Non-Targeted Analysis of Complex Environmental Samples Using Thermal Desorption, Multidimensional Gas Chromatography, Multi-Mode Ionization Methods, and High-Resolution Time-of-Flight Mass Spectrometry

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Introduction

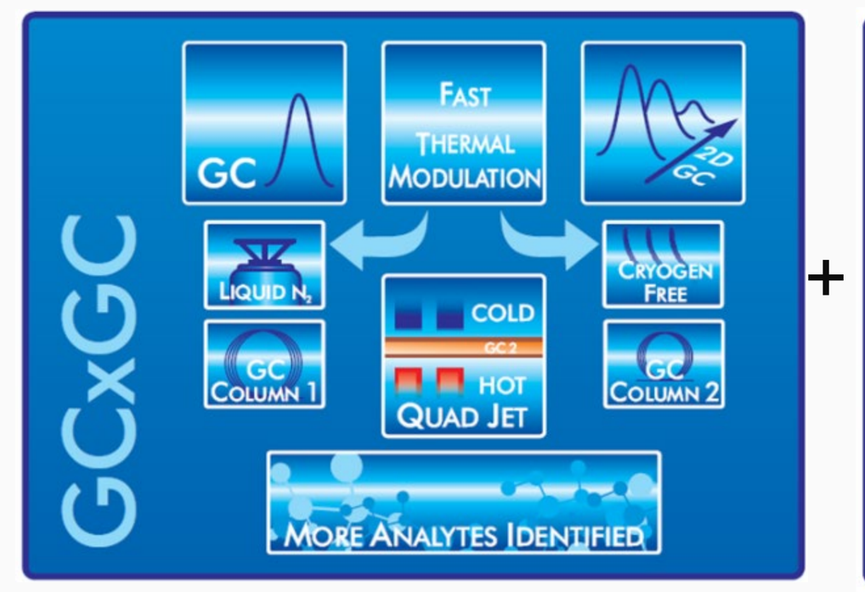
- Confident analysis of environmental samples (e.g., air, water, dust/soil) is critical for the monitoring of harmful substances such as persistent organic pollutants
- Many of these harmful chemical substances have been classified as carcinogens and endocrine disruptors
- Study Objective: To use GCxGC-HRTOFMS for the analysis of complex environmental samples.

Challenge: Complex environmental samples are difficult to analyze

- Very large number of sample constituents
- Wide concentration range
- Varying physiochemical properties

Solution: The utilization of powerful analytical discovery tools

Multidimensional Chromatography



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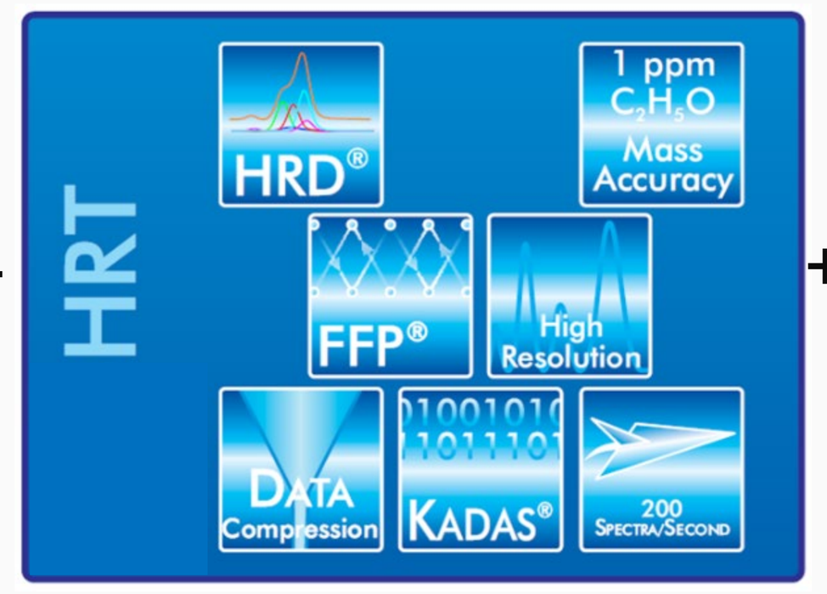
High-Resolution Time-of-Flight Mass Spectrometry



