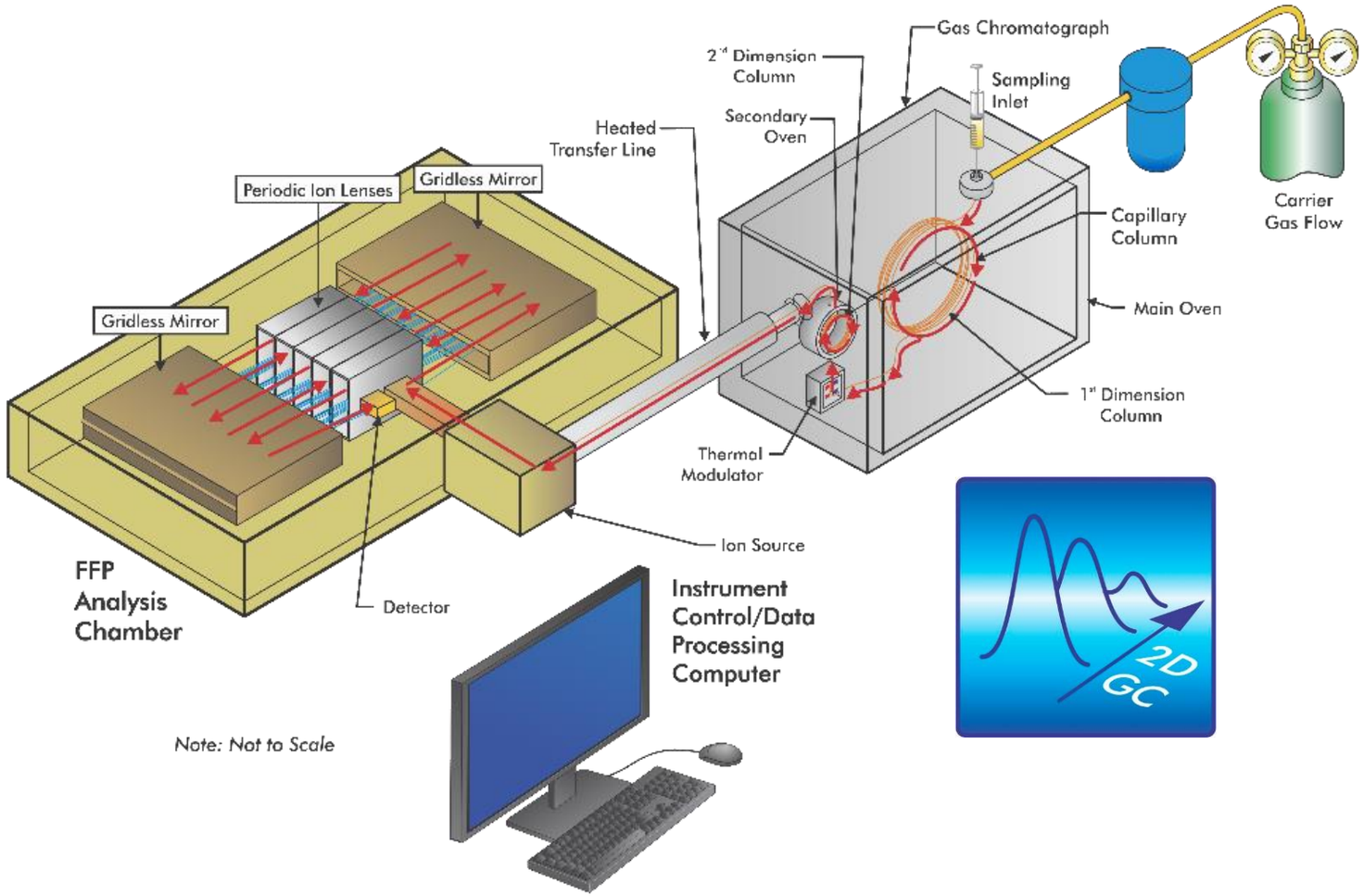
1) NIST SRM 2585
2) Household Dust
3) Office Dust



Experimental: Instrument

Pegasus HRT+ 4D



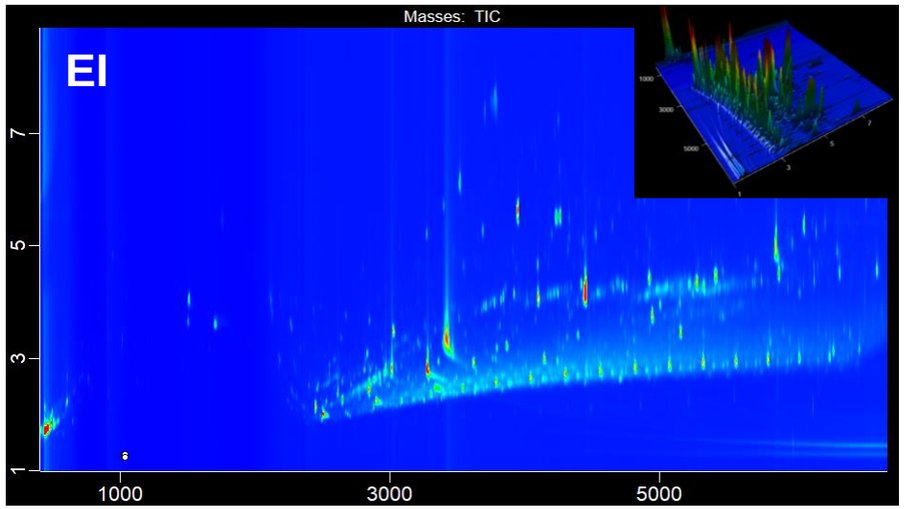


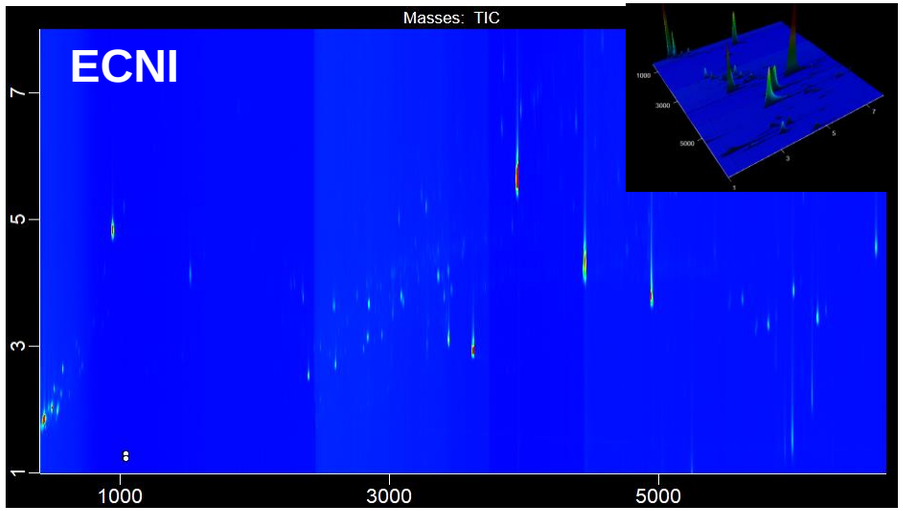
Mass Accuracy: 1 PPM
Resolution: Up to 50,000
Acquisition Speed: Up to 200 sps
Two Sources:

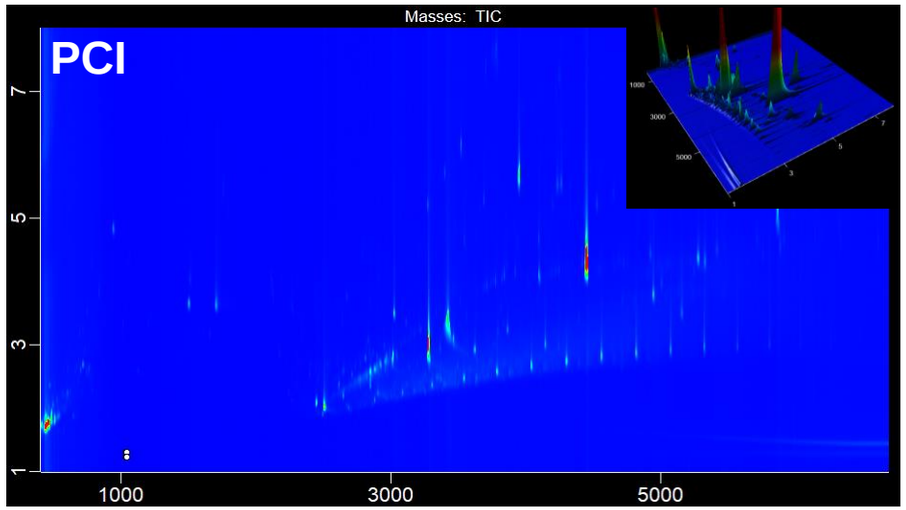
1) EI (Dedicated Source)
2) **Multimode Source (EI, PCI & ECNI)**

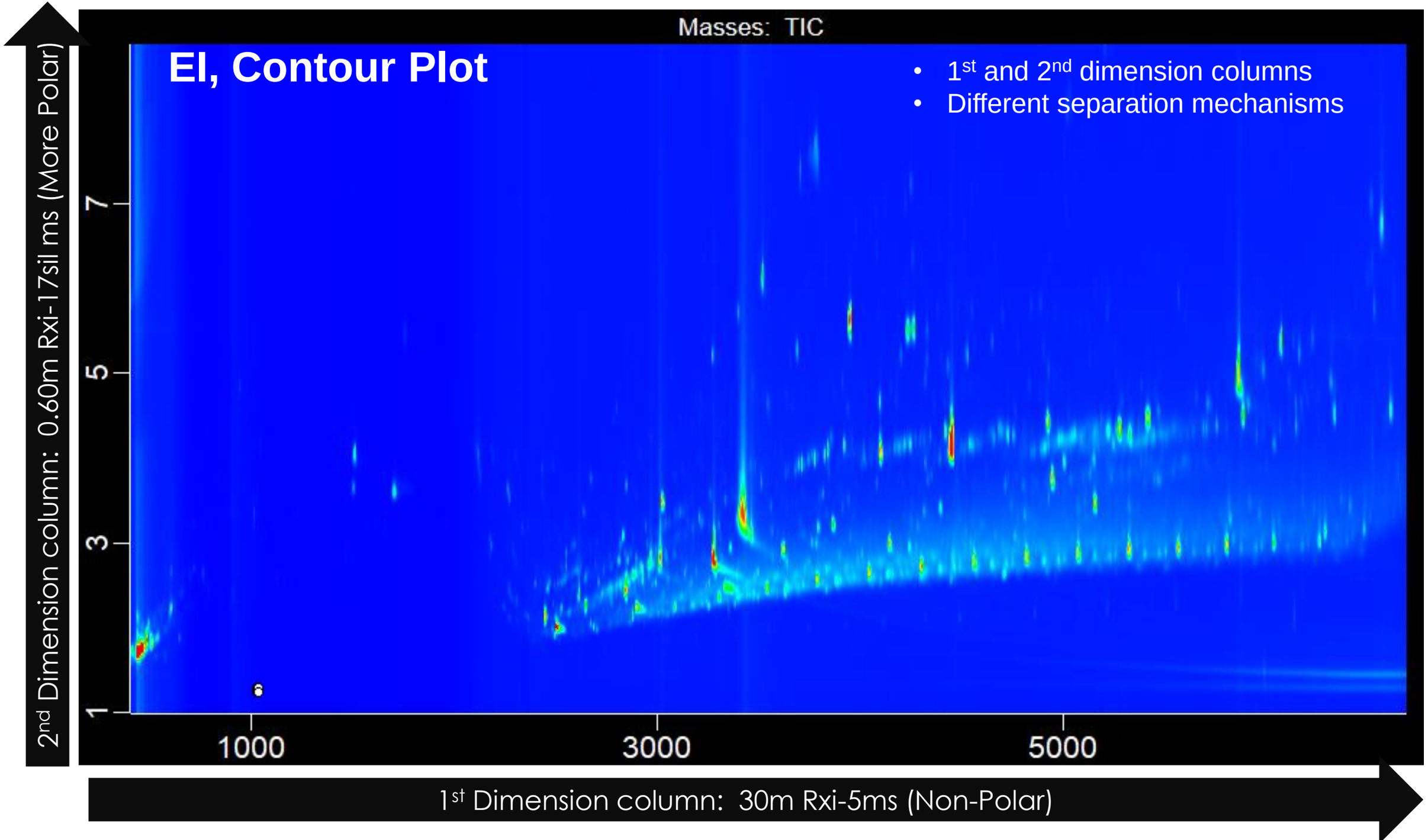
Part 1

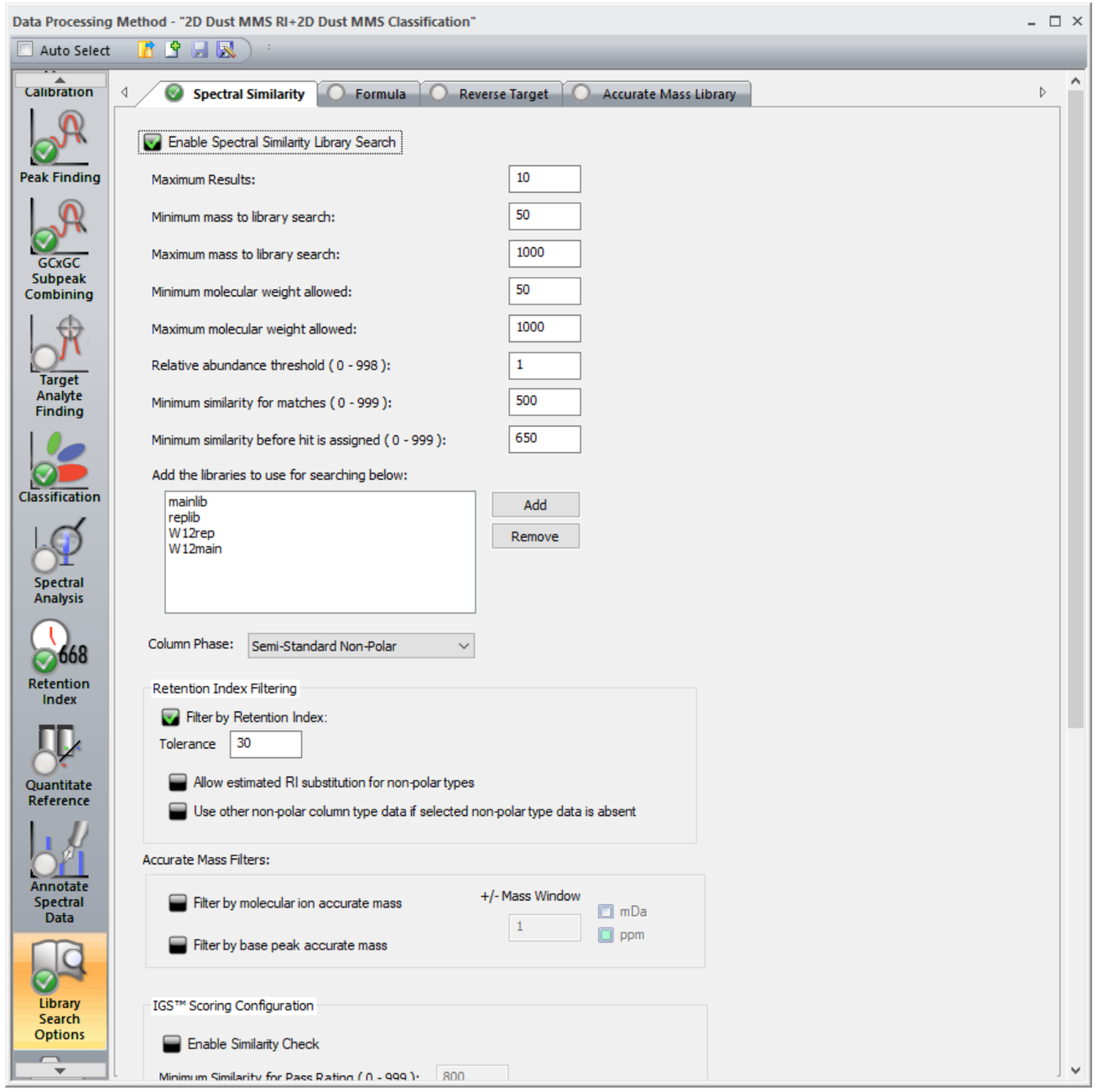
Non-targeted Screening (MMS)








Masses: TIC
EI, Contour Plot
• 1st and 2nd dimension columns
• Different separation mechanisms
2nd Dimension column: 0.60m Rxi-17sil ms (More Polar)
1
3
5
7
1000
3000
5000
1st Dimension column: 30m Rxi-5ms (Non-Polar)



Non-targeted Data Processing

- ✓ Peak Find (Deconvolution)
- ✓ Group Classification
- ✓ Database Searches
  - NIST 20,
  - Wiley 12
- ✓ Retention Index Filtering
- ✓ Formula Determinations
  - Mass Accuracy Calculations
  - Molecular, Fragment Ions

Representative Compounds

- ✓ Hydrocarbons
- ✓ Acids
- ✓ Aromatics
- ✓ Amines
- ✓ Alcohols
- ✓ Aldehydes
- ✓ Ketones
- ✓ Phenols
- ✓ Terpenes
- ✓ Fatty Acids
- ✓ Sterols
- ✓ Phosphates
- ✓ **More…**

Name	Formula	R.T. (s)	Similarity
Benzyl alcohol	C_7H_8O	496, 2.064	890
p-Cresol	C_7H_8O	520, 2.112	826
Acetophenone	C_8H_8O	528, 2.143	942
Phenylethyl Alcohol	$C_8H_{10}O$	576, 2.344	884
Octanoic acid	$C_8H_{16}O_2$	608, 2.240	908
Oxazolidin-2-one	$C_3H_5NO_2$	616, 3.967	950
Benzenamine, 2-methoxy-	C_7H_9NO	640, 2.768	839
3-Dodecene, (Z)-	$C_{12}H_{24}$	648, 1.893	917
Benzaldehyde, 3,4-dimethyl-	$C_9H_{10}O$	664, 2.592	888
p-Acetyltoluene	$C_9H_{10}O$	672, 2.678	937
Methyl salicylate	$C_8H_8O_3$	688, 2.632	771
Naphthalene	$C_{10}H_8$	688, 2.755	952
Ethanol, 2-phenoxy-	$C_8H_{10}O_2$	720, 3.064	809
Benzothiazole	C_7H_5NS	752, 3.504	909
Nonanoic acid	$C_9H_{18}O_2$	760, 2.648	873
1-Decanol	$C_{10}H_{22}O$	792, 2.456	920
1H-Inden-1-one, 2,3-dihydro-	C_9H_8O	864, 4.076	815
Indole	C_8H_7N	880, 4.418	870
5-Acetoxymethyl-2-furaldehyde	$C_8H_8O_4$	888, 4.200	915
Sesamol	$C_7H_6O_3$	912, 4.422	754
Benzamide	C_7H_7NO	968, 6.027	854
Capric acid	$C_{10}H_{20}O_2$	1008, 3.184	897
Capric acid	$C_{10}H_{20}O_2$	1016, 3.344	898
Benzaldehyde, 4-hydroxy-	$C_7H_6O_2$	1024, 5.384	935
Tropeolin	C_8H_7NS	1032, 5.216	864
E-11,13-Tetradecadien-1-ol	$C_{14}H_{26}O$	1064, 3.037	922
2(3H)-Furanone, dihydro-5-pentyl-	$C_9H_{16}O_2$	1064, 4.352	874
1-Tetradecene	$C_{14}H_{28}$	1128, 2.600	944
Dodecanal	$C_{12}H_{24}O$	1208, 3.352	916
Coumarin	$C_9H_6O_2$	1408, 8.263	901
Acenaphthylene	$C_{12}H_8$	1472, 6.872	925
1-Dodecanol	$C_{12}H_{26}O$	1504, 4.008	954
Diisobutyl maleate	$C_{12}H_{20}O_4$	1624, 4.464	900
1-Dodecanamine, N,N-dimethyl-	$C_{14}H_{31}N$	1704, 3.616	942
Tridecanal	$C_{13}H_{26}O$	1744, 4.485	890
Lauric acid	$C_{12}H_{24}O_2$	2120, 4.040	906

Name	Formula	R.T. (s)	Similarity
β-Calacorene	$C_{15}H_{20}$	2168, 3.810	807
n-Tridecan-1-ol	$C_{13}H_{28}O$	2184, 2.968	935
Amyl salicylate	$C_{12}H_{16}O_3$	2192, 3.600	940
Cetene	$C_{16}H_{32}$	2248, 2.240	934
2-Tetradecanone	$C_{14}H_{28}O$	2264, 2.512	920
Epicedrol	$C_{15}H_{26}O$	2304, 2.800	904
Diphenylamine	$C_{12}H_{11}N$	2344, 3.330	886
Benzophenone	$C_{13}H_{10}O$	2360, 3.247	937
Tributyl phosphate	$C_{12}H_{27}O_4P$	2400, 2.304	917
Cinnamaldehyde, α-pentyl-	$C_{14}H_{18}O$	2400, 2.520	913
8-Heptadecene	$C_{17}H_{34}$	2464, 1.950	919
n-Hexyl salicylate	$C_{13}H_{18}O_3$	2464, 2.448	929
Triaminotriazine	$C_3H_6N_6$	2472, 3.040	882
3-Phenoxy-4-fluorobenzaldehyde	$C_{13}H_9FO_2$	2472, 3.064	886
Tetradecanenitrile	$C_{14}H_{27}N$	2488, 2.288	884
4-(1,1-Dimethylheptyl)phenol	$C_{15}H_{24}O$	2512, 2.528	895
Veramoss	$C_{10}H_{12}O_4$	2520, 3.040	902
Oplopanone	$C_{15}H_{26}O_2$	2592, 2.816	803
Myristic acid	$C_{14}H_{28}O_2$	2616, 2.400	892
Benzyl Benzoate	$C_{14}H_{12}O_2$	2640, 3.360	926
Vertofix Coeur	$C_{17}H_{26}O$	2656, 2.672	856
9-Eicosene, (E)-	$C_{20}H_{40}$	2672, 2.053	903
Benzenemethanol, 3-phenoxy-	$C_{13}H_{12}O_2$	2680, 3.688	842
1H-Indole-3-carboxaldehyde	C_9H_7NO	2720, 5.016	920
Versalide	$C_{18}H_{26}O$	2840, 2.888	872
Methyl palmitate	$C_{17}H_{34}O_2$	2936, 2.455	795
Palmitic acid	$C_{16}H_{32}O_2$	3016, 2.848	898
Phenylethyl salicylate	$C_{15}H_{14}O_3$	3040, 3.920	854
Benzoguanamine	$C_9H_9N_5$	3176, 5.963	825
2-(2H-Benzotriazol-2-yl)-5-methylphenol	$C_{13}H_{11}N_3O$	3272, 4.584	845
Fluoranthene	$C_{16}H_{10}$	3272, 5.208	933
1-Octadecanol	$C_{18}H_{38}O$	3280, 2.808	945
Stearic acid	$C_{18}H_{36}O_2$	3464, 3.112	800
Hexadecanamide	$C_{16}H_{33}NO$	3512, 3.712	890
p-Terphenyl	$C_{18}H_{14}$	3560, 5.192	822
trans-3,5-Dimethoxystilbene	$C_{16}H_{16}O_2$	3656, 5.136	877