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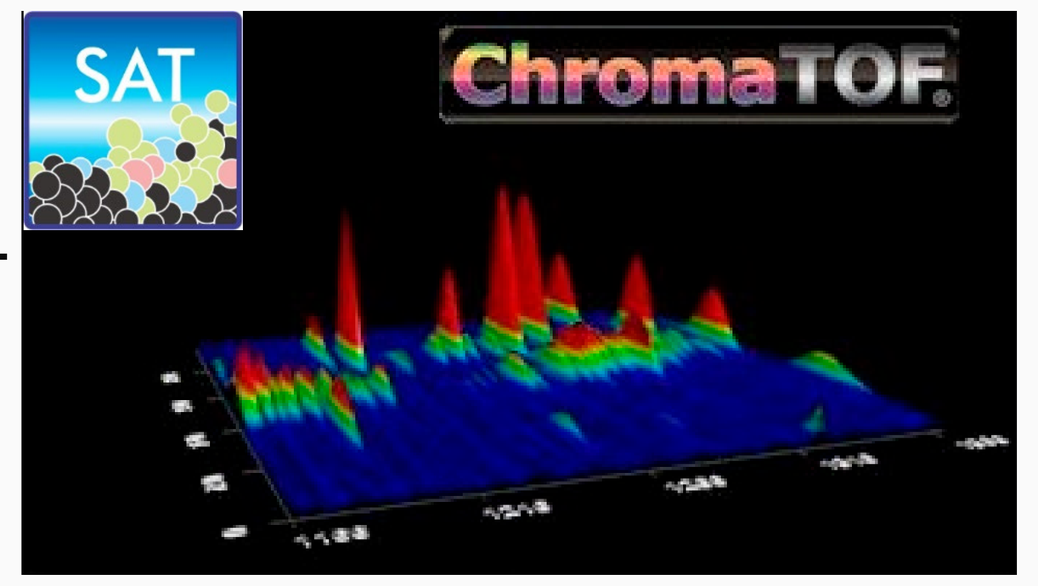
Powerful Software for Deriving Meaningful Information from Rich Data



Instrument Specifications

Mass Accuracy: 1 PPM
Acquisition Speed: 200 sps
Enhanced Chromatographic Resolution: GCxGC
Resolution: Up to 50,000
Multimode Source (MMS): EI, PCI & ECNI

Figure 1. Pegasus® HRT⁺ 4D and Multimode Source.