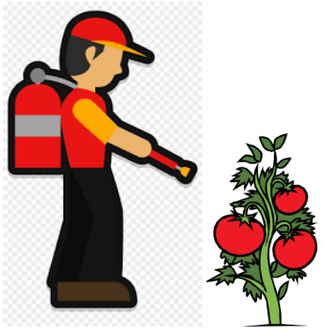
Name	Formula	R.T. (s)	Similarity
2,6-Diphenylpyridine	$C_{17}H_{13}N$	3672, 5.640	795
1,8-Diazacyclotetradecane-2,7-dione	$C_{12}H_{22}N_2O_2$	3704, 7.416	874
Tributyl acetylcitrate	$C_{20}H_{34}O_8$	3712, 3.592	874
Tert-octyldiphenylamine	$C_{20}H_{27}N$	3776, 4.472	768
N-Methyl-N-benzyltetradecanamine	$C_{22}H_{39}N$	3864, 3.228	850
Methyl dehydroabietate	$C_{21}H_{30}O_2$	3936, 4.576	864
Octadecanamide	$C_{18}H_{37}NO$	4016, 4.016	790
Benzo[ghi]fluoranthene	$C_{18}H_{10}$	4072, 6.888	879
Triphenyl phosphate	$C_{18}H_{15}O_4P$	4080, 6.432	878
Diphenyl 2-ethylhexyl phosphate	$C_{20}H_{27}O_4P$	4152, 4.824	802
Isopropylphenyl diphenyl phosphate	$C_{21}H_{21}O_4P$	4432, 6.004	815
Benz[a]anthracene, 7-methyl-	$C_{19}H_{14}$	4608, 7.312	865
Tri-m-tolylphosphate	$C_{21}H_{21}O_4P$	4800, 6.536	847
Tri-p-cresyl phosphate	$C_{21}H_{21}O_4P$	4880, 6.568	761
Perylene	$C_{20}H_{12}$	5032, 8.200	924
Squalene	$C_{30}H_{50}$	5152, 3.480	924
Cholesta-4,6-dien-3-ol, (3β)-	$C_{27}H_{44}O$	5272, 4.364	861
Cholesta-3,5-diene	$C_{27}H_{44}$	5328, 4.288	910
Piperine	$C_{17}H_{19}NO_3$	5344, 8.344	921
17αH-Trisnorhopane	$C_{27}H_{46}$	5384, 4.864	805
Benzo[b]chrysene	$C_{22}H_{14}$	5416, 7.983	790
p,p'-Dioctyldiphenylamine	$C_{28}H_{43}N$	5456, 4.752	909
28-Nor-17α(H)-hopane	$C_{29}H_{50}$	5712, 4.632	900
Cholesterol	$C_{27}H_{46}O$	5848, 4.848	895
α-Tocopheryl acetate	$C_{31}H_{52}O_3$	6040, 4.160	904
Cholesta-3,5-dien-7-one	$C_{27}H_{42}O$	6072, 5.394	922
Campesterol	$C_{28}H_{48}O$	6112, 4.872	844
Cholest-4-en-3-one	$C_{27}H_{44}O$	6160, 5.232	936
17α(H),21β(H)-Homohopane	$C_{31}H_{54}$	6168, 4.648	846
Stigmasterol	$C_{29}H_{48}O$	6184, 4.824	808
Cholesta-4,6-dien-3-one	$C_{27}H_{42}O$	6224, 5.416	876
γ-Sitosterol	$C_{29}H_{50}O$	6320, 4.880	919
Stigmasta-3,5-dien-7-one	$C_{29}H_{46}O$	6528, 5.765	825
Cholesterol, 7-oxo-	$C_{27}H_{44}O_2$	6568, 6.768	913

Similarity Ave. 880/1000

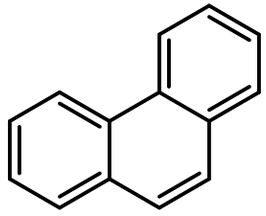
Pollutants

Polyaromatic Hydrocarbons

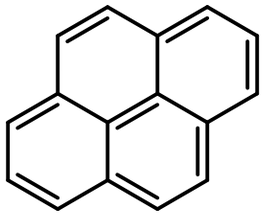
Flame Retardants



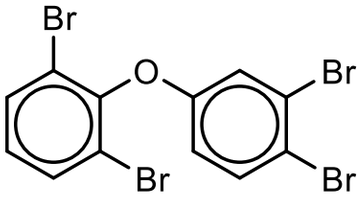
Pesticides



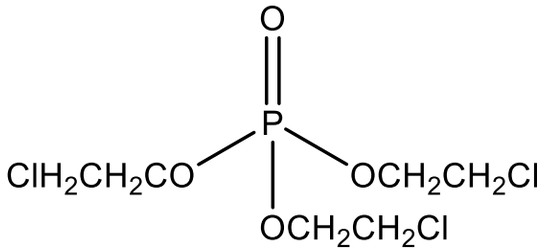
Phenanthrene



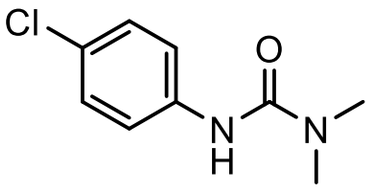
Pyrene



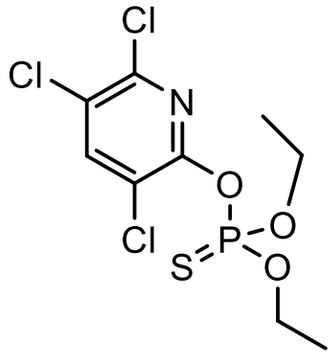
BDE-71



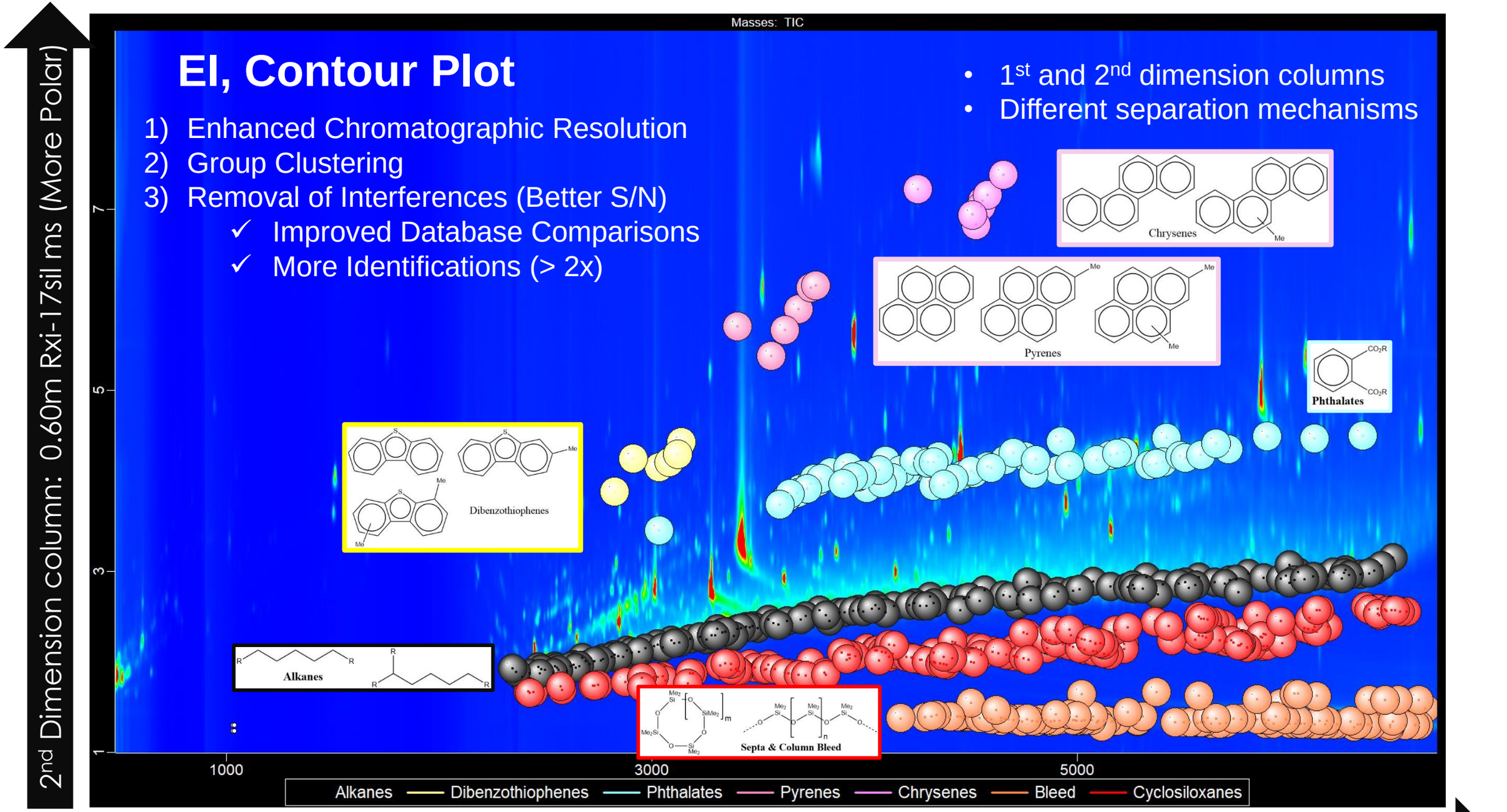
TCEP



Chlorfenidim



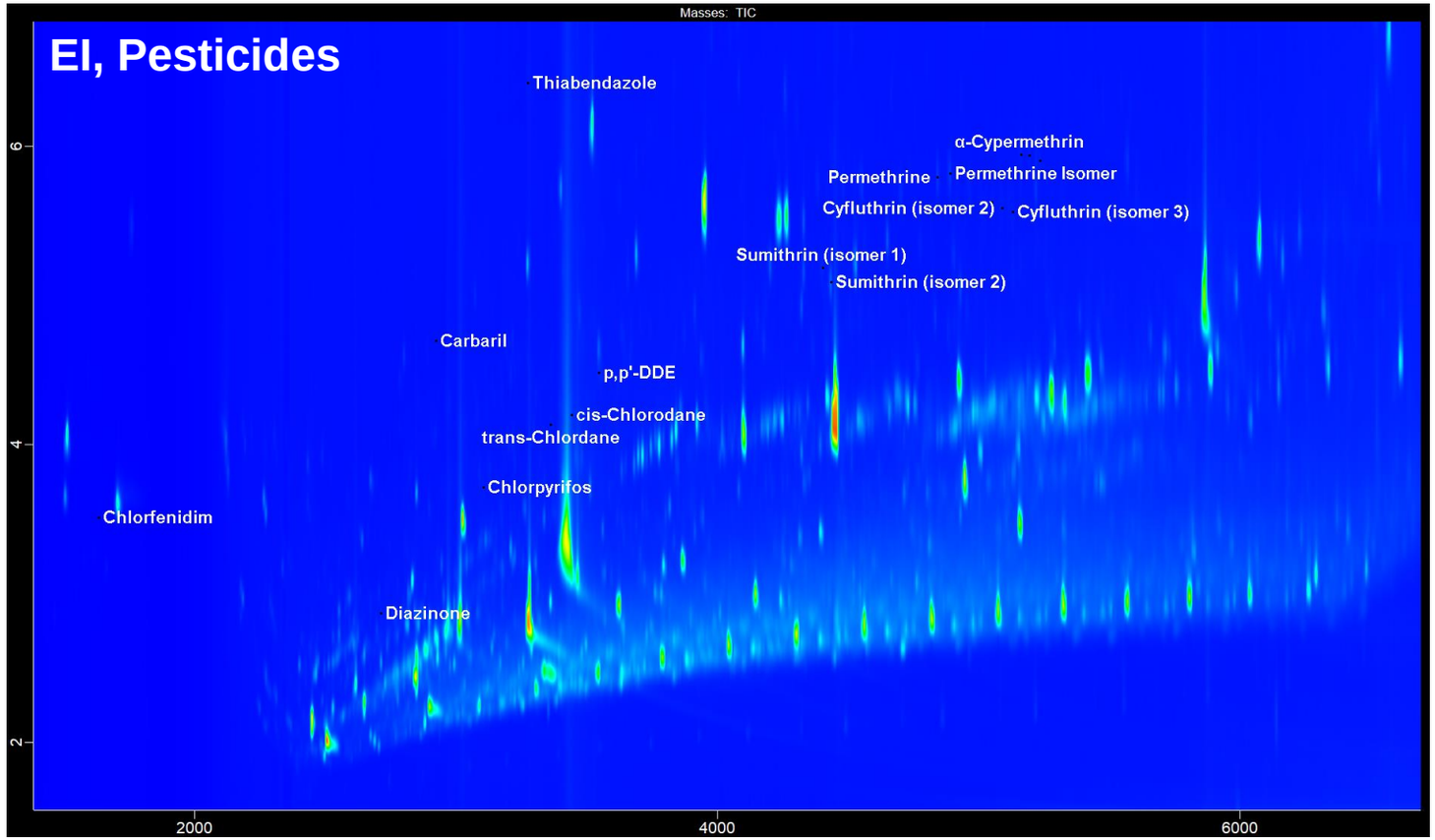
Chlorpyrifos


Masses: TIC
EI, Contour Plot
1) Enhanced Chromatographic Resolution
2) Group Clustering
3) Removal of Interferences (Better S/N)
✓ Improved Database Comparisons
✓ More Identifications (> 2x)
• 1st and 2nd dimension columns
• Different separation mechanisms
Chrysenes
Pyrenes
Phthalates
Dibenzothiophenes
Alkanes
Septa & Column Bleed
2nd Dimension column: 0.60m Rxi-17sil ms (More Polar)
1st Dimension column: 30m Rxi-5ms (Non-Polar)
1
3
5
7
1000
3000
5000
Alkanes
Dibenzothiophenes
Phthalates
Pyrenes
Chrysenes
Bleed
Cyclosiloxanes

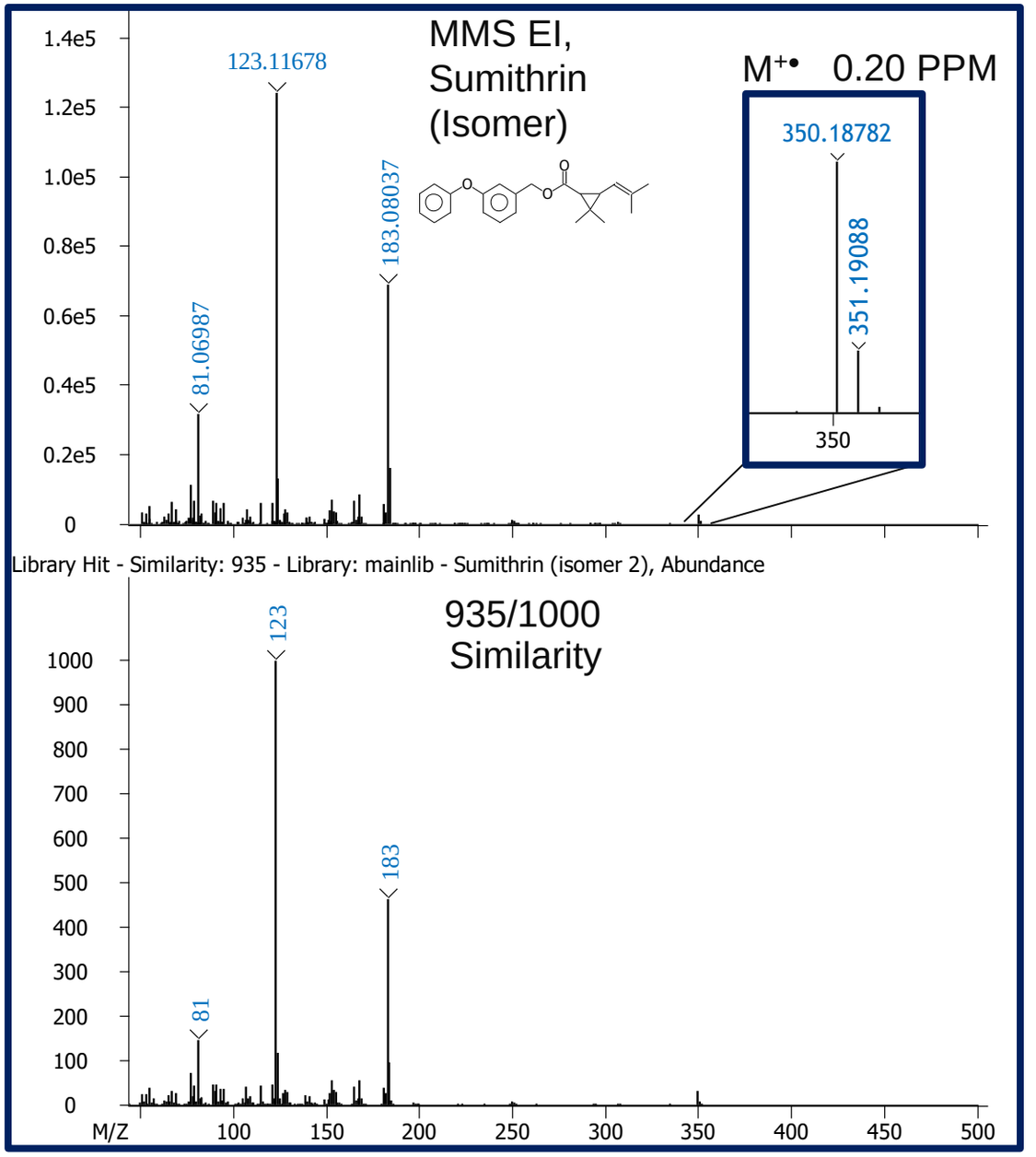
Selected Pesticides

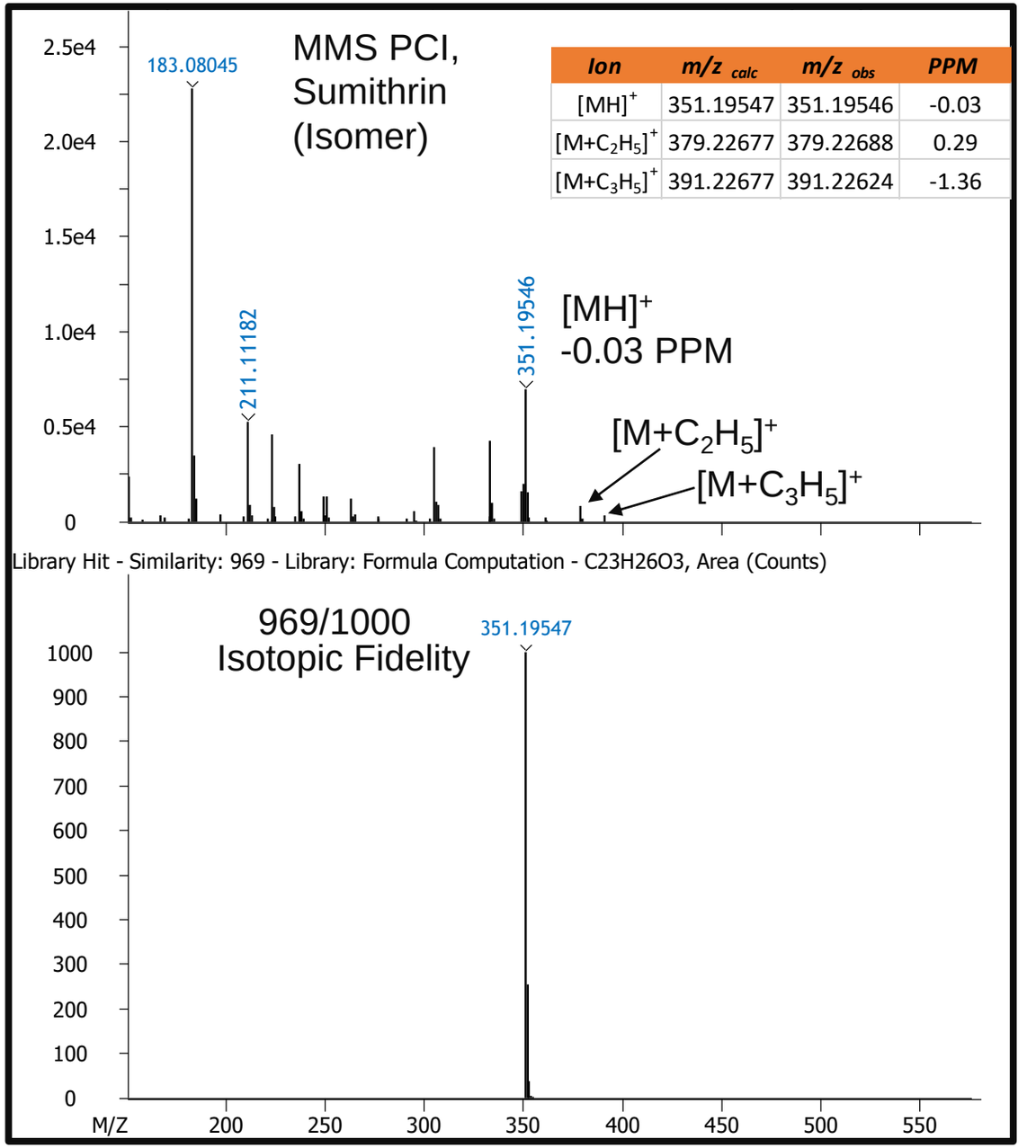
Name	*Formula*	*R.T. (s)*	*Similarity*	*Mass Accuracy (ppm)*
Chlorfenidim	$C_9H_{11}ClN_2O$	1632, 3.512	811	N/A
Diazinone	$C_{12}H_{21}N_2O_3PS$	2712, 2.872	818	-0.84
Carbaril	$C_{12}H_{11}NO_2$	2920, 4.696	818	N/A
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	3104, 3.712	827	N/A
Thiabendazole	$C_{10}H_7N_3S$	3272, 6.424	929	0.66
trans-Chlordane	$C_{10}H_6Cl_8$	3360, 4.136	788	N/A
cis-Chlorodane	$C_{10}H_6Cl_8$	3440, 4.200	772	N/A
p,p'-DDE	$C_{14}H_8Cl_4$	3544, 4.480	855	-0.62
Sumithrin (isomer 1)	$C_{23}H_{26}O_3$	4400, 5.184	871	-0.21
Sumithrin (isomer 2)	$C_{23}H_{26}O_3$	4432, 5.084	935	0.2
Permethrine	$C_{21}H_{20}Cl_2O_3$	4840, 5.792	909	-0.28
Permethrine Isomer	$C_{21}H_{20}Cl_2O_3$	4888, 5.816	914	-0.55
Cyfluthrin	$C_{22}H_{18}Cl_2FNO_3$	5048, 5.624	751	N/A
Cyfluthrin (isomer 2)	$C_{22}H_{18}Cl_2FNO_3$	5088, 5.584	805	N/A
Cyfluthrin (isomer 3)	$C_{22}H_{18}Cl_2FNO_3$	5128, 5.560	817	N/A
α-Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	5160, 5.944	844	N/A
β-Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	5192, 5.936	883	N/A
Cypermethrin (isomer 3)	$C_{22}H_{19}Cl_2NO_3$	5232, 5.904	869	N/A

Ave. Similarity: 845/1000



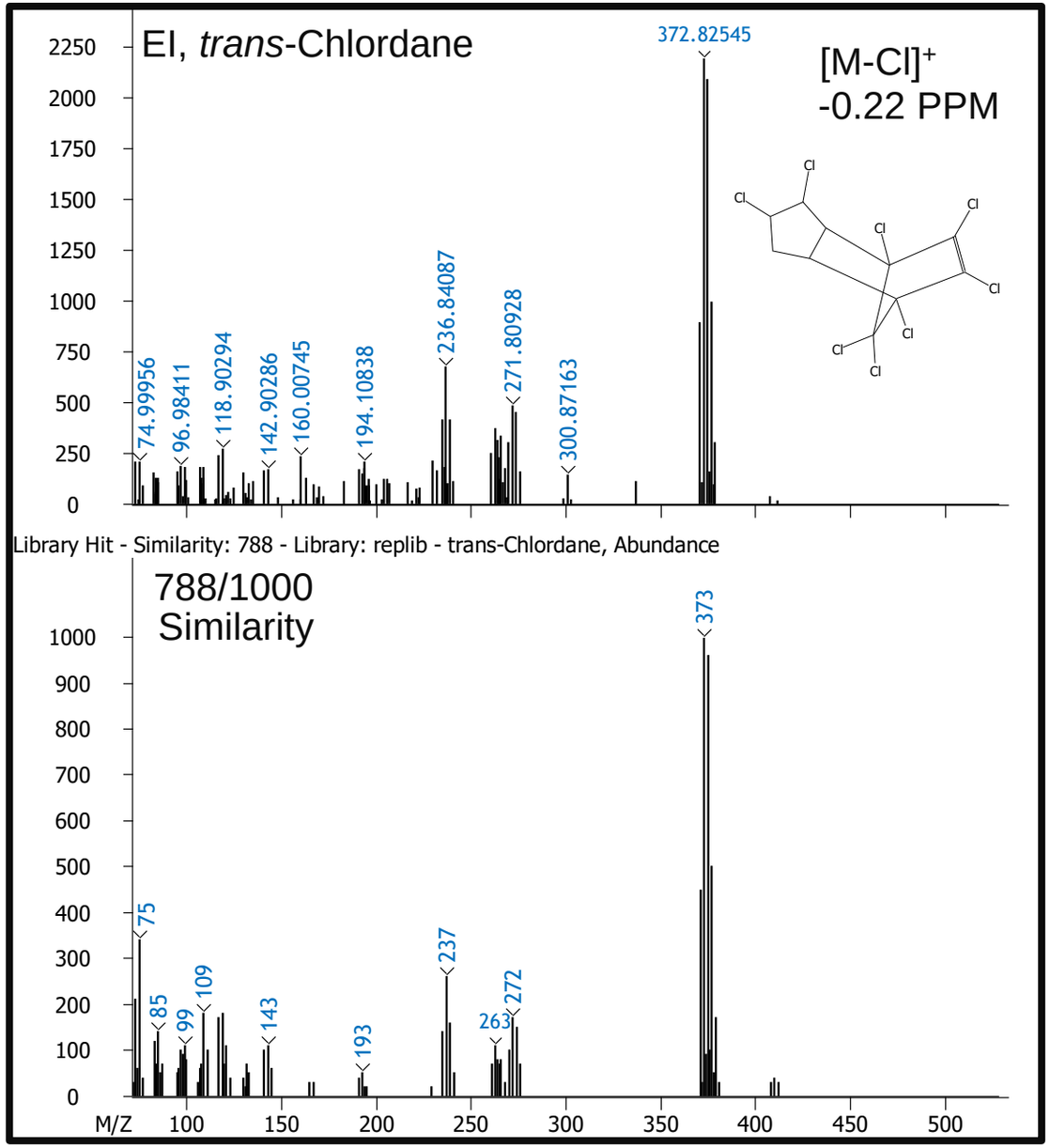
Pesticide Example 1: Complementary EI & PCI



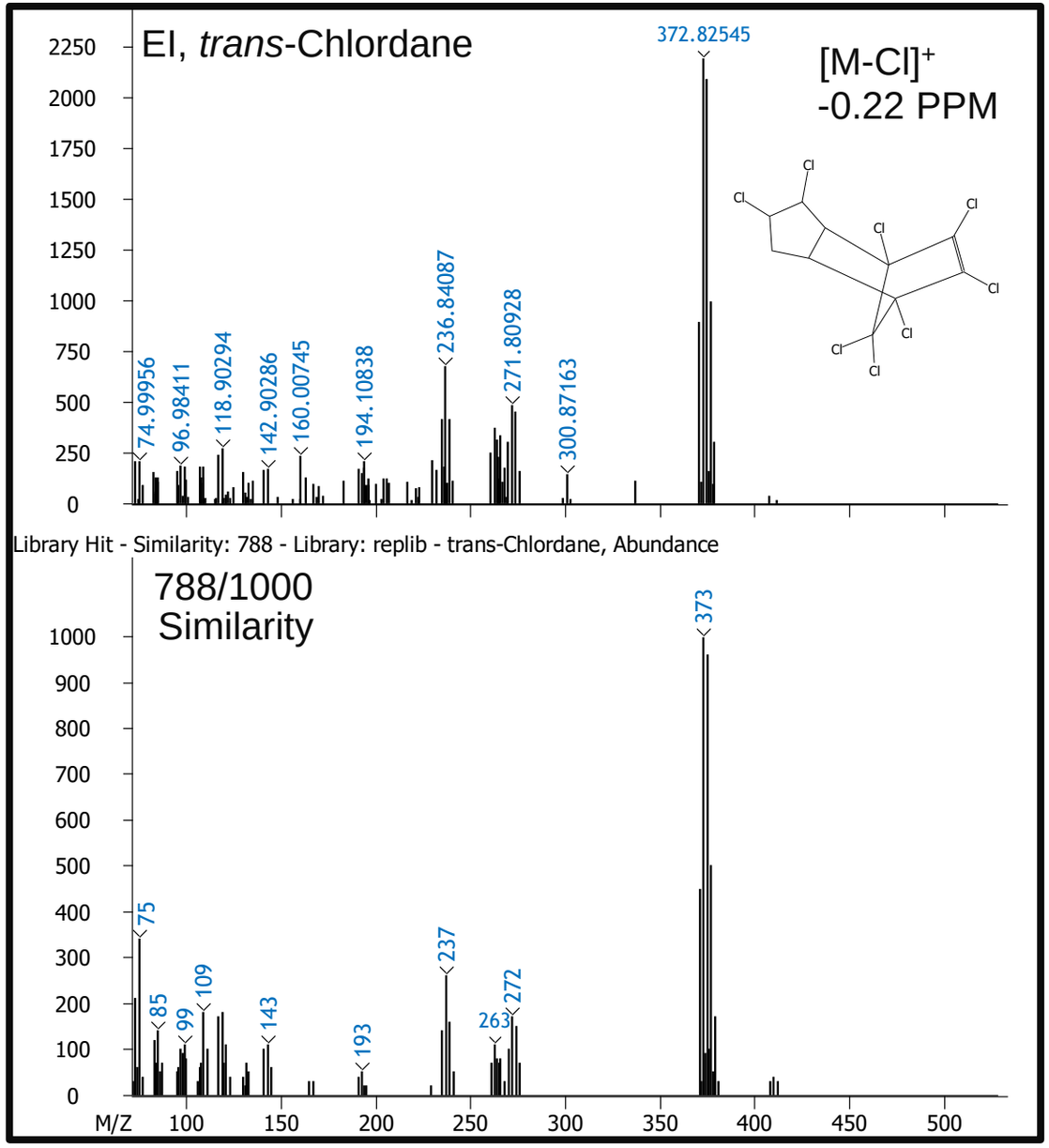


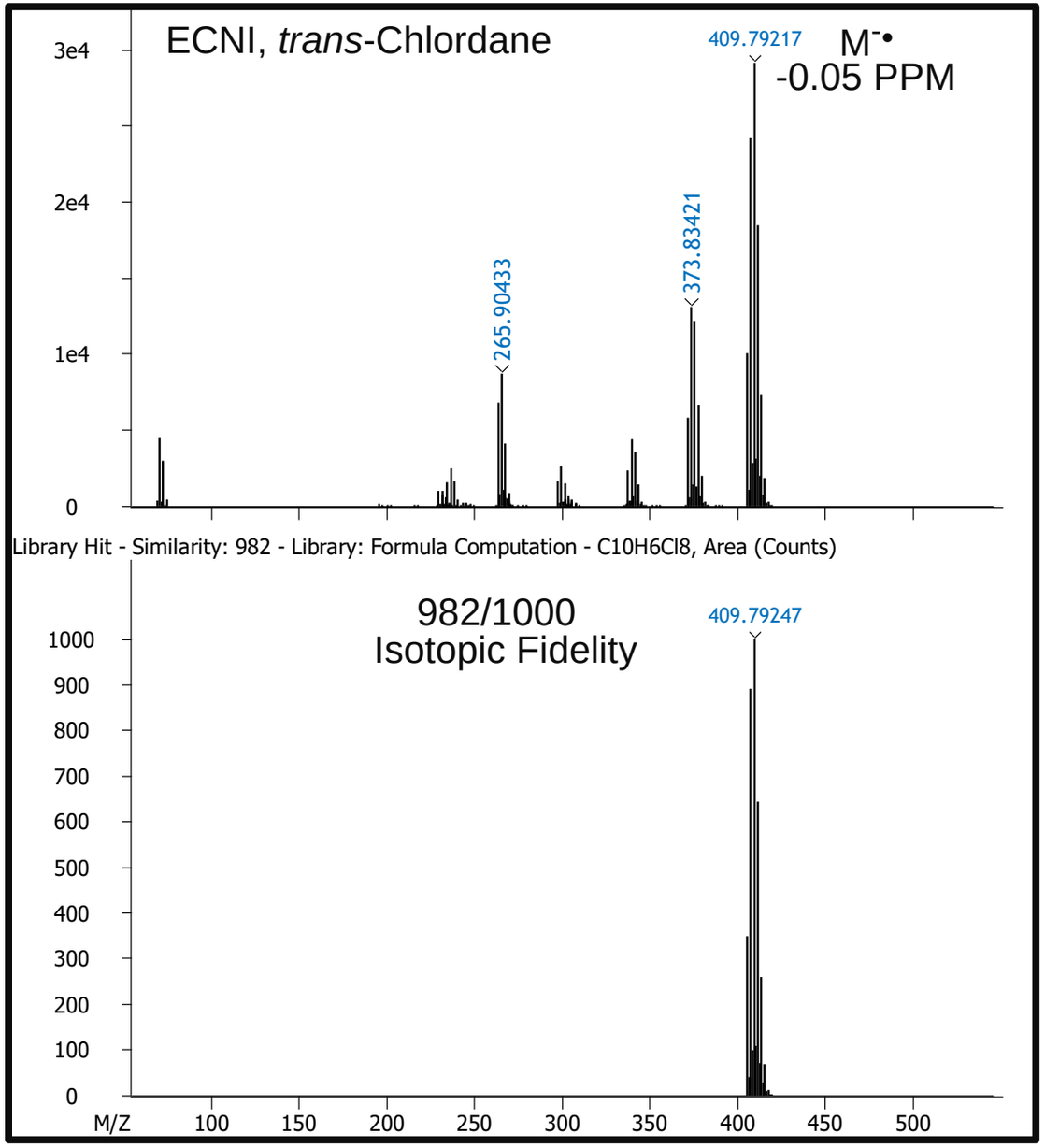
Ion	m/z calc	m/z obs	PPM
$[MH]^+$	351.19547	351.19546	-0.03
$[M+C_2H_5]^+$	379.22677	379.22688	0.29
$[M+C_3H_5]^+$	391.22677	391.22624	-1.36

Pesticide Example 2: *trans*-Chlordane, EI



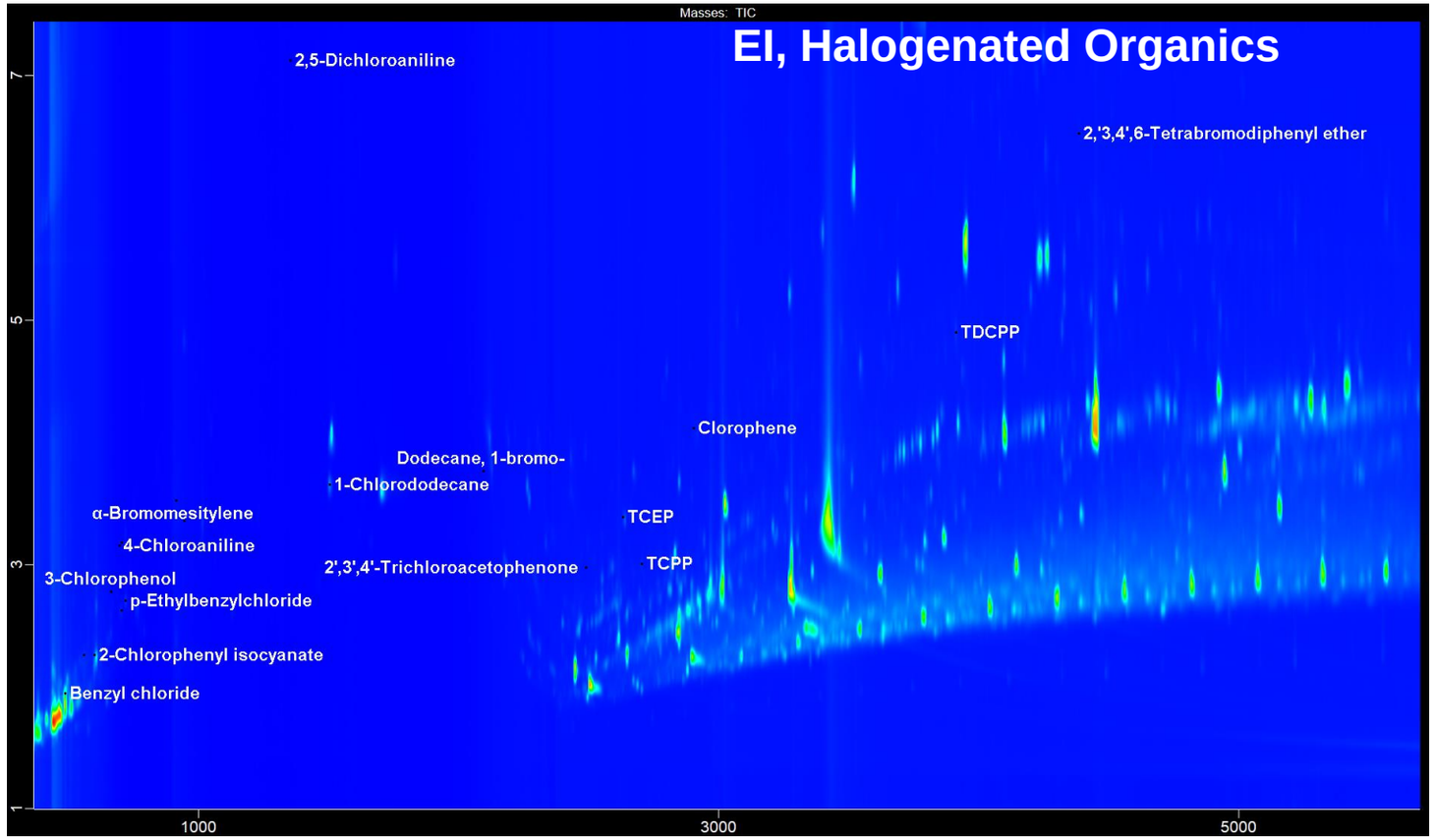
Pesticide Example 2: *trans*-Chlordane, EI & ECNI





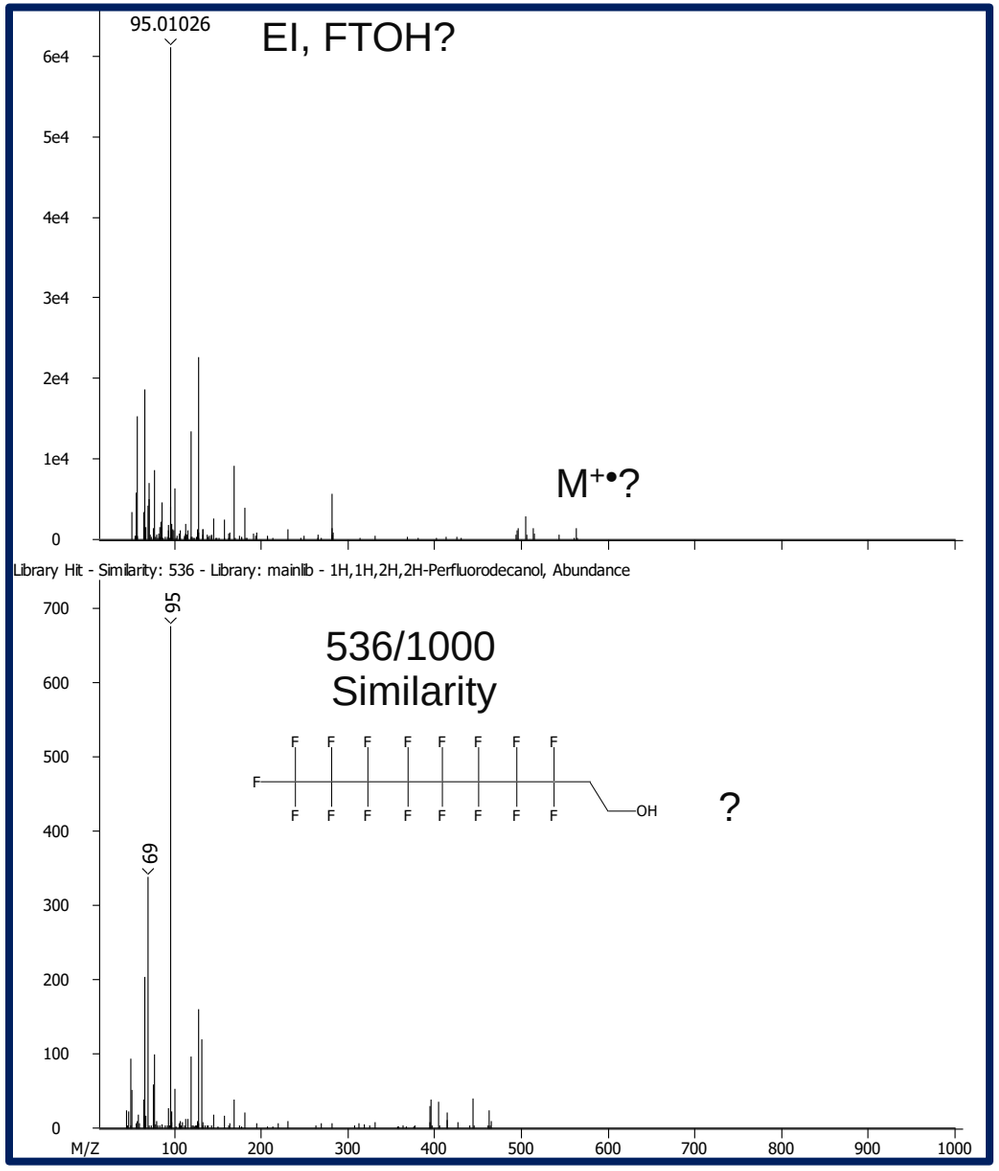
Representative Halogenated Organics

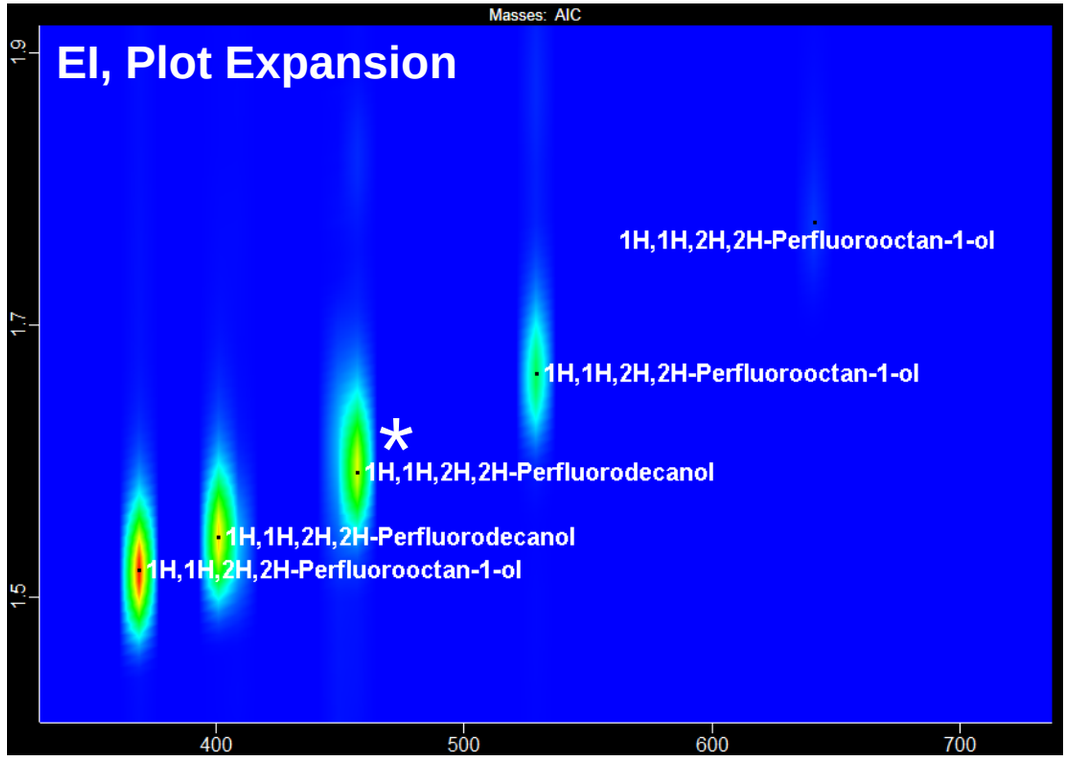
Name	*Formula*	*R.T. (s)*	*Similarity*	*PPM*
Benzyl chloride	C_7H_7Cl	488, 1.952	873	0.87
Benzyl Bromide	C_7H_7Br	560, 2.263	866	0.54
3-Chlorophenyl isocyanate	C_7H_4ClNO	600, 2.264	927	0.31
3-Chlorophenol	C_6H_5ClO	664, 2.784	896	1.32
4-Chloroaniline	C_6H_6ClN	696, 3.160	913	1.52
p-Ethylbenzylchloride	$C_9H_{11}Cl$	720, 2.704	931	0.21
α-Bromomesitylene	$C_9H_{11}Br$	912, 3.528	861	-0.23
3,4-Dichlorophenyl isocyanate	$C_7H_3Cl_2NO$	944, 3.358	820	1.93
2,5-Dichloroaniline	$C_6H_5Cl_2N$	984, 7.124	933	0.59
1-Chlorododecane	$C_{12}H_{25}Cl$	1504, 3.656	949	-0.8
1-Bromododecane	$C_{12}H_{25}Br$	2096, 3.768	873	N/A
2',3',4'-Trichloroacetophenone	$C_8H_5Cl_3O$	2488, 2.976	781	N/A
TCEP	$C_6H_{12}Cl_3O_4P$	2632, 3.392	893	N/A
TCPP	$C_9H_{18}Cl_3O_4P$	2728, 3.064	918	N/A
Chorophene	$C_{13}H_{11}ClO$	2904, 4.120	824	1.22
TDCPP	$C_9H_{15}Cl_6O_4P$	3912, 4.904	902	N/A
2,3',4'6-Tetrabromodiphenyl ether	$C_{12}H_6Br_4O$	4384, 6.528	831	0.34
2,3',4,4',5-Pentabromodiphenyl ether	$C_{12}H_5Br_5O$	5056, 7.296	892	-0.45