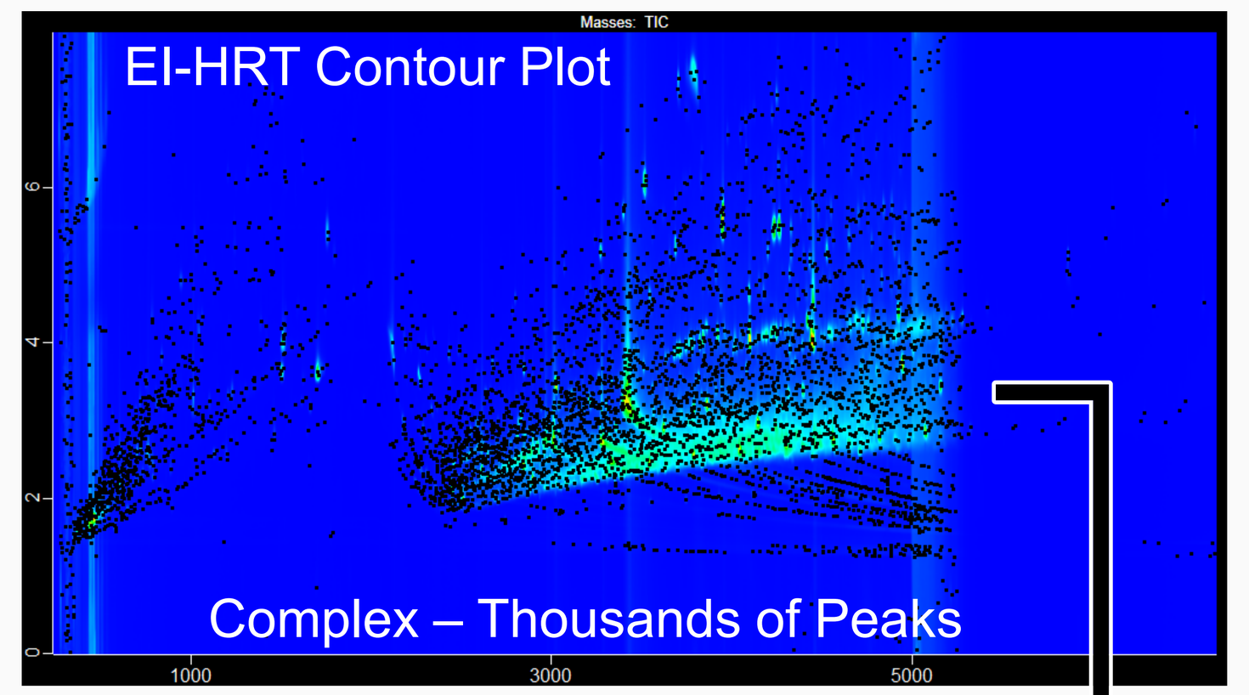
Table 1: Instrument Parameters

Gas Chromatograph	Agilent 7890B with LECO Dual Stage QuadJet™ Modulator
Sample Introduction A	TD, Split 10:1 (3 mins) → Splitless, 50 °C to 300 °C at 10 °C/s
Sample Introduction B	Pyr, 10:1 → Splitless (3 mins), 50 °C to 600 °C at 60 °C/s
Carrier Gas	He @ 1.4 mL/min, Corrected Constant Flow
Primary Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 µm
Secondary Column	Rxi-17sil ms, 1.3 m x 0.10 mm x 0.10 µm
Temperature Program	50 °C (2 min) ramp 10 °C/min to 250 °C, then ramp to 300 °C at 20 °C/min to 300 °C (Hold 15 mins) Secondary oven maintained +5 °C relative to primary oven
Modulation Period	3.0 seconds; modulator maintained +15 °C relative to secondary oven
Transfer Line	300 °C
Mass Spectrometer	**LECO *Pegasus* HRT⁺ 4D**
Source Temperature	EI, 250 °C; PCI, ECNI, 165 °C
Acquisition Mode	High Resolution, R ≥ 25,000 for m/z 219, Mass Accuracy ≤ 1 ppm
Ionization	EI, PCI/ECNI (Reagent Gas = CH_4)
Mass Range (m/z)	EI 50-1000; PCI 60-1000; ECNI 30-1000
Acquisition Rate	200 sps

Complex Environmental Samples

Monitoring where we live and work

1) Dust



- Hydrocarbons
- Acids
- Aromatics
- Amines
- Alcohols
- Aldehydes
- Ketones
- Terpenes
- Phenols
- Fatty Acids
- Sterols
- Phosphates
- OTC Drugs
- Illicit Drugs
- Pollutants….

Figure 2. Contour plot of a complex dust sample.