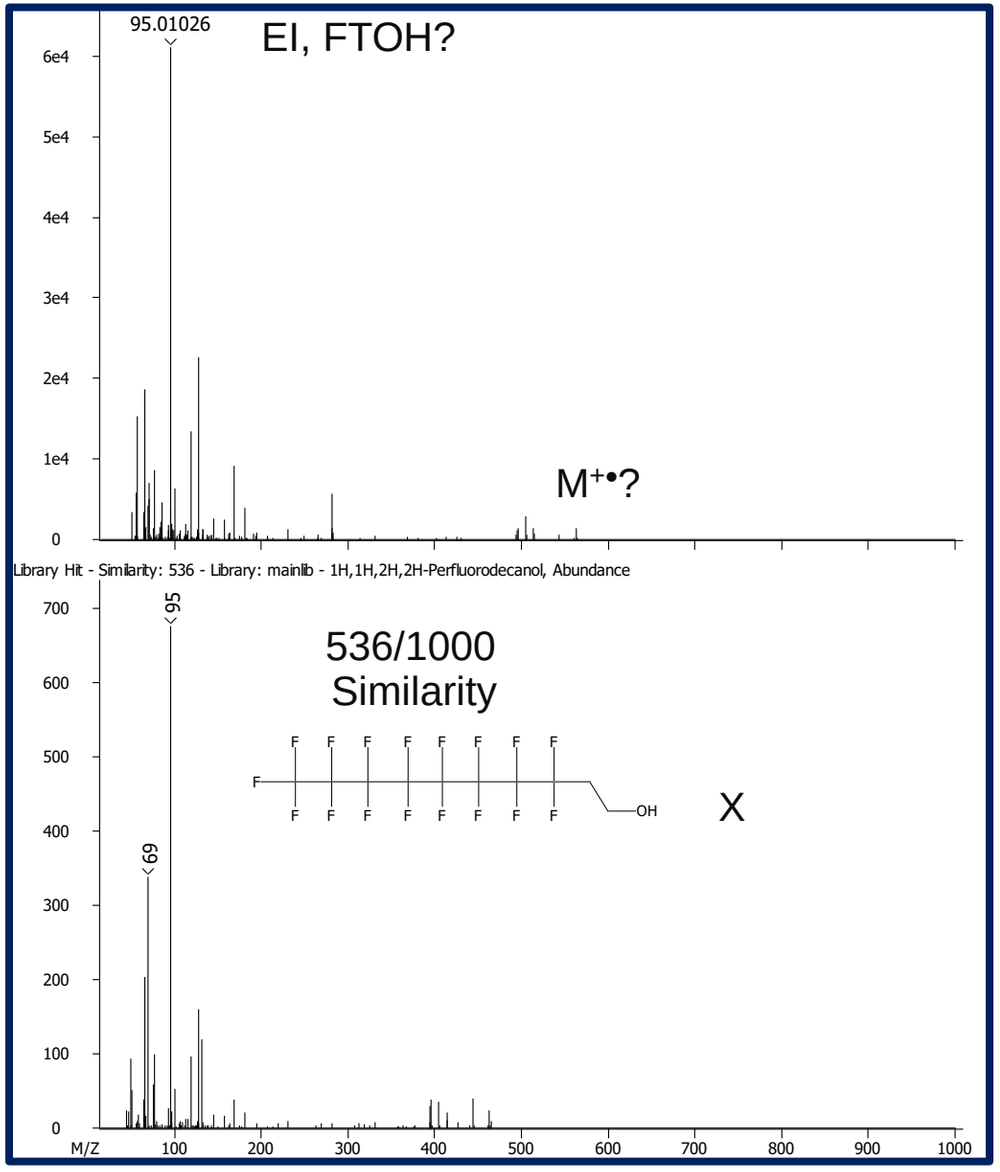
Ave. Similarity: 876/1000

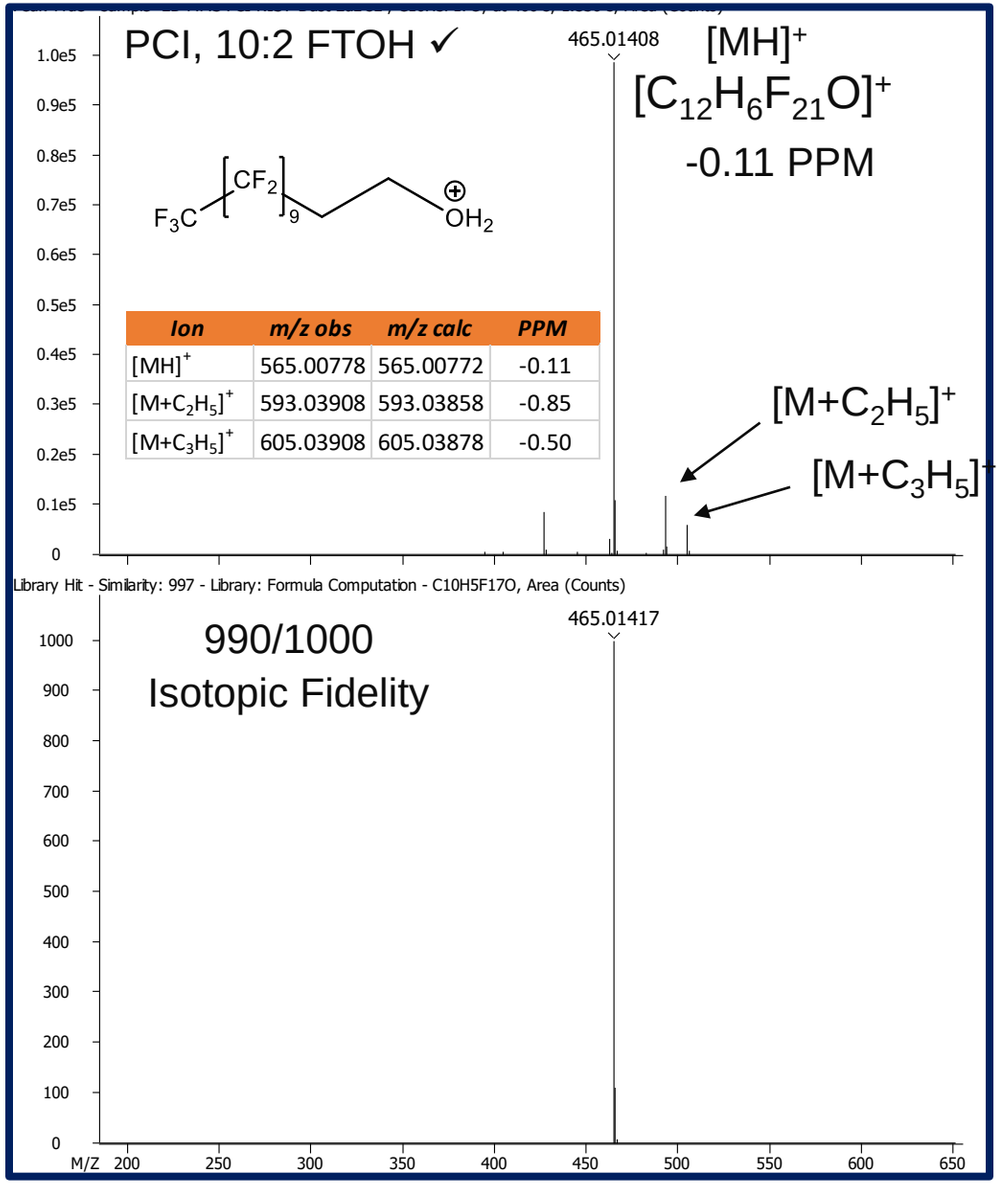
EI: Unknown FTOHs



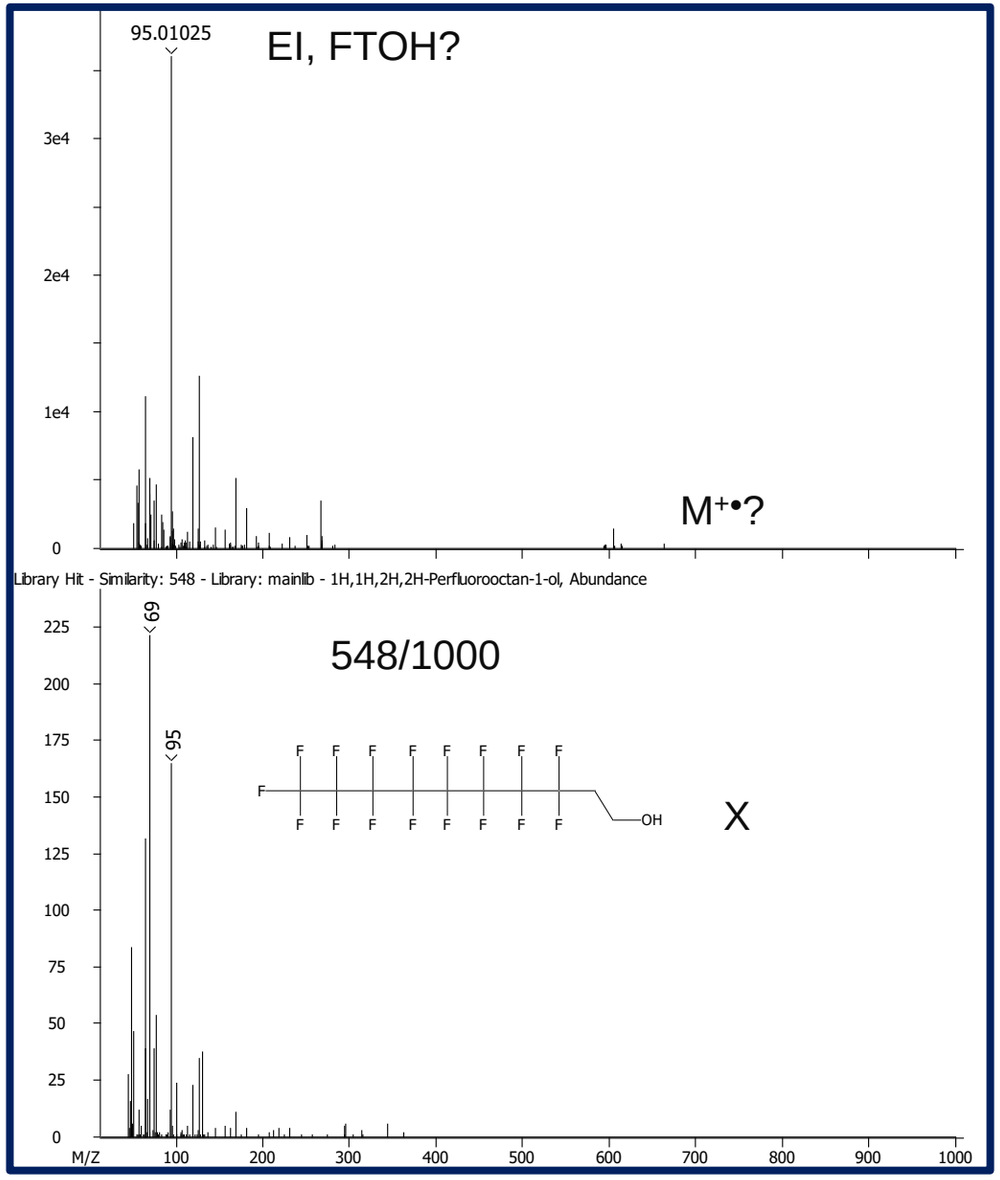


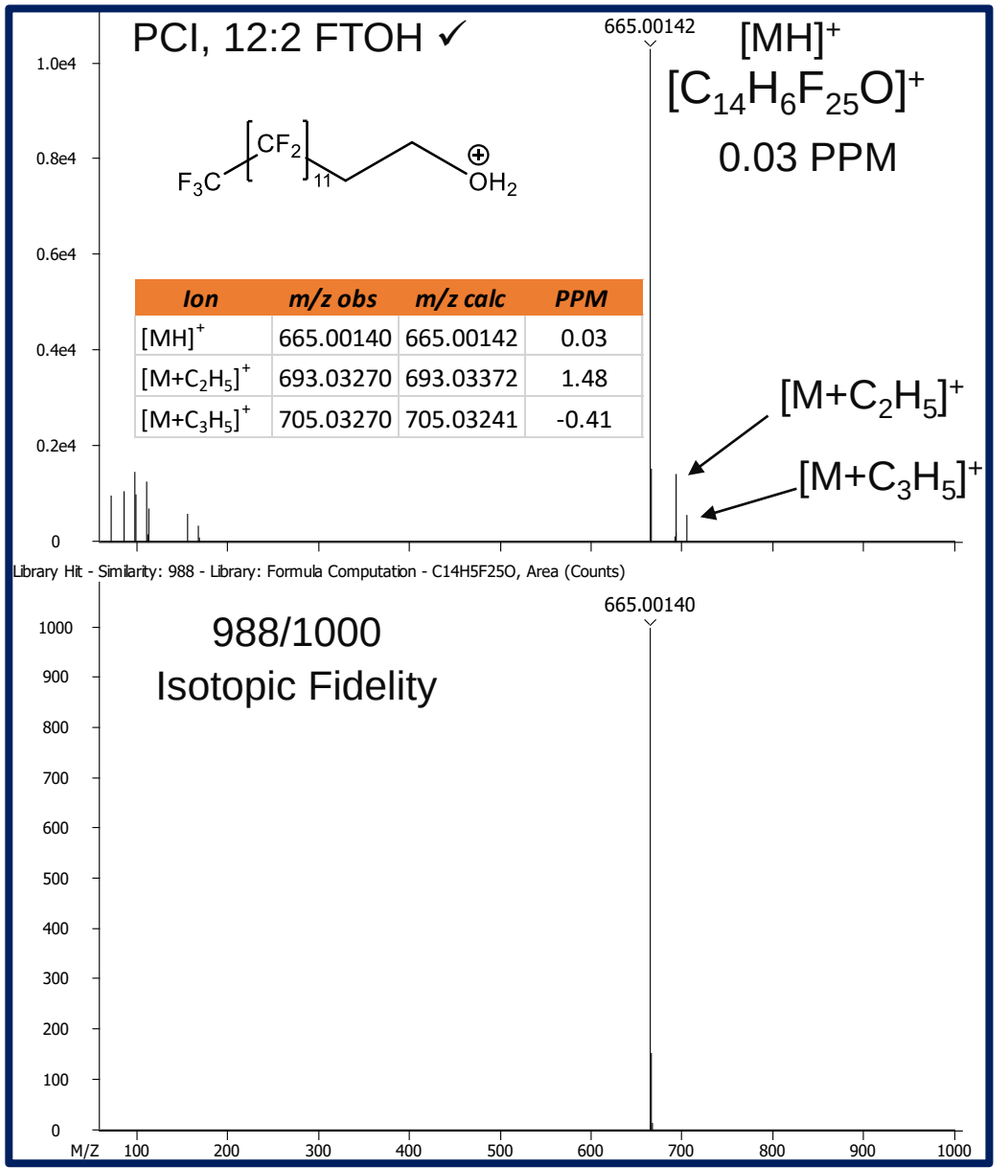
EI & PCI: Annotated 10:2 FTOH



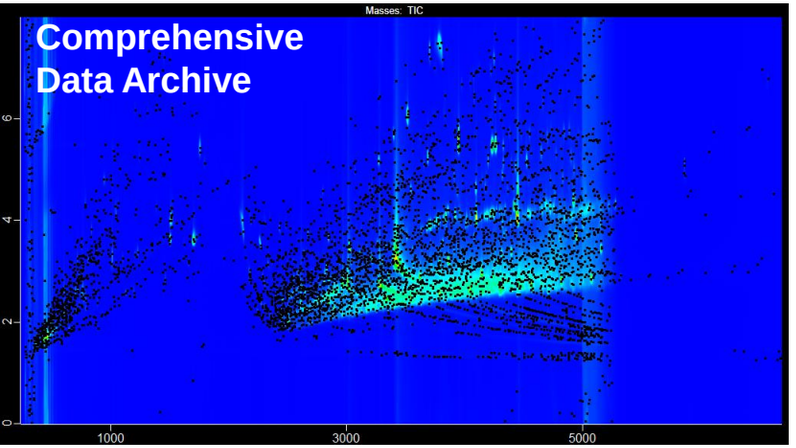


EI: Annotated 12:2 FTOH

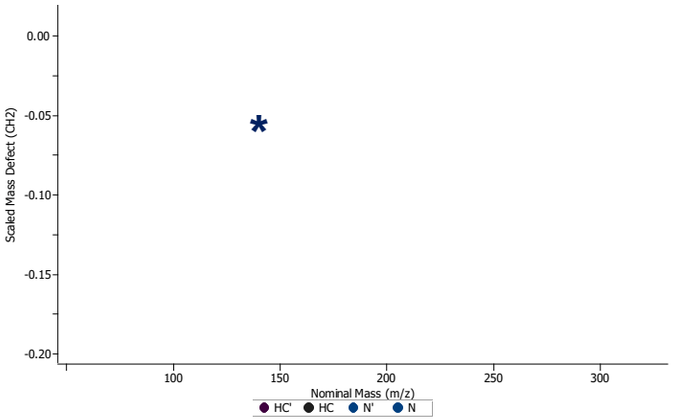




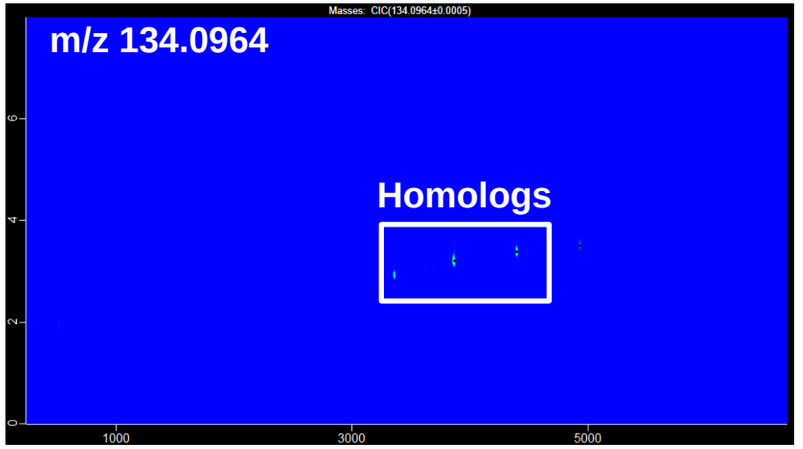
Part 2
Retrospective Analysis of Data Archives



Peak Find

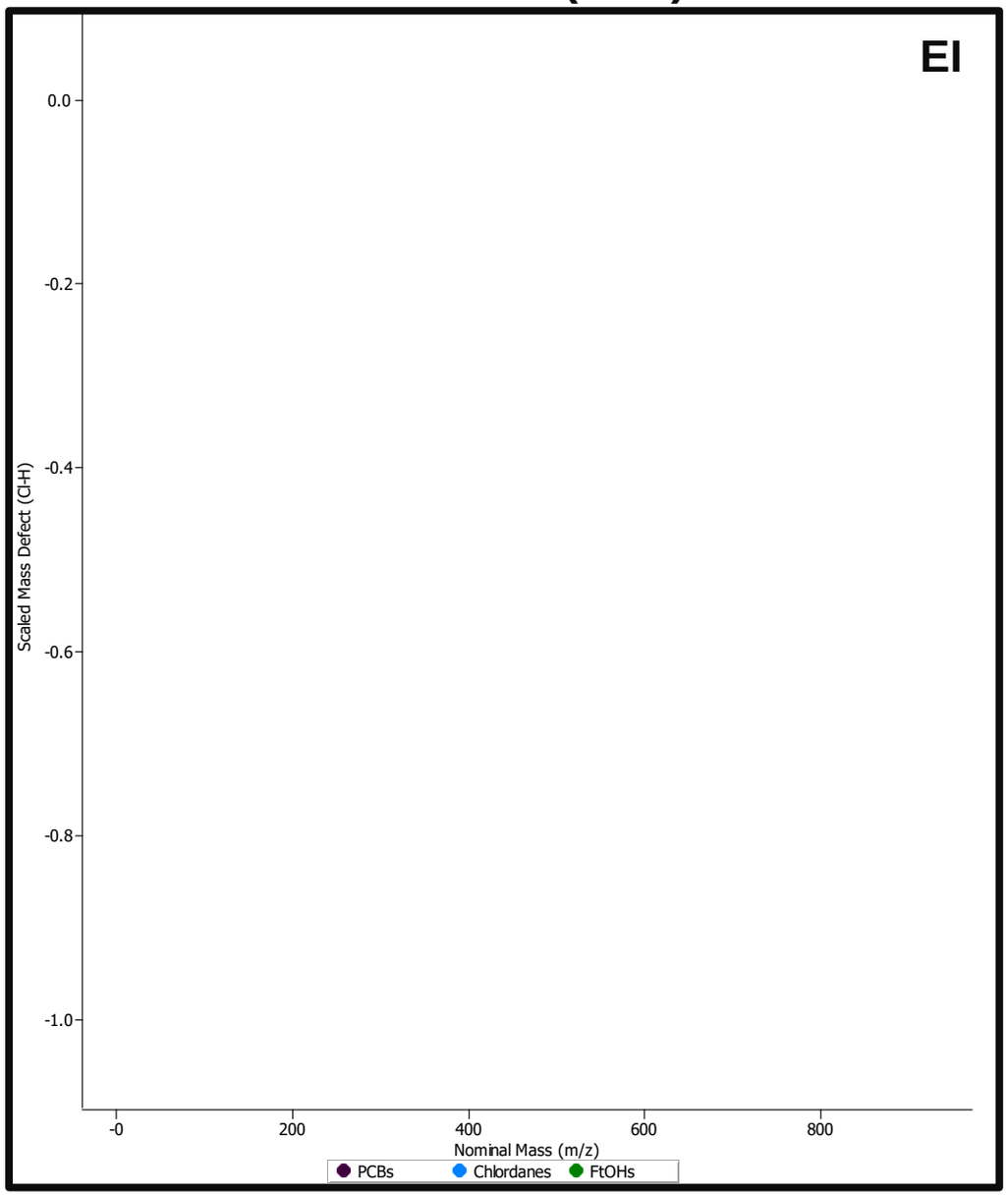


Mass Defect



Target Analyte Finding

Scaled Mass Defect Plots



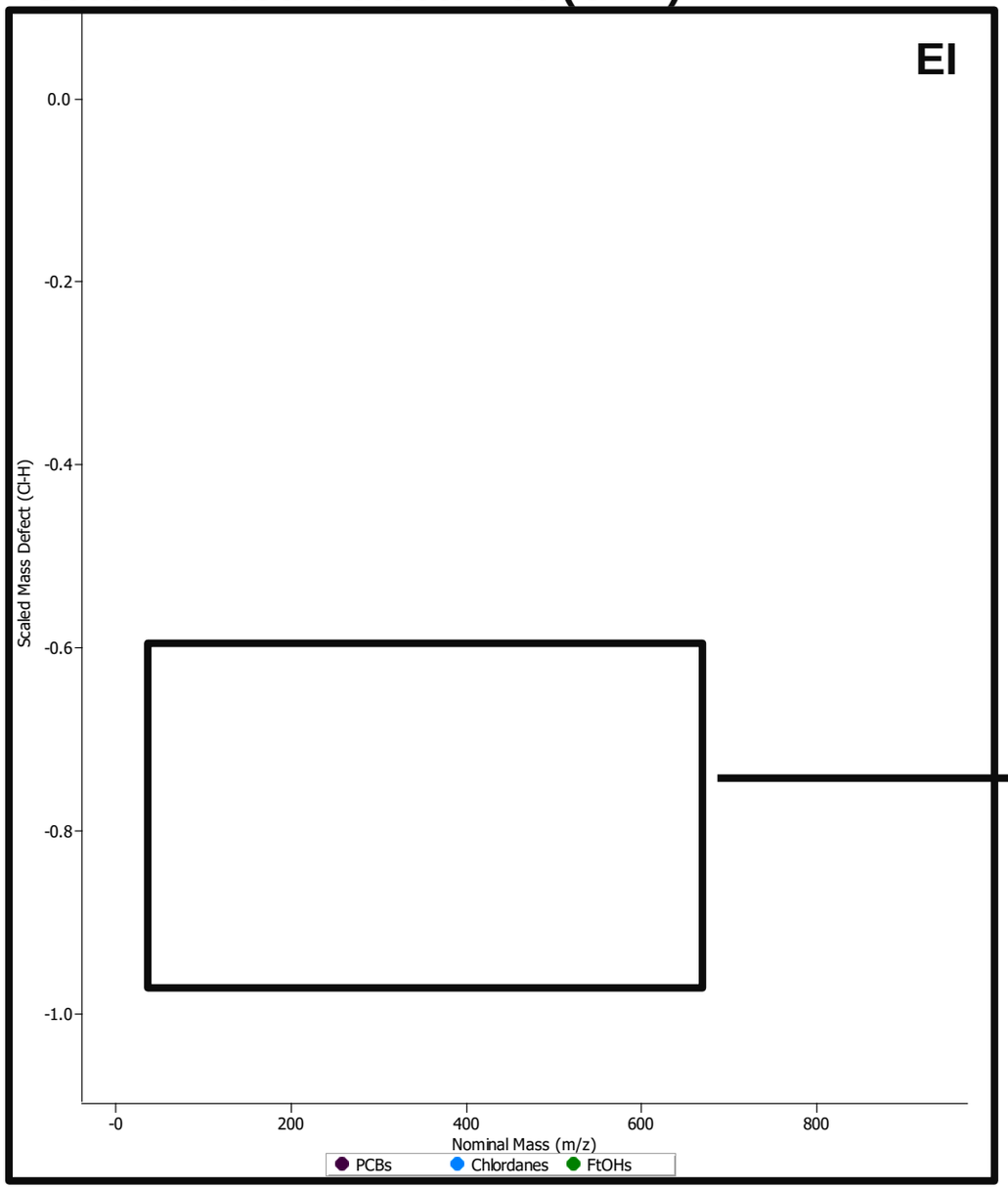
Cl-H defect = Cl-H mass - nominal mass

Cl-H mass = IUPAC mass x (34/33.96102)

Taguchi, et al, *J. Am. Mass Spectrom,* **2010**, *21*, 1918-1921.

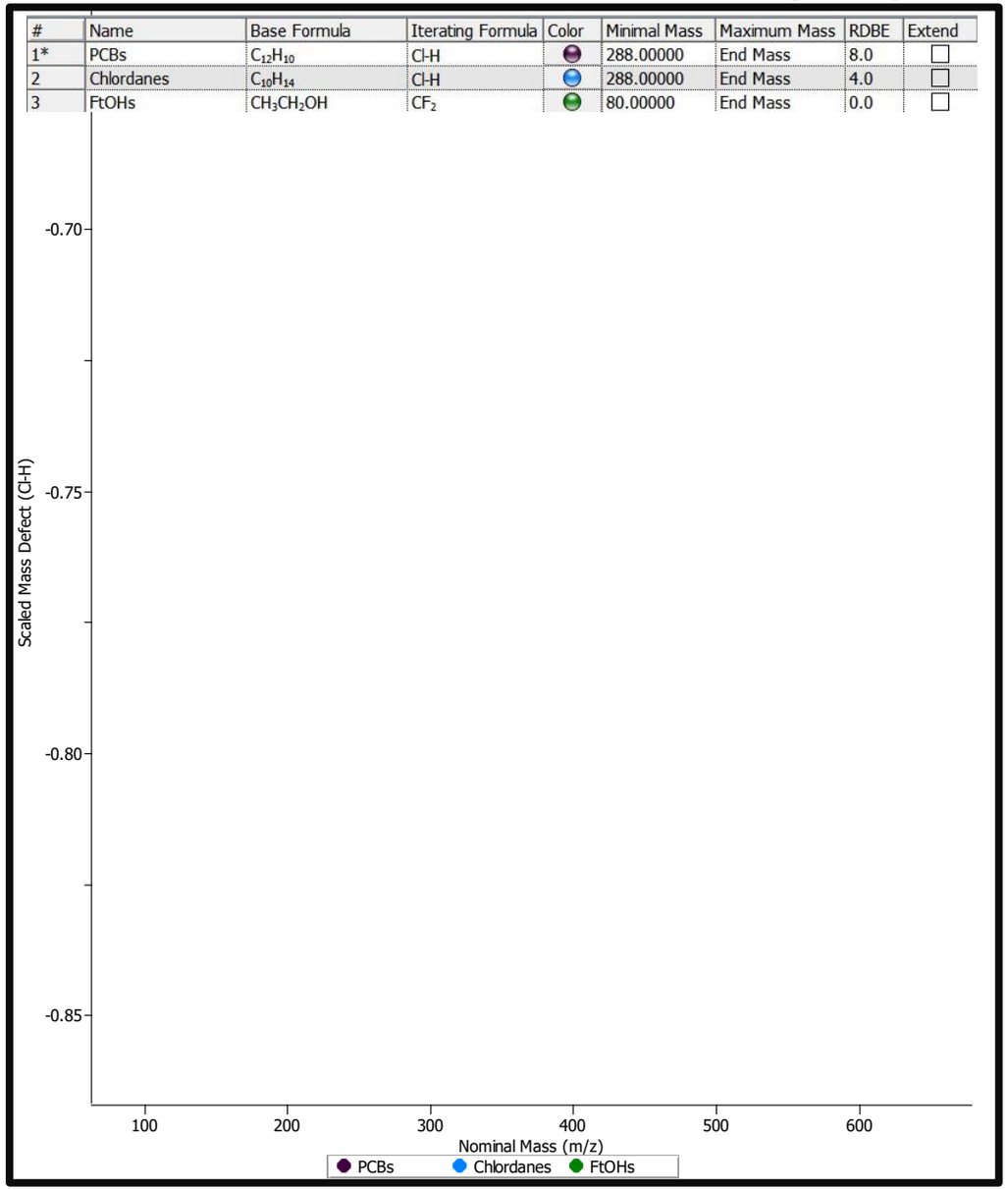
Spectral Analysis Tools

Scaled Mass Defect Plot (Cl-H)



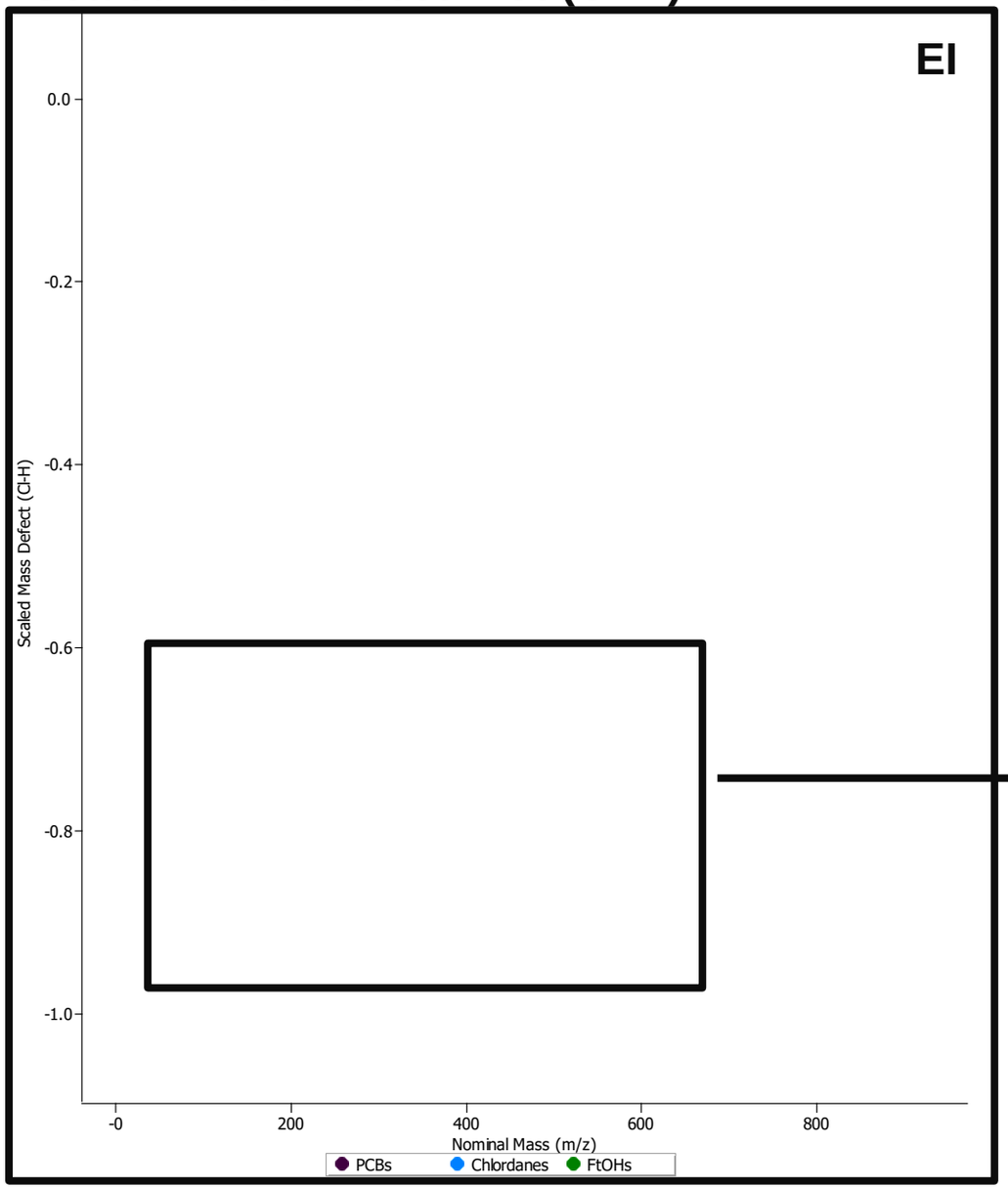
Filtered & Scaled Mass Defect Plot (Cl-H)

#	Name	Base Formula	Iterating Formula	Color	Minimal Mass	Maximum Mass	RDBE	Extend
1*	PCBs	$C_{12}H_{10}$	Cl-H		288.00000	End Mass	8.0	☐
2	Chlordanes	$C_{10}H_{14}$	Cl-H		288.00000	End Mass	4.0	☐
3	FtOHs	CH_3CH_2OH	CF_2		80.00000	End Mass	0.0	☐



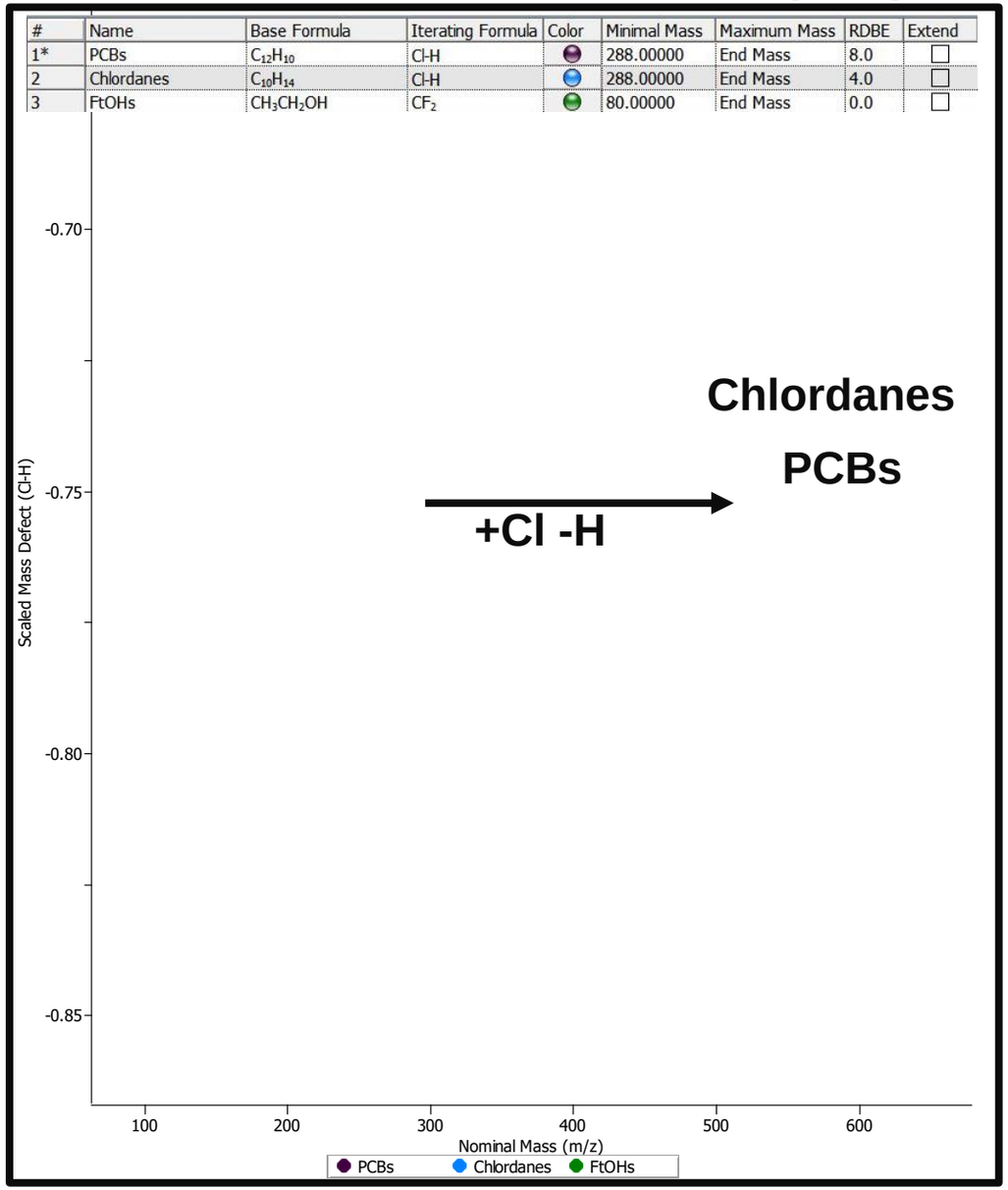
SMD (Cl-H): PCBs & Chlordanes

Scaled Mass Defect Plot (Cl-H)



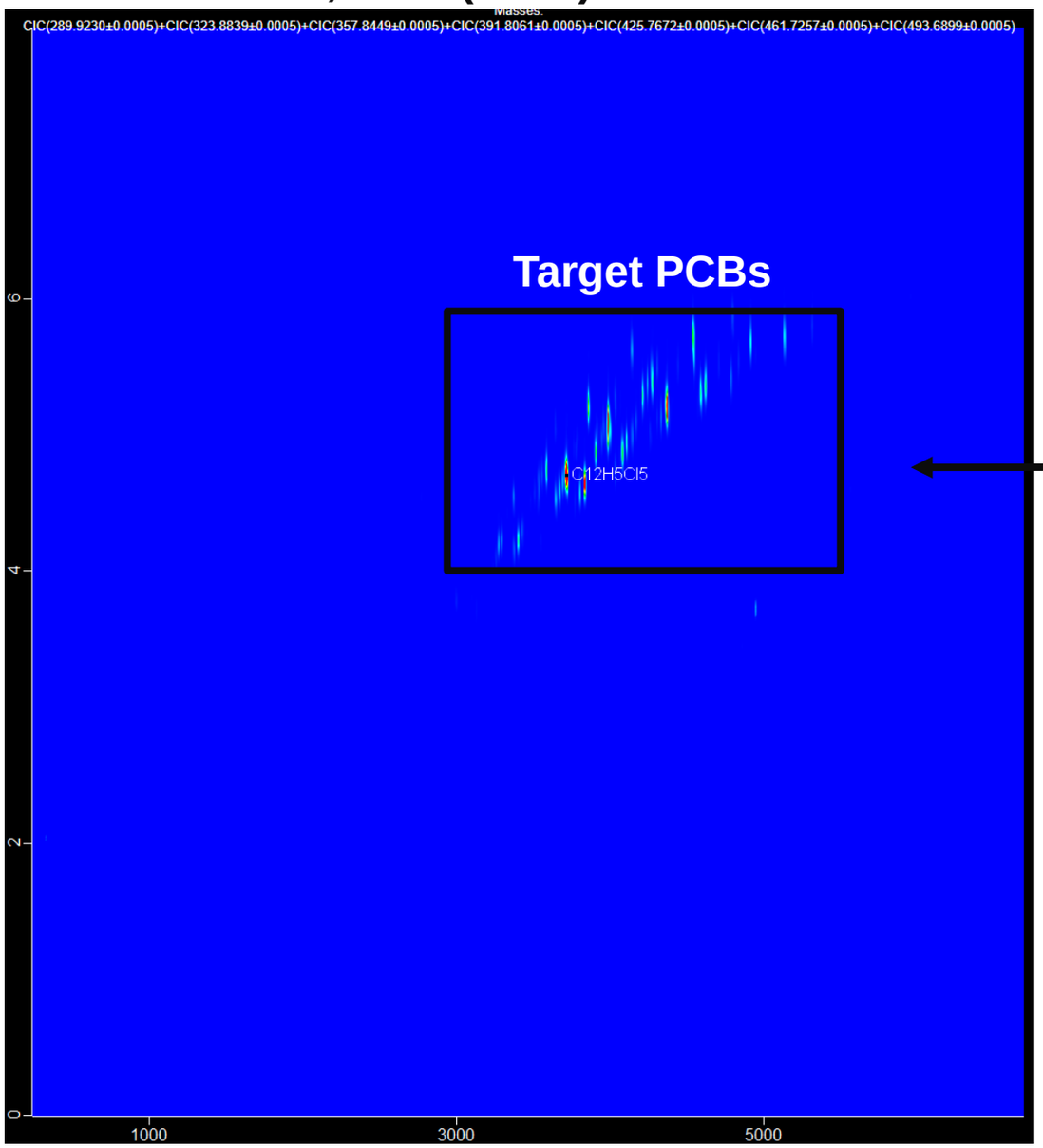
Filtered & Scaled Mass Defect Plot (Cl-H)

#	Name	Base Formula	Iterating Formula	Color	Minimal Mass	Maximum Mass	RDBE	Extend
1*	PCBs	$C_{12}H_{10}$	Cl-H		288.00000	End Mass	8.0	
2	Chlordanes	$C_{10}H_{14}$	Cl-H		288.00000	End Mass	4.0	
3	FtOHs	CH_3CH_2OH	CF_2		80.00000	End Mass	0.0	



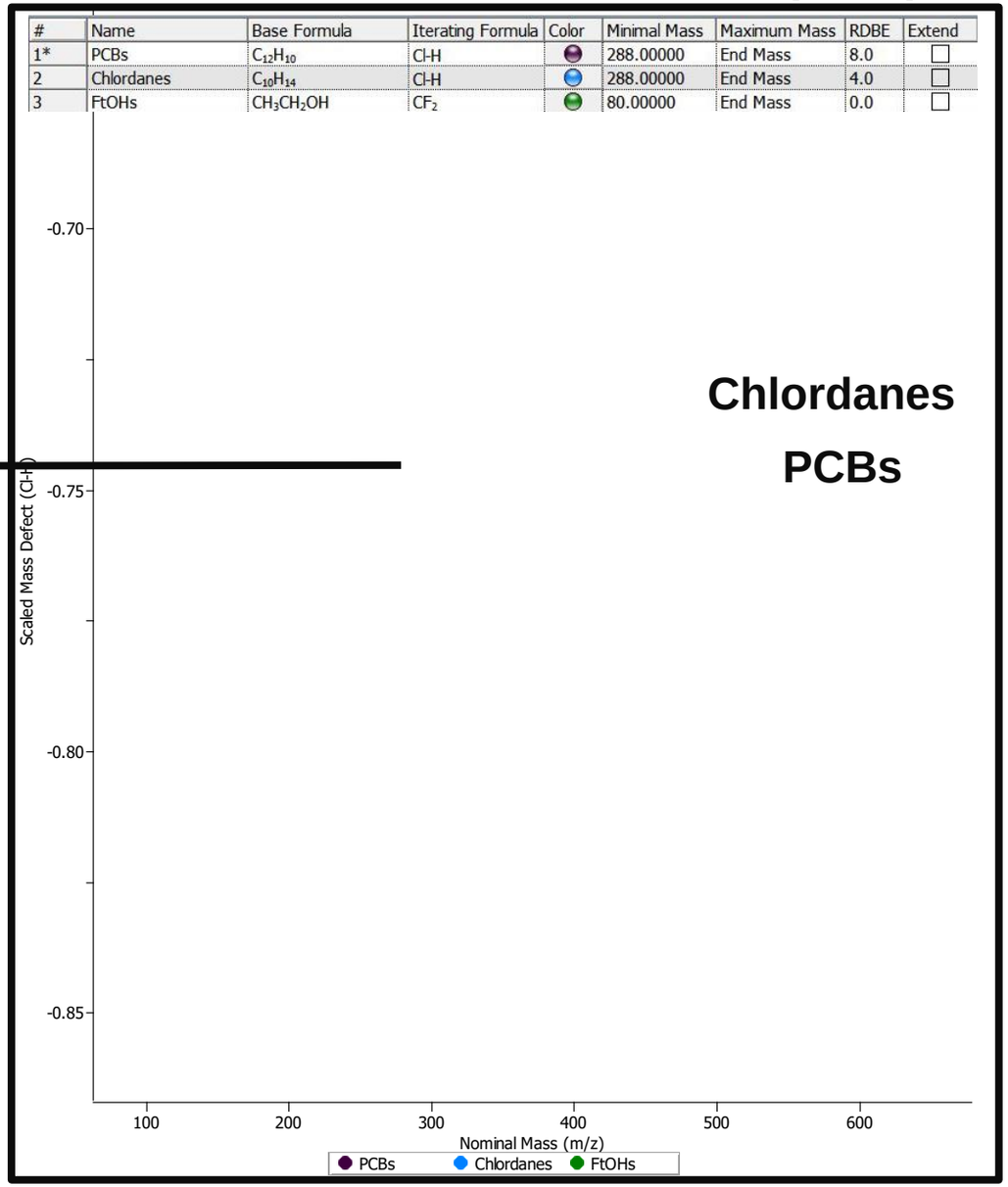
PCBs: SMD (Cl-H) to Contour Plot

Contour Plot, XICs (ECNI)

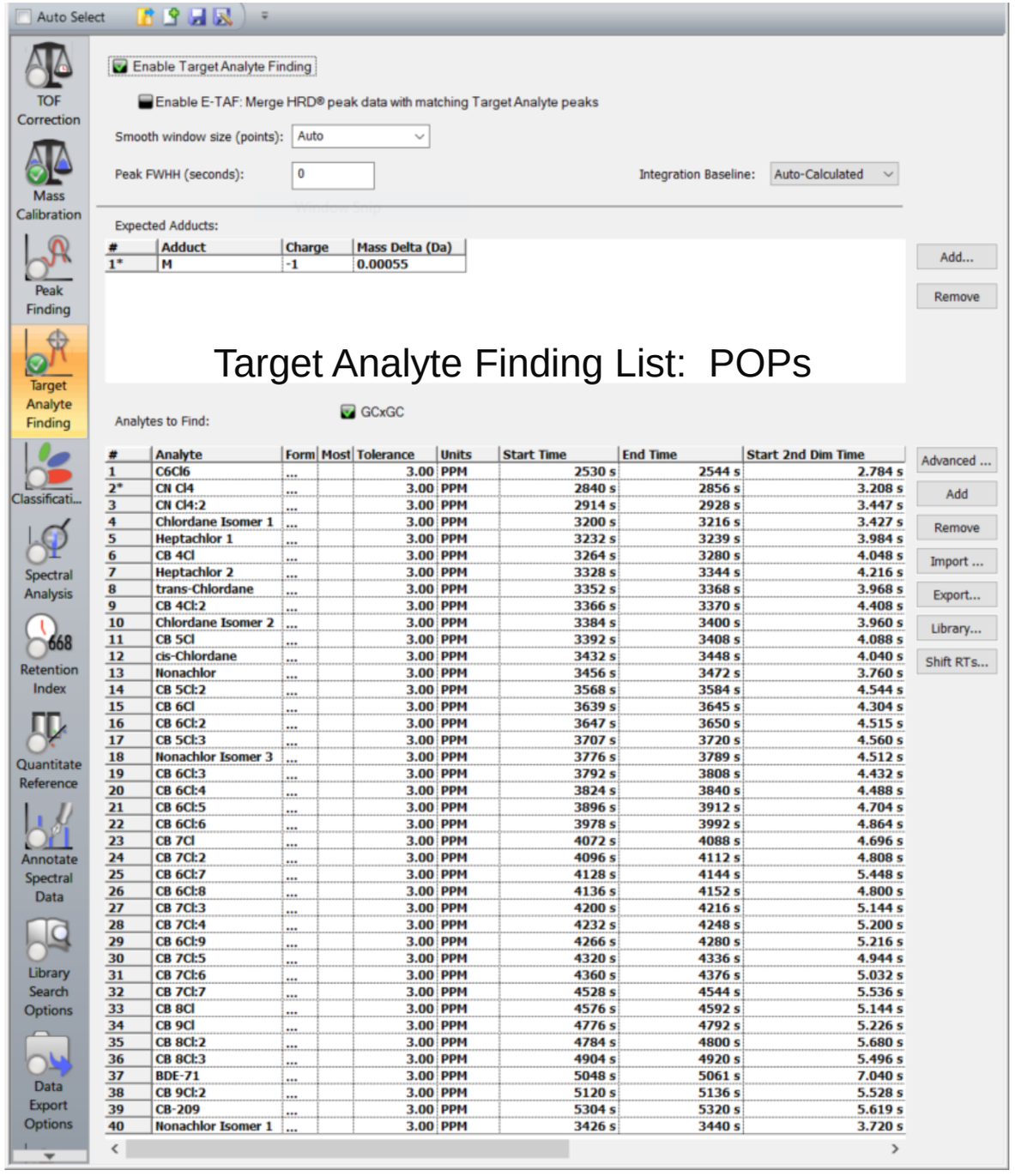


Filtered & Scaled Mass Defect Plot (ECNI)