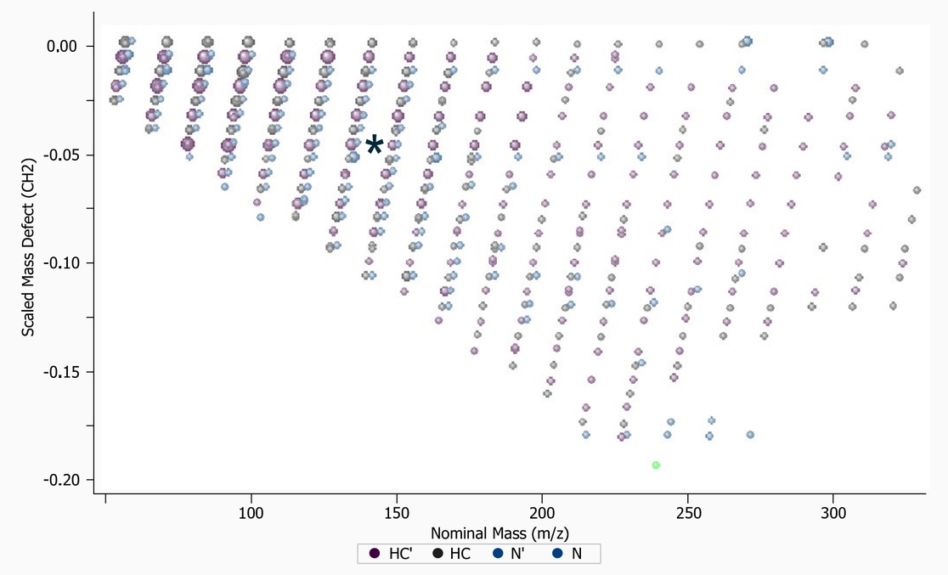


Figure 3. Spectral Analysis Tools (SAT) for complex sample simplification. Mass defect plot of dust sample.

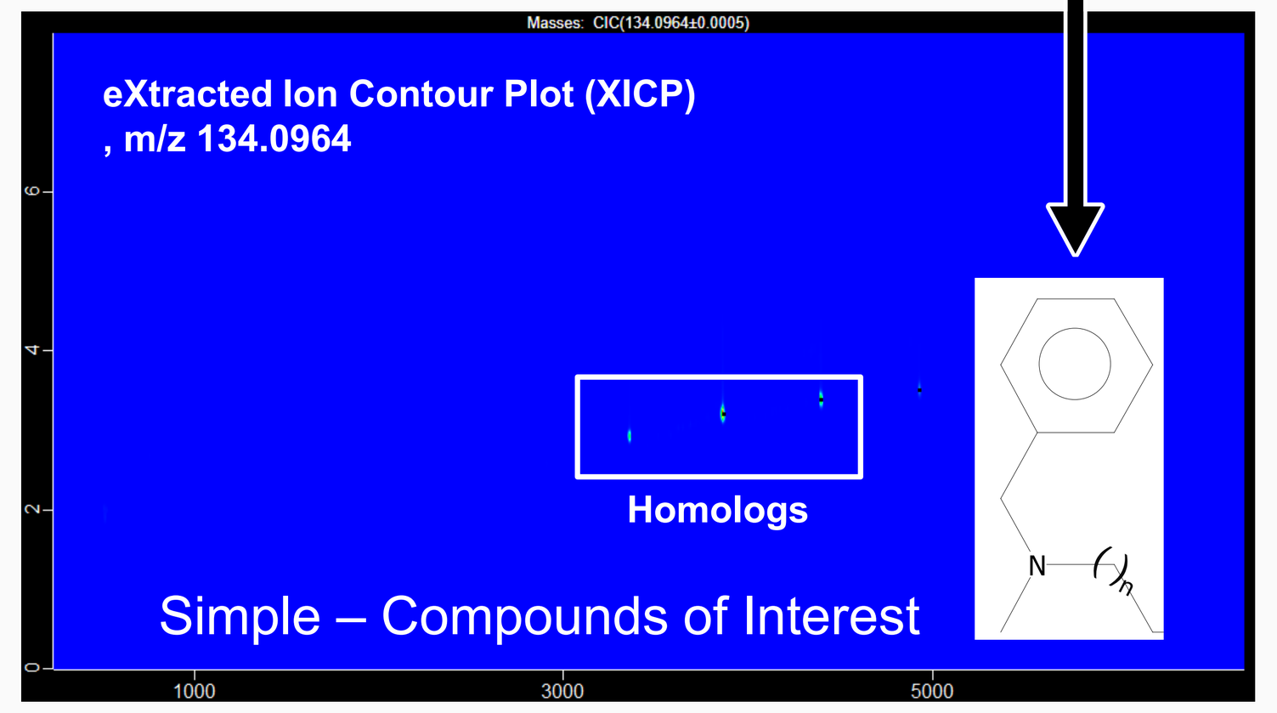


Figure 4. Filtered (XICP) contour plot displaying a homologous series of alkylmethylbenzylamines.