#	Name	Base Formula	Iterating Formula	Color	Minimal Mass	Maximum Mass	RDBE	Extend
1*	PCBs	$C_{12}H_{10}$	Cl-H		288.00000	End Mass	8.0	
2	Chlordanes	$C_{10}H_{14}$	Cl-H		288.00000	End Mass	4.0	
3	FtOHs	CH_3CH_2OH	CF_2		80.00000	End Mass	0.0	



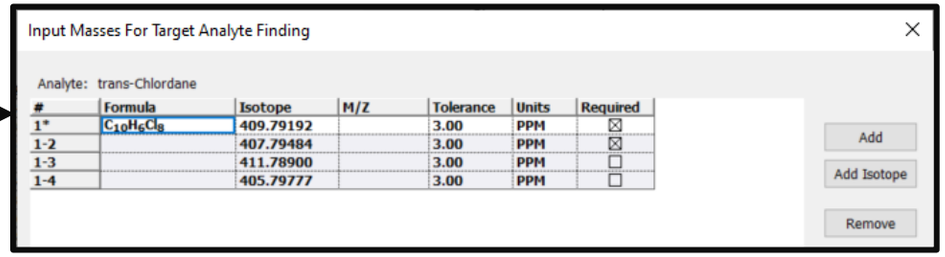
Targeting POPs in ECNI

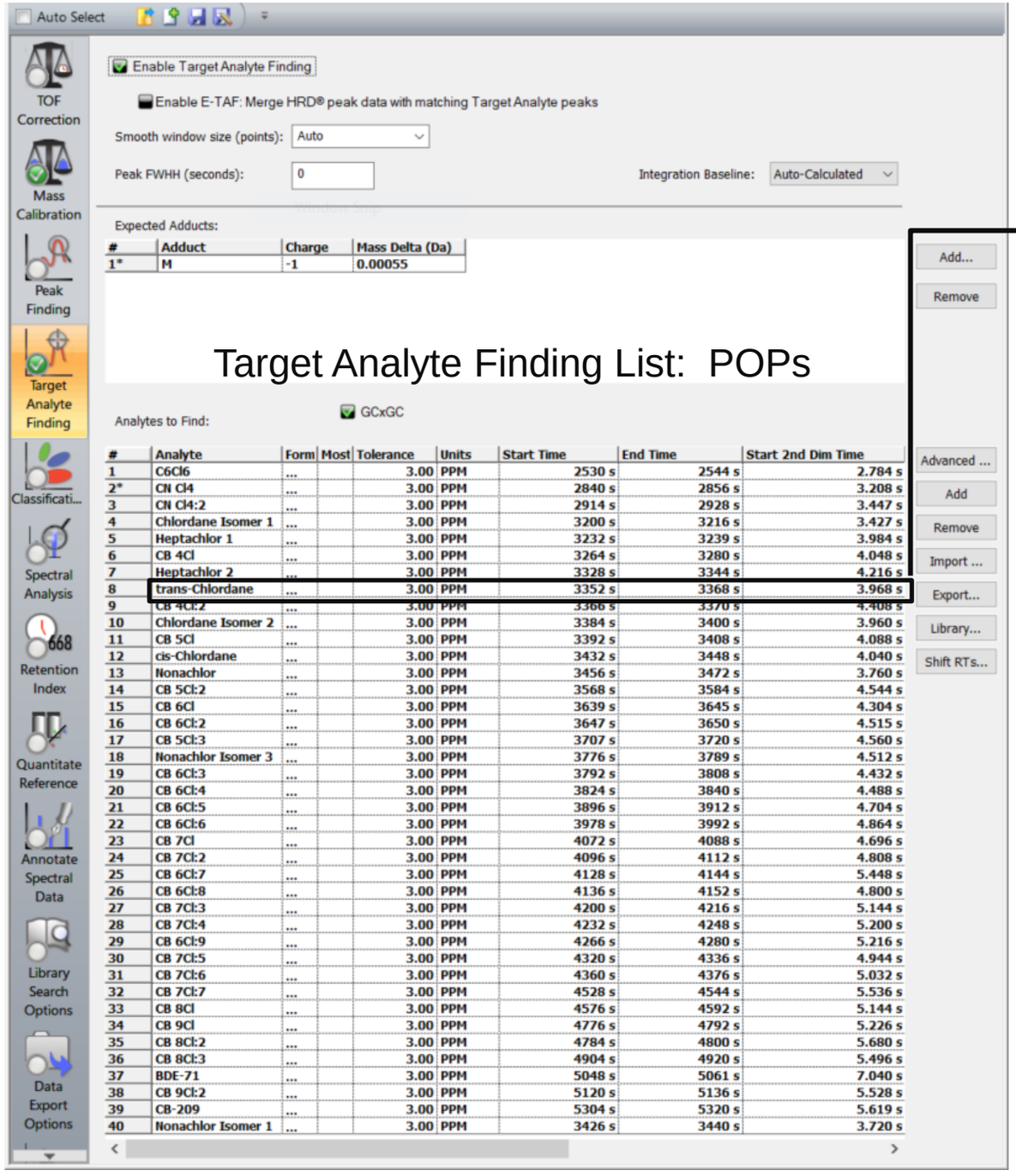


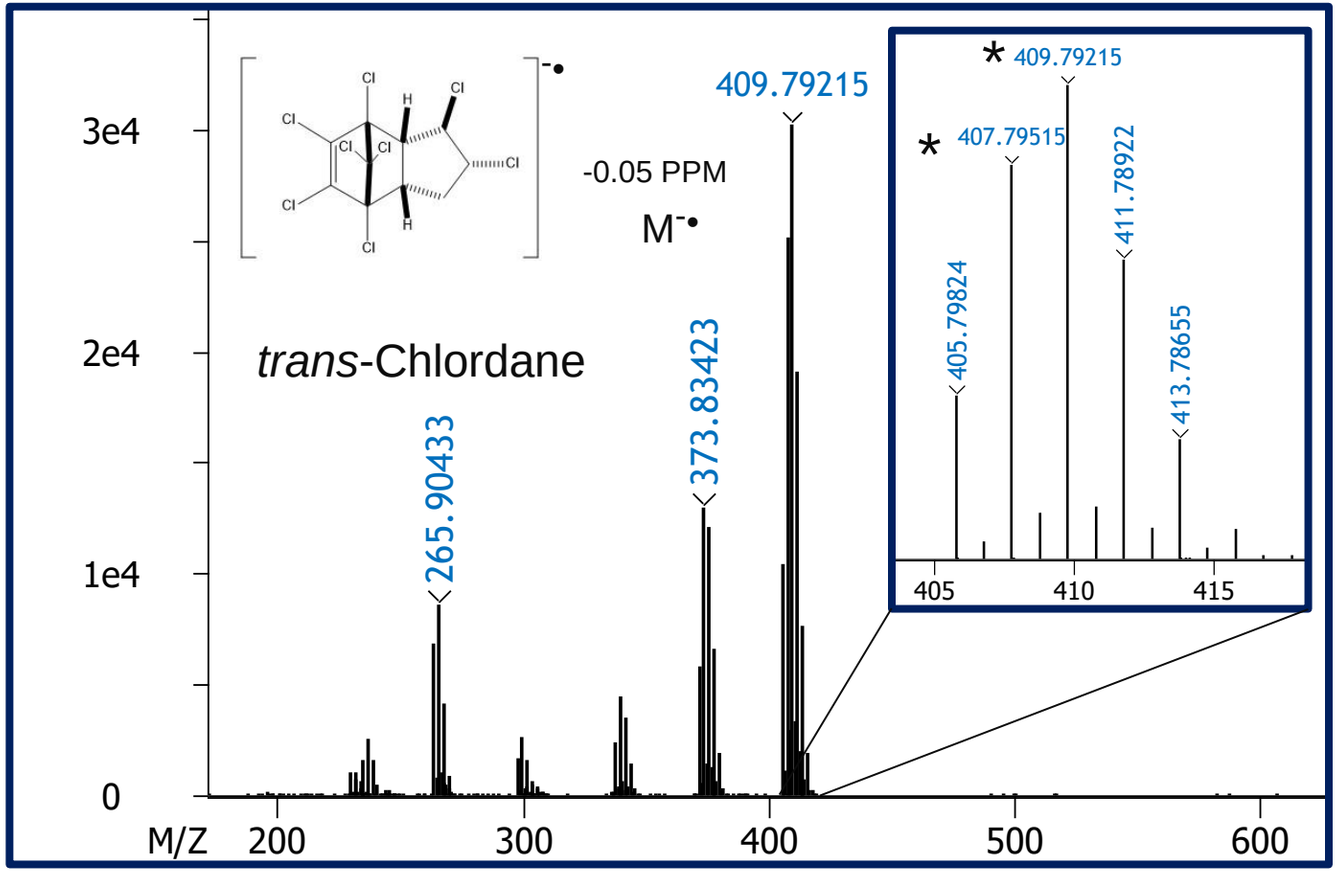
- ✓ Trace Analysis
- ✓ Quantitative Analysis
- ✓ Fast Processing

Targeting Trace POPs in ECNI

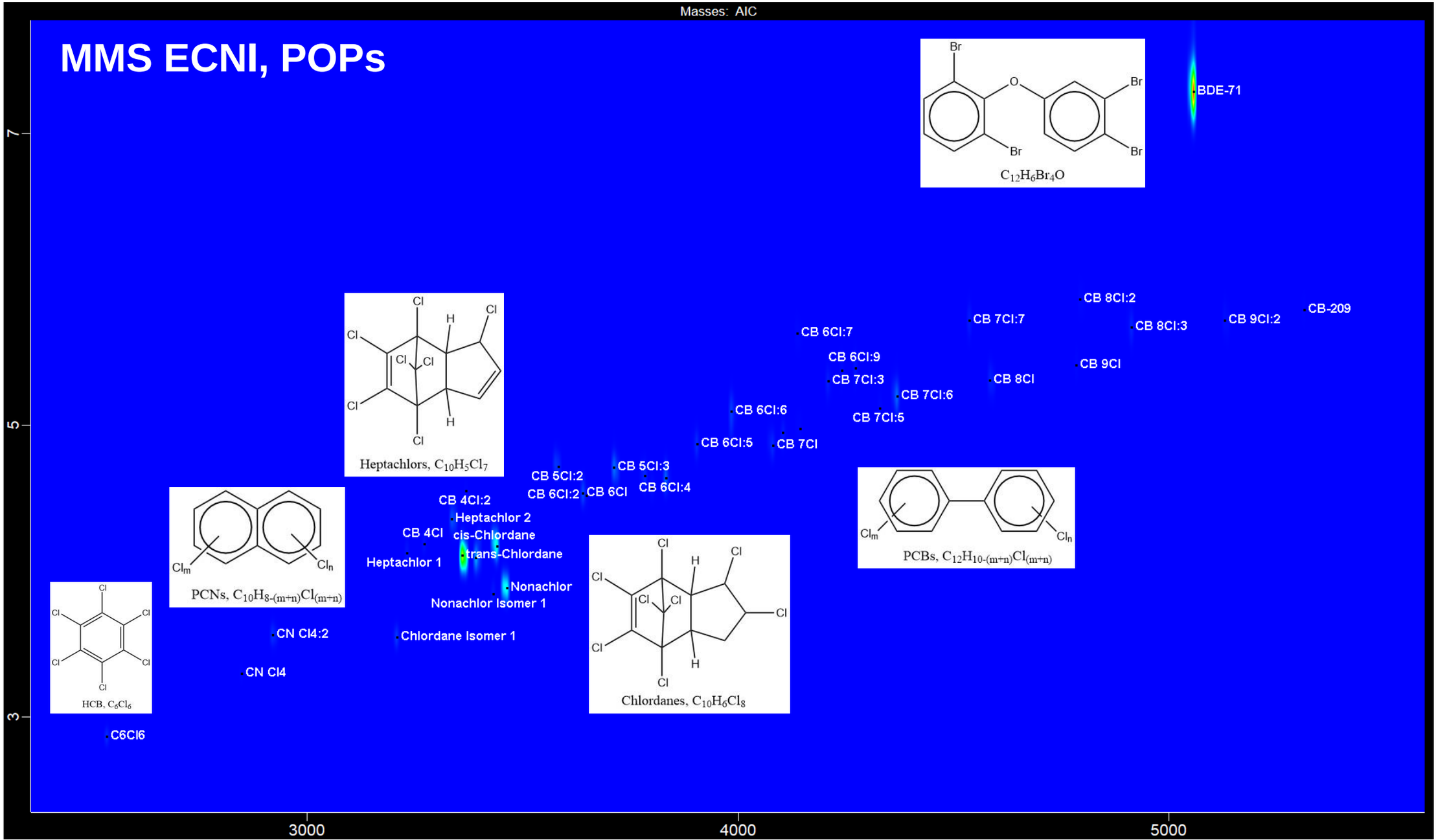
HRAM Ions







TAF Results: Trace POPs in NIST SRM



TAF Results: NIST SRM, Household, and Office Dust

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
C_6Cl_6	2536, 2.872	66777	10364	485688
CN Cl4	2848, 3.304	13710		
CN Cl4:2	2920, 3.568	143301		
Chlordane Isomer 1	3208, 3.552	62129		
Heptachlor 1	3232, 4.128	15887		
CB 4Cl	3272, 4.192	21645	8827	
Heptachlor 2	3336, 4.360	215913		
trans-Chlordane	3360, 4.112	1730979	3025	11470
CB 4Cl:2	3368, 4.552	10321	1454	
Chlordane Isomer 2	3392, 4.096	266412		
CB 5Cl	3400, 4.224	54160	50338	
Nonachlor Isomer 1	3432, 3.848	9577		
cis-Chlordane	3440, 4.176	624489		
Nonachlor	3464, 3.888	596640		3023
CB 5Cl:2	3584, 4.720	44766	55571	
CB 6Cl	3640, 4.536	23649	33324	
CB 6Cl:2	3648, 4.520	23937		
CB 5Cl:3	3712, 4.712	304119	305058	
Nonachlor Isomer 3	3784, 4.656	98500		
CB 6Cl:3	3800, 4.576	44400	46349	

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
CB 6Cl:4	3832, 4.640	285099	324443	
CB 6Cl:5	3904, 4.872	85405	83716	
CB 6Cl:6	3984, 5.096	280450	328292	
CB 7Cl	4080, 4.864	149348	108803	
CB 7Cl:2	4104, 4.952	68723	50837	
CB 6Cl:7	4136, 5.632	39203	47433	
CB 6Cl:8	4144, 4.976	27026	22346	
CB 7Cl:3	4208, 5.304	92038	91365	
CB 7Cl:4	4240, 5.376	38110	38962	
CB 6Cl:9	4272, 5.392	67431	66771	
CB 7Cl:5	4328, 5.120	26105	19932	
CB 7Cl:6	4368, 5.200	397534	369028	
CB 7Cl:7	4536, 5.720	86694	109695	
CB 8Cl	4584, 5.312	119235	53370	
CB 9Cl	4784, 5.416	13906		
CB 8Cl:2	4792, 5.864	27430	15635	
CB 8Cl:3	4912, 5.672	94752	58564	
BDE-71	5056, 7.288	5480469	433778	663837
CB 9Cl:2	5128, 5.720	51490	10114	
CB-209	5312, 5.792	9879		

Results: NIST SRM, Household, and Office Dust

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
C_6Cl_6	2536, 2.872	66777	10364	485688
CN Cl4	2848, 3.304	13710		
CN Cl4:2	2920, 3.568	143301		
Chlordane Isomer 1	3208, 3.552	62129		
Heptachlor 1	3232, 4.128	15887		
CB 4Cl	3272, 4.192	21645	8827	
He[illegible]	3[illegible]6, 4.360	21591		
tr[illegible]	3360, [illegible]12	17309[illegible]9	3025	1147[illegible]
CB 4Cl:2	3368, 4.552	10321	1454	
Chlordane Isomer 2	3392, 4.696	266412		
CB 5Cl	3400, 4.224	54160	50338	
Nonachlor Isomer 1	3432, 3.848	9577		
cis-Chlordane	3440, 4.176	624489		
Nonachlor	3464, 3.888	596640		3023
CB 5Cl:2	3584, 4.720	44766	55571	
CB 6Cl	3640, 4.536	23649	33324	
CB 6Cl:2	3648, 4.520	23937		
CB 5Cl:3	3712, 4.712	304119	305058	
Nonachlor Isomer 3	3784, 4.656	98500		
CB 6Cl:3	3800, 4.576	44400	46349	

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
CB 6Cl:4	3832, 4.640	285099	324443	
CB 6Cl:5	3904, 4.872	85405	83716	
CB 6Cl:6	3984, 5.096	280450	328292	
CB 7Cl	4080, 4.864	149348	108803	
CB 7Cl:2	4104, 4.952	68723	50837	
CB 6Cl:7	4136, 5.632	39203	47433	
CB 6Cl:8	4144, 4.976	2[illegible]026	22346	
CB 7Cl:3	42[illegible], 5.304	2[illegible]03[illegible]	9[illegible]36	
CB 7Cl:4	4240, 5.376	38110	38962	
CB 6Cl:9	4272, 5.392	67431	66771	
CB 7Cl:5	4328, 5.120	26105	19932	
CB 7Cl:6	4368, 5.200	397534	369028	
CB 7Cl:7	4536, 5.720	86694	109695	
CB 8Cl	4584, 5.312	119235	53370	
CB 9Cl	4784, 5.416	13906		
CB 8Cl:2	4792, 5.864	27430	15635	
CB 8Cl:3	4912, 5.672	94752	58564	
BDE-71	5056, 7.288	5480469	433778	663837
CB 9Cl:2	5128, 5.720	51490	10114	
CB-209	5312, 5.792	9879		

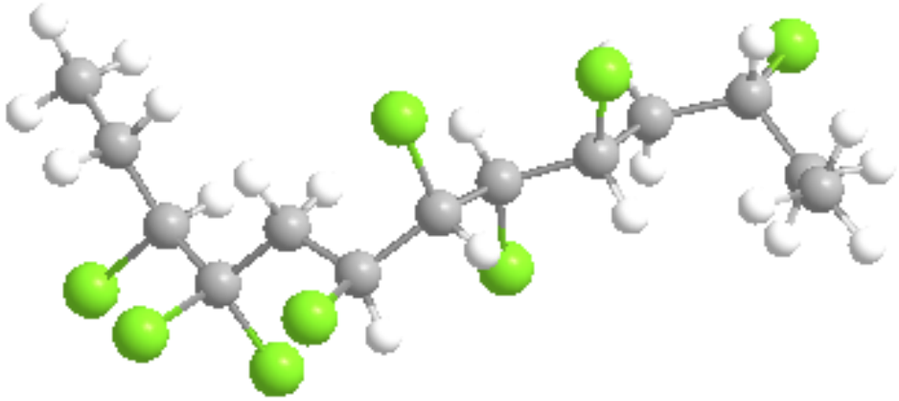
POPs: NIST>Office>House

Part 3

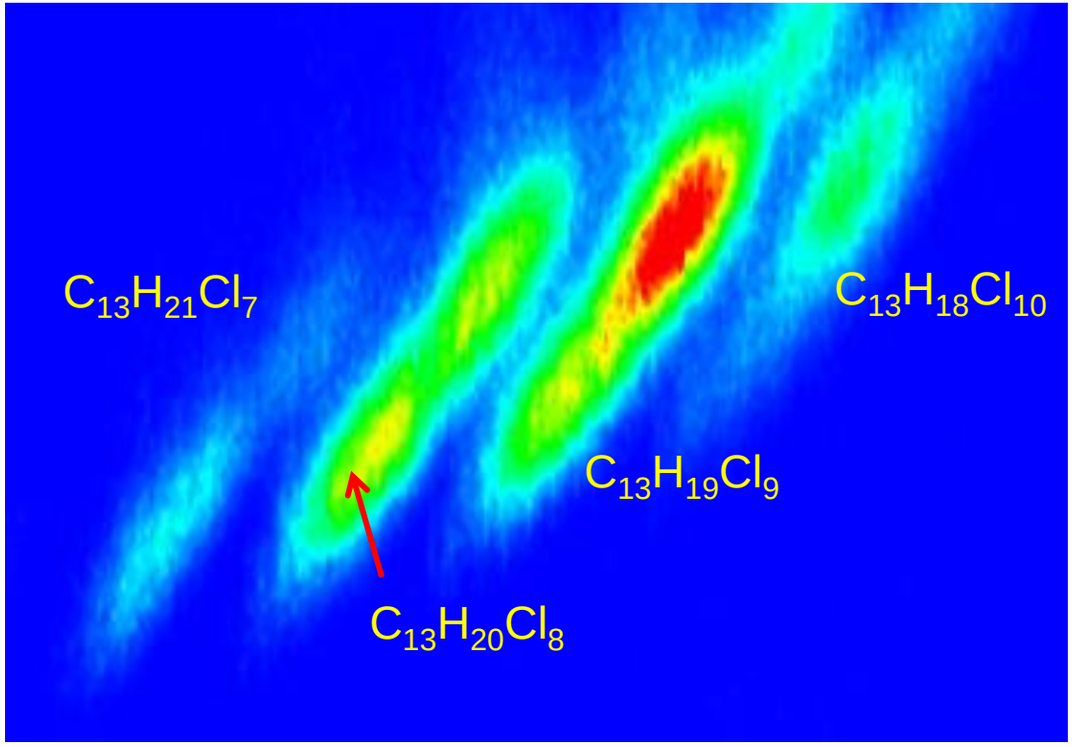
Quantitative Analysis of Polychlorinated Paraffins

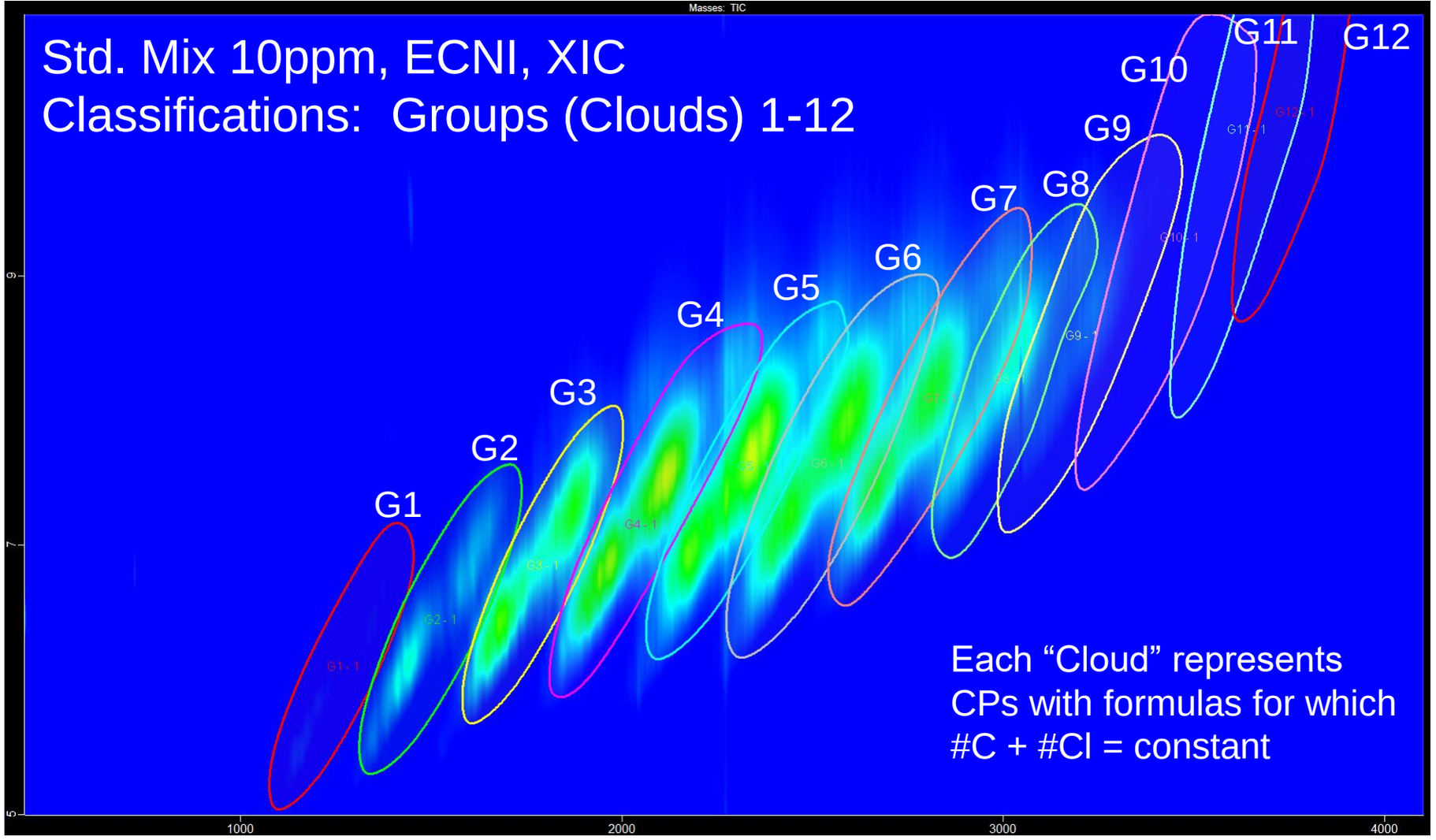
Short Chain (SCCPs): C_{10} to C_{13}

Medium Chain (MCCPs): C_{14} to C_{17}



$C_{13}H_{20}Cl_8$



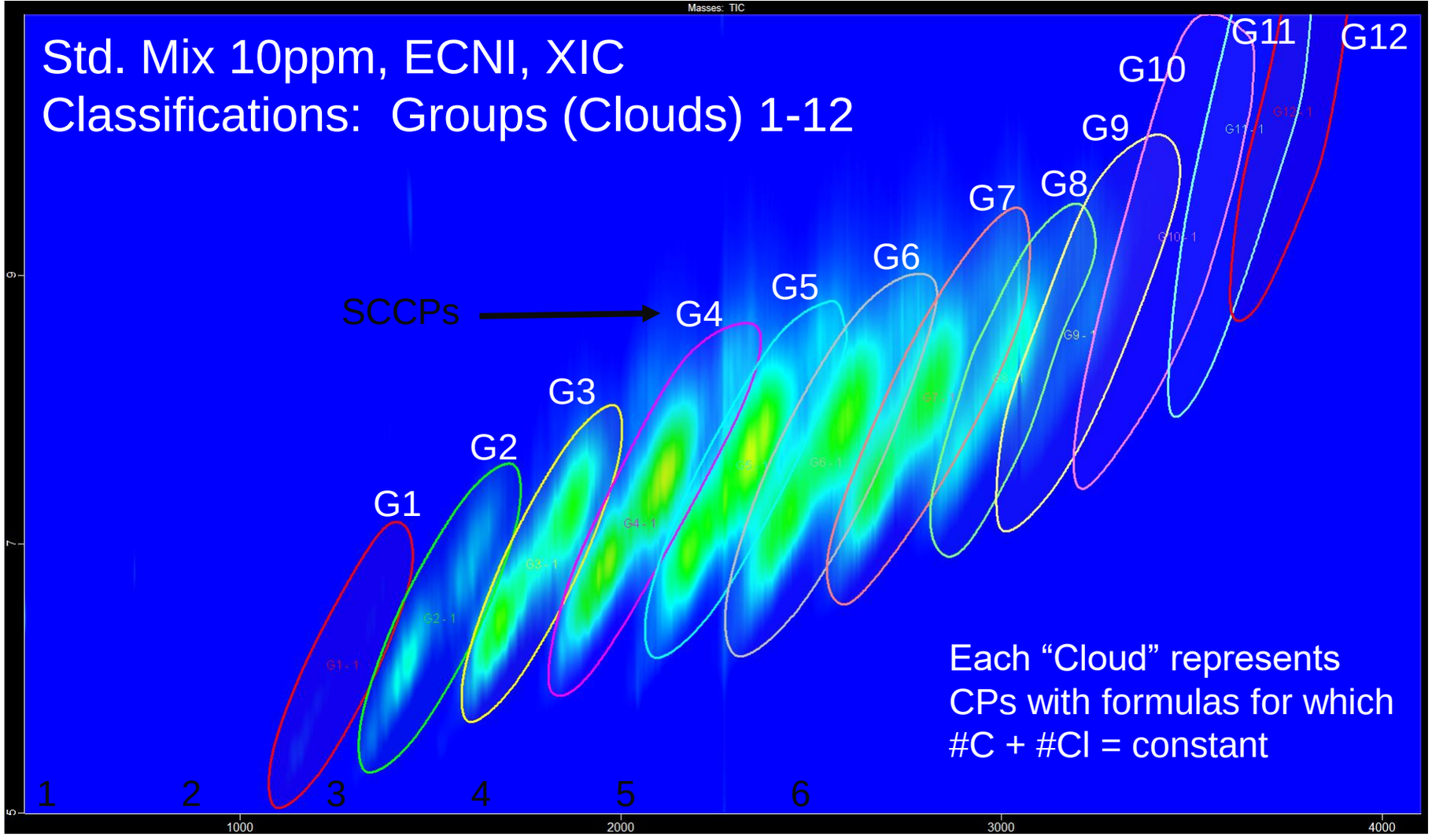


Standard Mix :

SCCP 51.5%, 55.5%, 63% ;

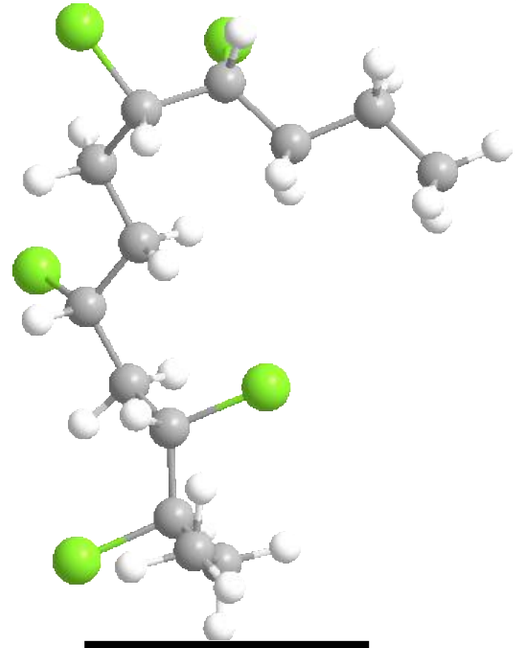
MCCP 42%, 52%, 57%

- CS1 0.25 ppm
- CS2 0.50 ppm
- CS3 1.0 ppm
- CS4 3.0 ppm
- CS5 5.0 ppm
- CS6 7.0 ppm
- CS7 10.0 ppm*
- CS8 15.0 ppm



SCCPs: C_{10} to C_{13}

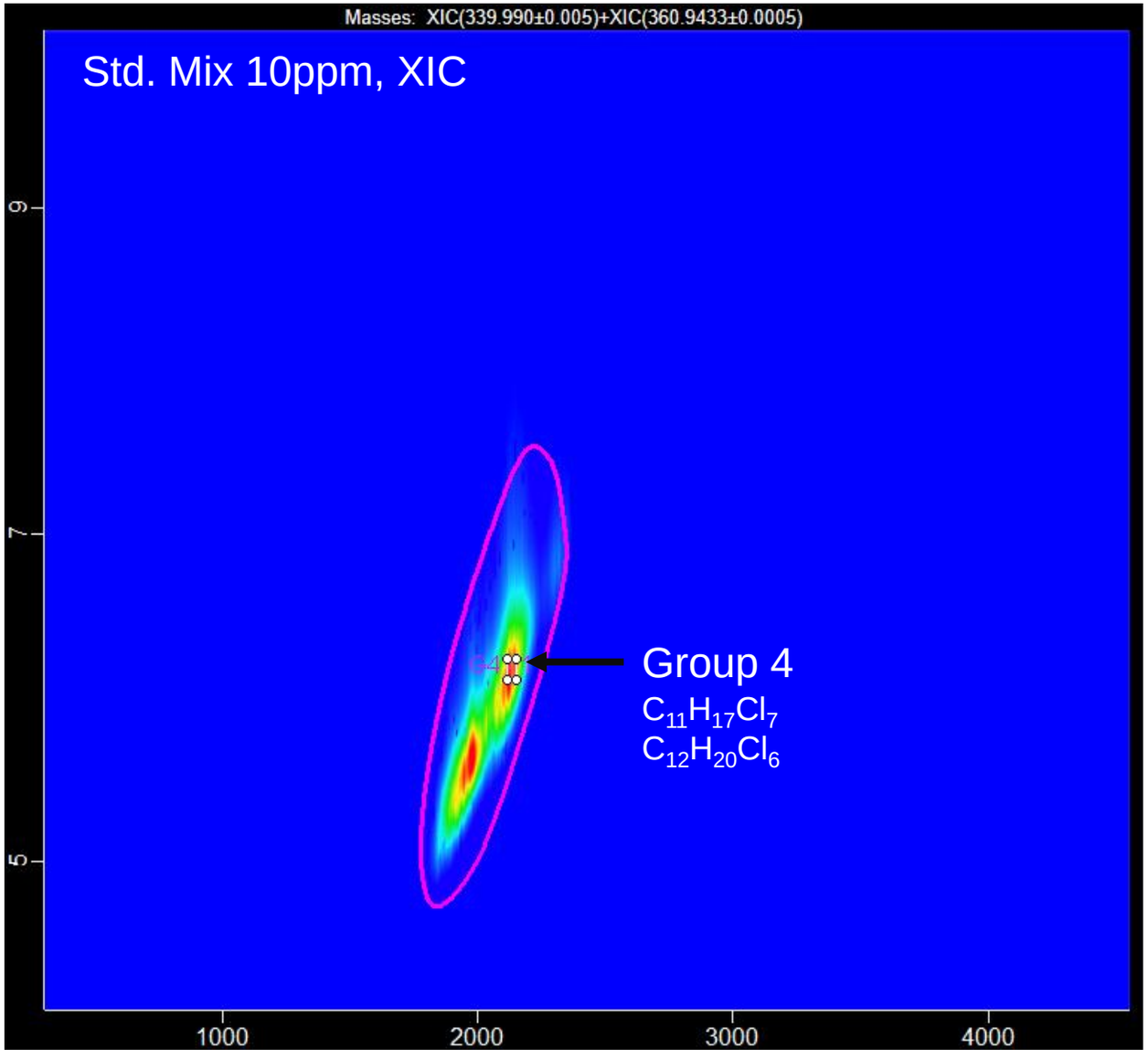
MCCPs: C_{14} to C_{17}

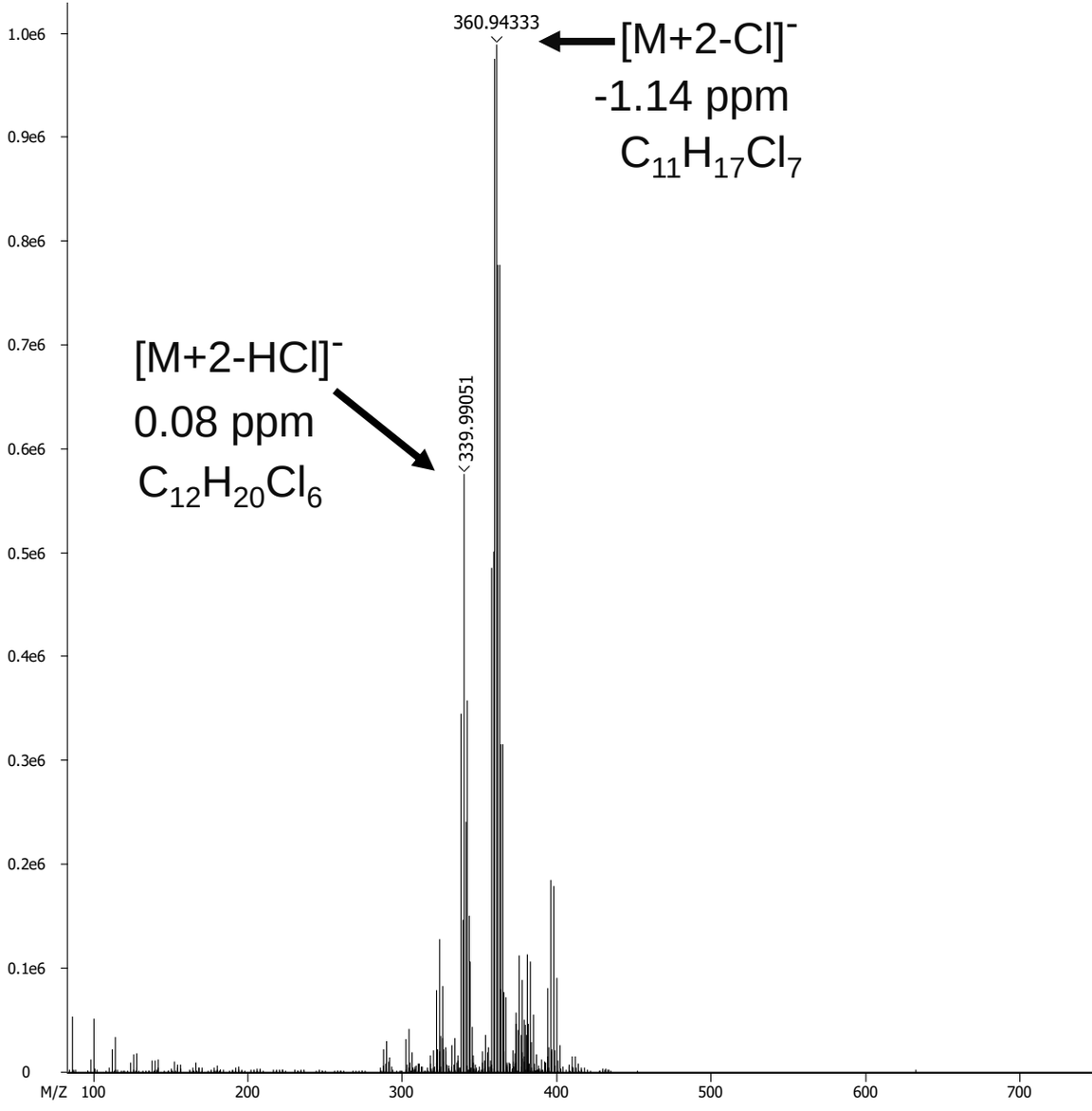


$C_{13}H_{23}Cl_5$

1	2	3	4	5	6	7	8	9	10	11	12
$C_{10}H_{17}Cl_5$	$C_{10}H_{16}Cl_6$	$C_{10}H_{15}Cl_7$	$C_{10}H_{14}Cl_8$	$C_{10}H_{13}Cl_9$	$C_{10}H_{12}Cl_{10}$	$C_{11}H_{14}Cl_{10}$	$C_{12}H_{16}Cl_{10}$	$C_{13}H_{18}Cl_{10}$	$C_{14}H_{20}Cl_{10}$	$C_{15}H_{22}Cl_{10}$	$C_{16}H_{24}Cl_{10}$
$C_{11}H_{20}Cl_4$	$C_{11}H_{19}Cl_5$	$C_{11}H_{18}Cl_6$	$C_{11}H_{17}Cl_7$	$C_{11}H_{16}Cl_8$	$C_{11}H_{15}Cl_9$	$C_{12}H_{17}Cl_9$	$C_{13}H_{19}Cl_9$	$C_{14}H_{21}Cl_9$	$C_{15}H_{23}Cl_9$	$C_{16}H_{25}Cl_9$	$C_{17}H_{27}Cl_9$
	$C_{12}H_{22}Cl_4$	$C_{12}H_{21}Cl_5$	$C_{12}H_{20}Cl_6$	$C_{12}H_{19}Cl_7$	$C_{12}H_{18}Cl_8$	$C_{13}H_{20}Cl_8$	$C_{14}H_{22}Cl_8$	$C_{15}H_{24}Cl_8$	$C_{16}H_{26}Cl_8$	$C_{17}H_{28}Cl_8$	
		$C_{13}H_{24}Cl_4$	$C_{13}H_{23}Cl_5$	$C_{13}H_{22}Cl_6$	$C_{13}H_{21}Cl_7$	$C_{14}H_{23}Cl_7$	$C_{15}H_{25}Cl_7$	$C_{16}H_{27}Cl_7$	$C_{17}H_{29}Cl_7$		
				$C_{14}H_{25}Cl_5$	$C_{14}H_{24}Cl_6$	$C_{15}H_{26}Cl_6$	$C_{16}H_{28}Cl_6$	$C_{17}H_{30}Cl_6$			
					$C_{15}H_{27}Cl_5$	$C_{16}H_{27}Cl_5$	$C_{17}H_{31}Cl_5$				

Std. Mix: Contour Plot & Mass Spectra for G4 Region





Cloud Quant Data Processing

Method: Mass Calibration, Signal Processing & Classification

Auto Select

#	Show	Class	Comp	Region	Color	Formula 1	Data I	Mass Toleran	Formula 2	Data I	Mass Toleran	Formula 3	Data I	Mass Toleran	Formula 4	Data Dc	Mass Toleran	Formula 5	Data I	Mass Toleran	Formula 6
1	☒	G1				277.9982 279.9952	Signal	5 PPM		Signal			Signal			Signal			Signal		
2	☒	G2				312.9671 314.9664	Signal	5 PPM	292.0132 294.0199	Signal	5 PPM		Signal			Signal			Signal		
3	☒	G3				346.9285 348.9257	Signal	5 PPM	325.9752 327.9730	Signal	5 PPM	304.0340 306.0301	Signal	5 PPM		Signal			Signal		
4	☒	G4				360.9438 362.9407	Signal	5 PPM	339.9909 341.9888	Signal	5 PPM		Signal			Signal			Signal		
5	☒	G5				380.8888 382.8862	Signal	5 PPM	394.9048 396.9006	Signal	5 PPM	374.9594 376.9556	Signal	5 PPM	354.0056 356.0036	Signal	5 PPM		Signal		
6	☒	G6				430.8621 432.8593	Signal	5 PPM	408.9207 410.9168	Signal	5 PPM	388.9745 390.9722	Signal	5 PPM	368.0223 370.0195	Signal	5 PPM		Signal		
7	☒	G7				464.8241 466.8210	Signal	5 PPM	444.8788 446.8760	Signal	5 PPM	422.9361 424.9334	Signal	5 PPM	402.9906 404.9877	Signal	5 PPM	382.0370 384.0349	Signal	5 PPM	366.0053 368.0022
8	☒	G8				478.8385 480.8350	Signal	5 PPM	458.8927 460.8896	Signal	5 PPM	436.9519 438.9486	Signal	5 PPM	417.0063 419.0030	Signal	5 PPM	396.0527 398.0511	Signal	5 PPM	
9	☒	G9				492.8536 494.8505	Signal	5 PPM	472.9098 474.9066	Signal	5 PPM	450.9686 452.9657	Signal	5 PPM	431.0151 433.0197	Signal	5 PPM	411.0767 413.0739	Signal	5 PPM	
10	☒	G10				506.8710 508.8684	Signal	5 PPM	486.9258 488.9231	Signal	5 PPM	464.9828 466.9802	Signal	5 PPM	445.0368 447.0342	Signal	5 PPM		Signal		
11	☒	G11				520.8865 522.8838	Signal	5 PPM	500.9415 502.9389	Signal	5 PPM	480.9955 482.9932	Signal	5 PPM		Signal			Signal		
12	☒	G12				534.9021 536.9006	Signal	5 PPM	514.9581 516.9546	Signal	5 PPM		Signal			Signal			Signal		
13*	☒	ISTD				260.9087 262.90577	Signal	5 PPM		Signal			Signal			Signal			Signal		
14		Unclass					Signal	5 PPM		Signal	5 PPM		Signal			Signal			Signal		

- SCCP & MCCP formula congeners analyzed simultaneously in one injection
- Analysis restricted to SCCP/MCCP congeners with 10-17 Carbon & 5-10 Chlorine atoms
- CP formula congener group quantification of cloud group patterns (Classification) with HRAM Formulas
- Utilized the most abundant m/z values in the $[M\text{-}Cl]^-$ or $[M\text{-}HCl]^-$ isotope clusters

Cloud Quant Data Processing

Method: Mass Calibration, Signal Processing & Classification

Auto Select

#	Show	Class	Comp	Region	Color	Formula 1	Data I	Mass Toleran	Formula 2	Data I	Mass Toleran	Formula 3	Data I	Mass Toleran	Formula 4	Data Dc	Mass Toleran	Formula 5	Data I	Mass Toleran	Formula 6
1	☒	G1				277.9982 279.9952	Signal	5 PPM		Signal			Signal			Signal			Signal		
2	☒	G2				312.9671 314.9664	Signal	5 PPM	292.0132 294.0199	Signal	5 PPM		Signal			Signal			Signal		
3	☒	G3				346.9285 348.9257	Signal	5 PPM	325.9752 327.9730	Signal	5 PPM	304.0340 306.0301	Signal	5 PPM		Signal			Signal		
4	☒	G4				360.9438 362.9407	Signal	5 PPM	339.9909 341.9888	Signal	5 PPM		Signal			Signal			Signal		
5	☒	G5				380.8888 382.8862	Signal	5 PPM	394.9048 396.9006	Signal	5 PPM	374.9594 376.9556	Signal	5 PPM	354.0056 356.0036	Signal	5 PPM		Signal		
6	☒	G6				430.8621 432.8593	Signal	5 PPM	408.9207 410.9168	Signal	5 PPM	388.9745 390.9722	Signal	5 PPM	368.0223 370.0195	Signal	5 PPM		Signal		
7	☒	G7				464.8241 466.8210	Signal	5 PPM	444.8788 446.8760	Signal	5 PPM	422.9361 424.9334	Signal	5 PPM	402.9906 404.9877	Signal	5 PPM	382.0370 384.0349	Signal	5 PPM	366.0053 368.0022
8	☒	G8				478.8385 480.8350	Signal	5 PPM	458.8927 460.8896	Signal	5 PPM	436.9519 438.9486	Signal	5 PPM	417.0063 419.0030	Signal	5 PPM	396.0527 398.0511	Signal	5 PPM	
9	☒	G9				492.8536 494.8505	Signal	5 PPM	472.9098 474.9066	Signal	5 PPM	450.9686 452.9657	Signal	5 PPM	431.0151 433.0197	Signal	5 PPM	411.0767 413.0739	Signal	5 PPM	
10	☒	G10				506.8710 508.8684	Signal	5 PPM	486.9258 488.9231	Signal	5 PPM	464.9828 466.9802	Signal	5 PPM	445.0368 447.0342	Signal	5 PPM		Signal		
11	☒	G11				520.8865 522.8838	Signal	5 PPM	500.9415 502.9389	Signal	5 PPM	480.9955 482.9932	Signal	5 PPM		Signal			Signal		
12	☒	G12				534.9021 536.9006	Signal	5 PPM	514.9581 516.9546	Signal	5 PPM		Signal			Signal			Signal		
13*	☒	ISTD				260.9087 262.90577	Signal	5 PPM		Signal			Signal			Signal			Signal		
14		Unclass					Signal	5 PPM		Signal	5 PPM		Signal			Signal			Signal		

Results: Mass Calibration (PFTBA)

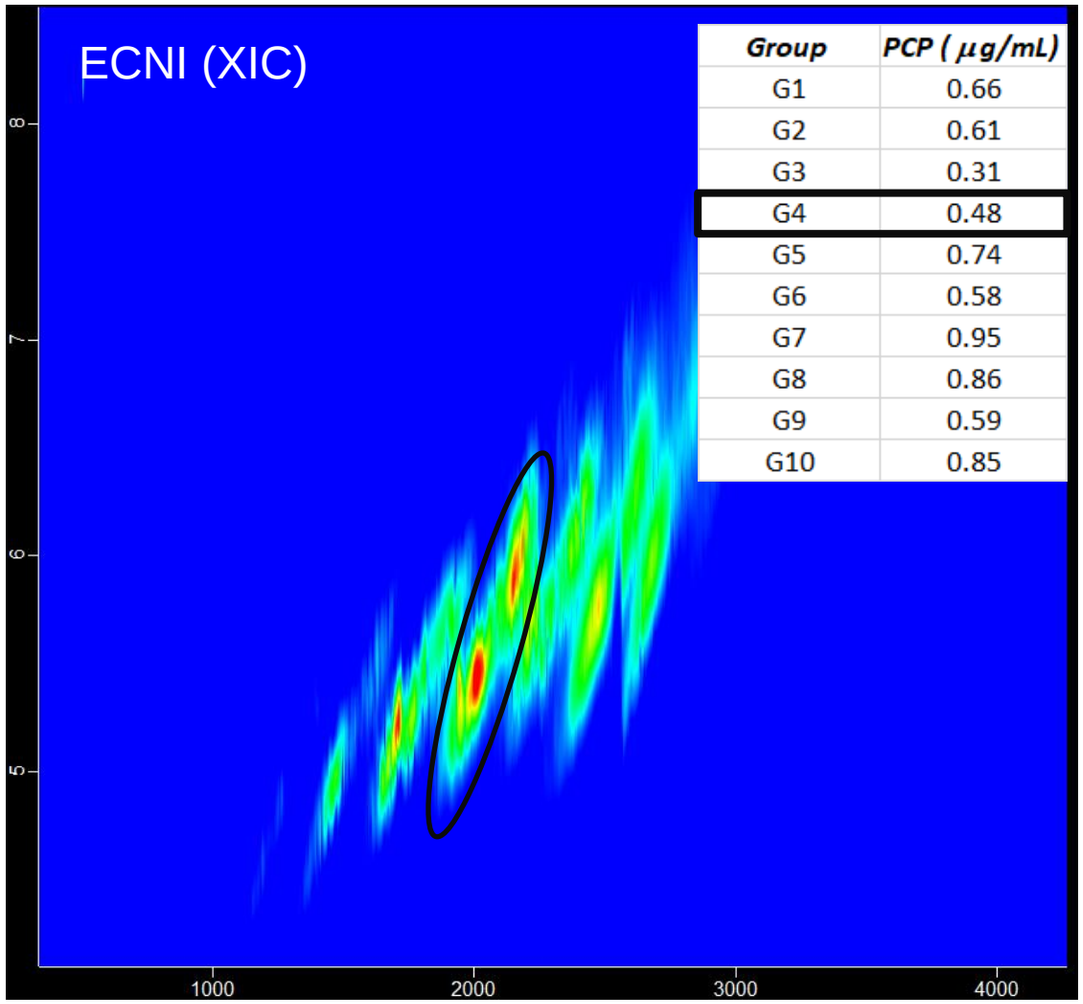
Ion	*Formula*	*m/z calc*	*m/z obs*	*PPM*
PFTBA200	C_4F_8	199.9878	199.9878	0.11
PFTBA283	$C_5F_{11}N$	282.9861	282.9860	-0.15
PFTBA395	$C_8F_{15}N$	394.9797	394.9796	-0.28
PFTBA414	$C_8F_{16}N$	413.9781	413.9780	-0.27
PFTBA433	$C_8F_{17}N$	432.9765	432.9765	0.04
PFTBA452	$C_8F_{18}N$	451.9749	451.9749	0.03
PFTBA514	$C_{10}F_{20}N$	513.9717	513.9716	-0.24
PFTBA595	$C_{12}F_{23}N$	594.9669	594.9668	-0.14
PFTBA633	$C_{12}F_{25}N$	632.9637	632.9637	0.03

Signal Processing/Classification

#	Class	Formula 1	Formula 2	Formula 3	Formula 4	Formula 5
1*	G1	5647020.8				
2	G2	5337271.5	656267.5			
3	G3	5255488.5	44026336.7	4689636.2		
4	G4	79009169.5	37677291.8			
5	G5	6728968.5	36301486.7	41784563.4	13809033.1	
6	G6	4339475.0	38949714.0	17461083.8	27230197.5	
7	G7	2067782.9	23885494.7	21835898.0	30198738.6	4551473.4
8	G8	344645.8	120905.5	36278044.2	4257813.1	237496.1
9	G9	49485.0	8679982.3	140282.9	61940.5	49.1
10	G10	869019.4	2087095.8	483837.0	5876.8	
11	G11	211600.2	181369.9	8775.4		
12	G12	9366.9	5732.6			
13	ISTD	1179072.9				
	Total	95176852.4	.54544763.9	82847158.6	44695910.7	4615599.4

Cloud Quant Results: NIST SRM, Group 4

NIST SRM

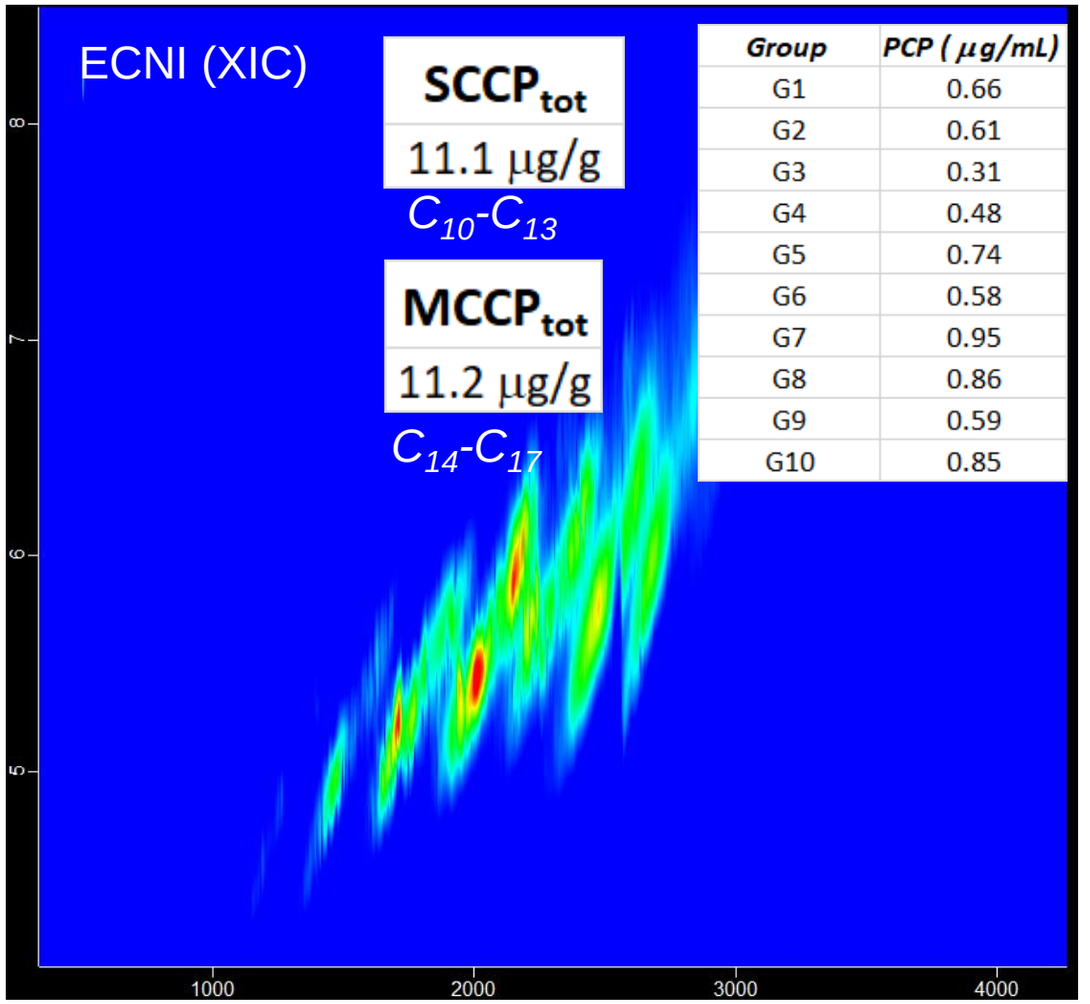


Group	PCP (µg/mL)
G1	0.66
G2	0.61
G3	0.31
G4	0.48
G5	0.74
G6	0.58
G7	0.95
G8	0.86
G9	0.59
G10	0.85

G4 conc.
1.4 µg/g

Cloud Quant Results: NIST SRM, SCCP & MCCP

NIST SRM



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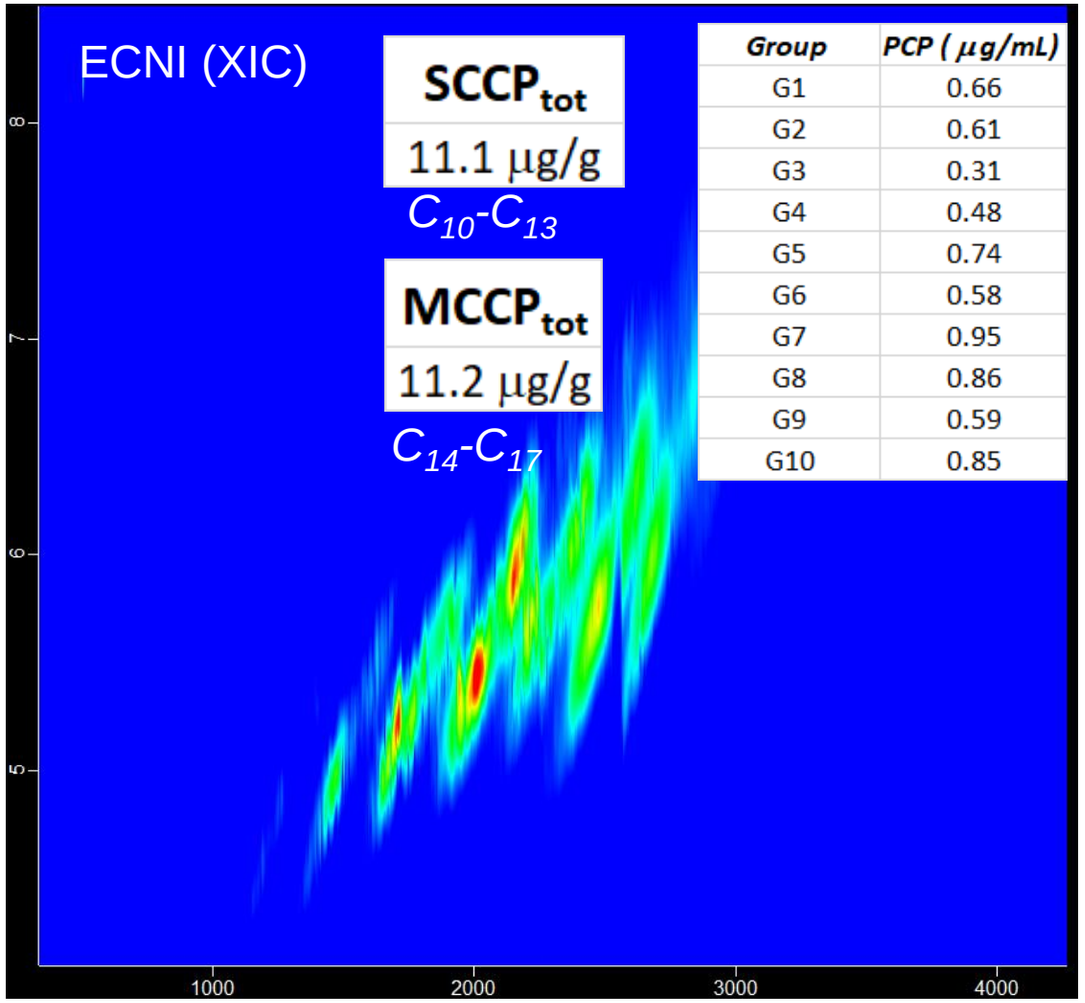
G10	0.85

Cloud Quant Results: NIST SRM, SCCP & MCCP

NIST SRM



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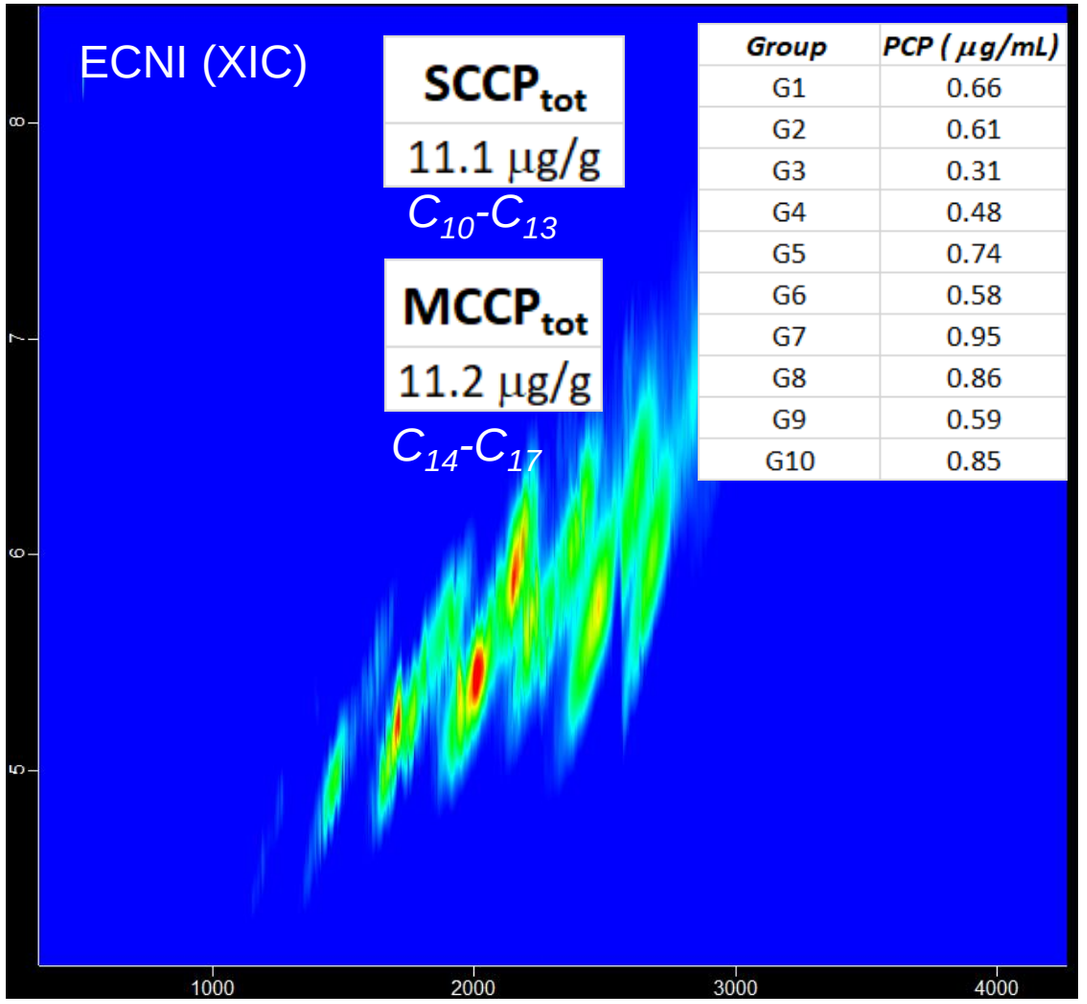
G4	0.48
G5	0.74
G6	0.58
G7	0.95
G8	0.86
G9	0.59
G10	0.85

	Ref. 1	Ref. 2	Ref. 3
SCCP (µg/g)	7.6	8.7	7.1
MCCP (µg/g)	16.4	12.0	10.0

1) Shang, et al, *Environ. Sci. Pollut. Res.* **2019,** *26*, 7453-7462.
2) Brits, et al, *Chemosphere* **2020**, *238*, 124643.
3) Brandsma, et al, *Environ. Sci. Technol.* **2019**, *53*, 7595-7604.

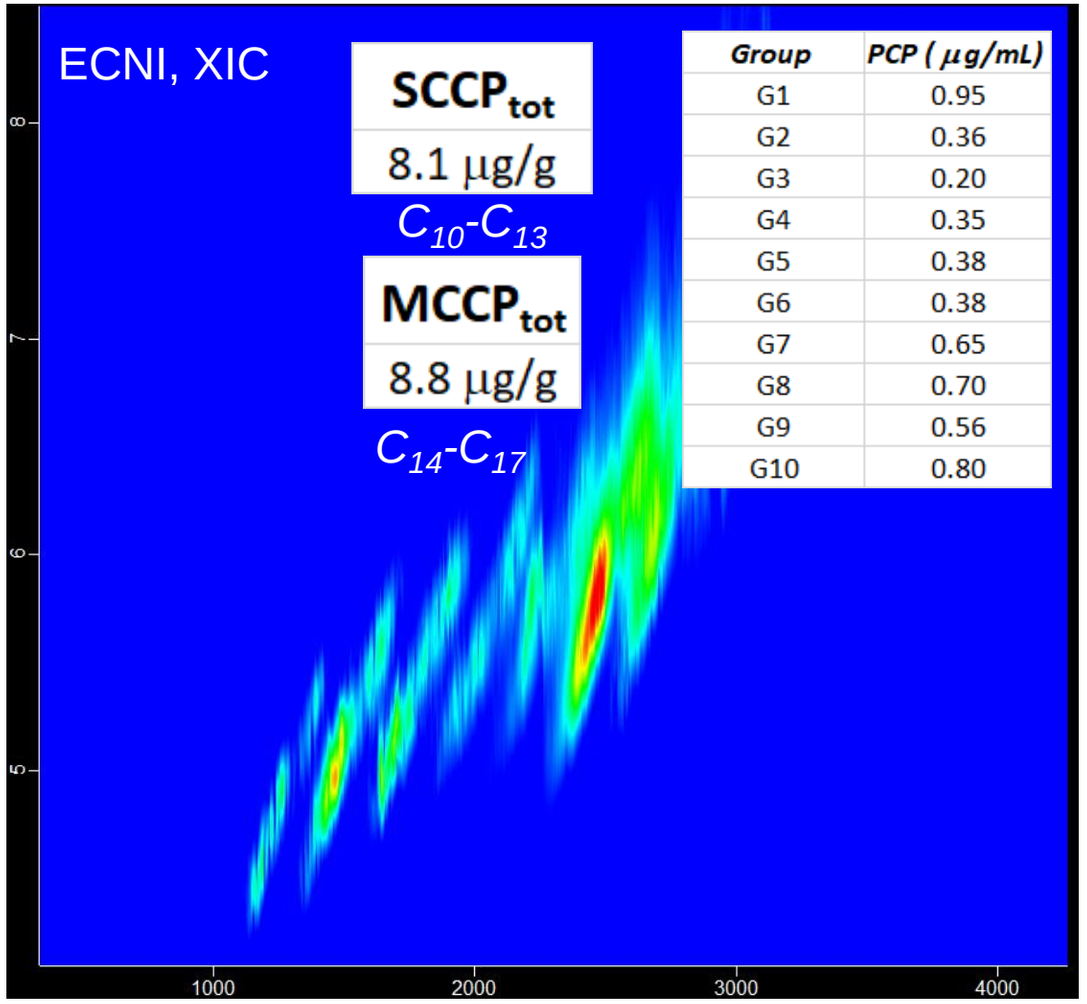
Cloud Quant Results: NIST SRM & Household Dust

NIST SRM



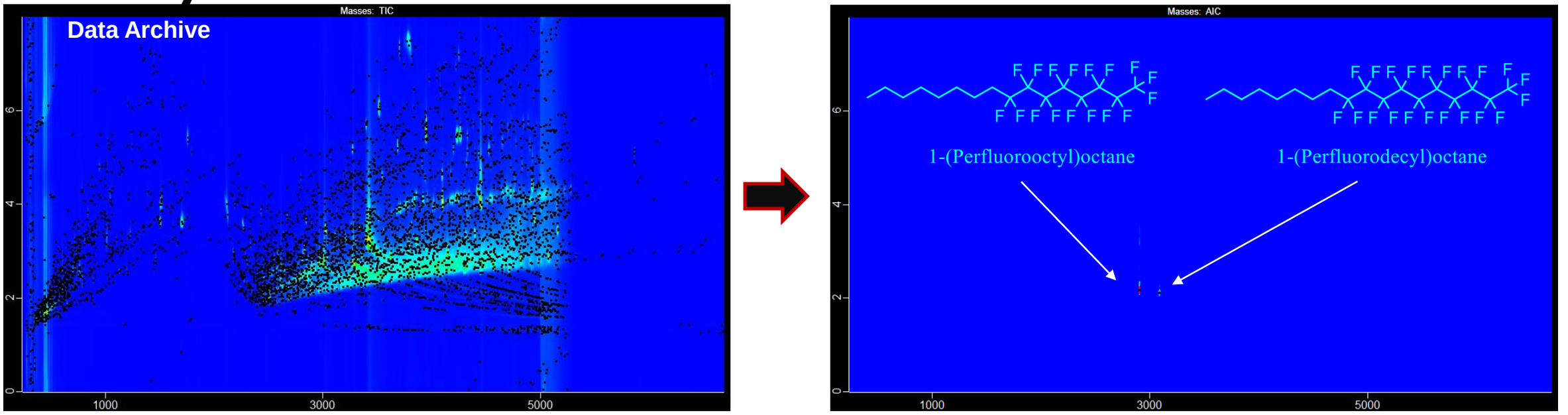
Group	PCP (µg/mL)
G1	0.66
G2	0.61
G3	0.31
G4	0.48
G5	0.74
G6	0.58
G7	0.95
G8	0.86
G9	0.59
G10	0.85

Household



Group	PCP (µg/mL)
G1	0.95
G2	0.36
G3	0.20
G4	0.35
G5	0.38
G6	0.38
G7	0.65
G8	0.70
G9	0.56
G10	0.80

Summary



- GCxGC-HRTOFMS is a powerful discovery tool
  - MMS EI mode: Compound characterization samples
    - ✓ Database comparisons
    - ✓ Formula determinations (HRAM ions)
  - Complementary Ionization modes for compound annotation
  - Retrospective Analysis using software tools (e.g., scaled mass defect plots)

Summary

- GCxGC-HRTOFMS is a powerful discovery tool
  - MMS EI mode: Compound characterization samples
    - ✓ Database comparisons
    - ✓ Formula determinations (HRAM ions)
  - Complementary Ionization modes for compound annotation
  - Retrospective Analysis using software tools (e.g., scaled mass defect plots)
- Effective Dust PCP Cloud Quant Analysis
  - Mass calibration (HRAM ions)
  - Group classification + signal processing

LECO

EMPOWERING RESULTS

Thank you very much for your attention.