Monitoring the food we consume

2) Food (Fish)

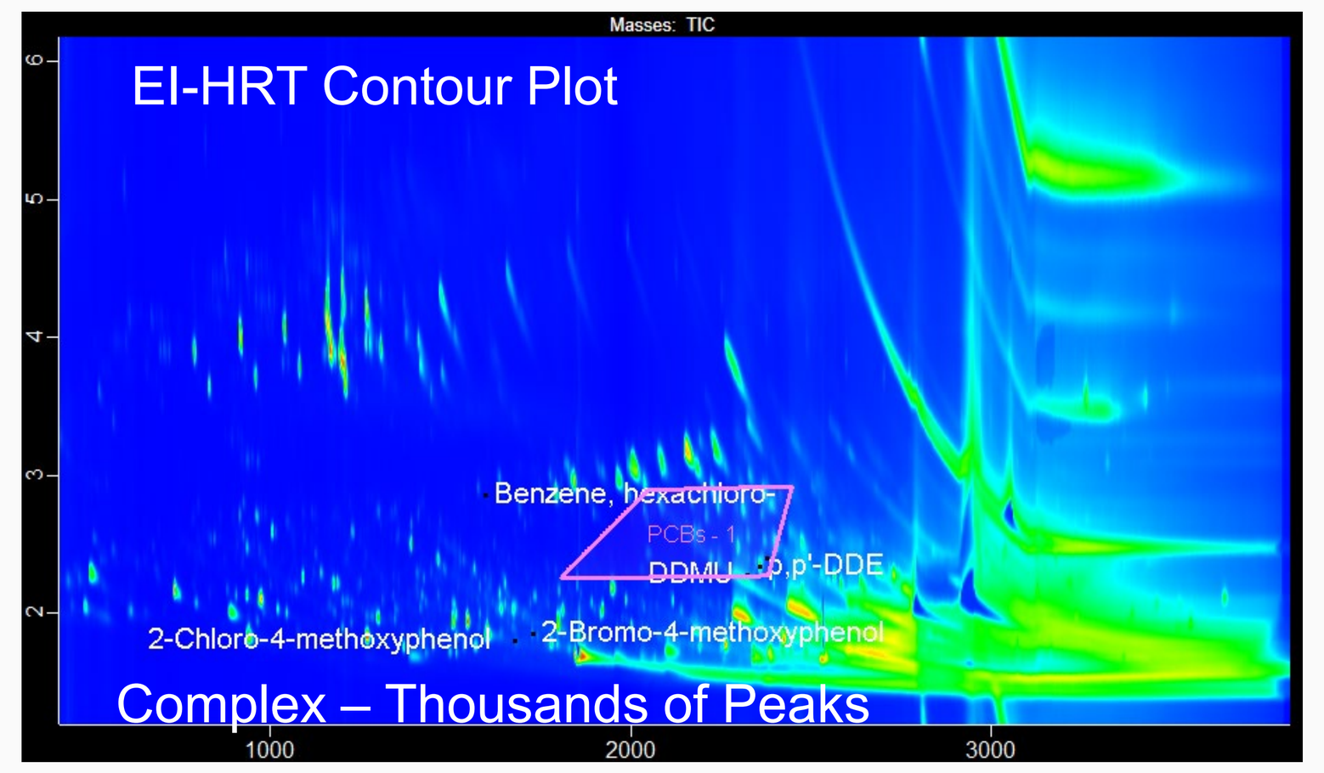


Figure 5. Contour plot displaying polychlorinated biphenyl region and selected halogenated organic compounds.

Table 2: Selected Halogenated Compounds

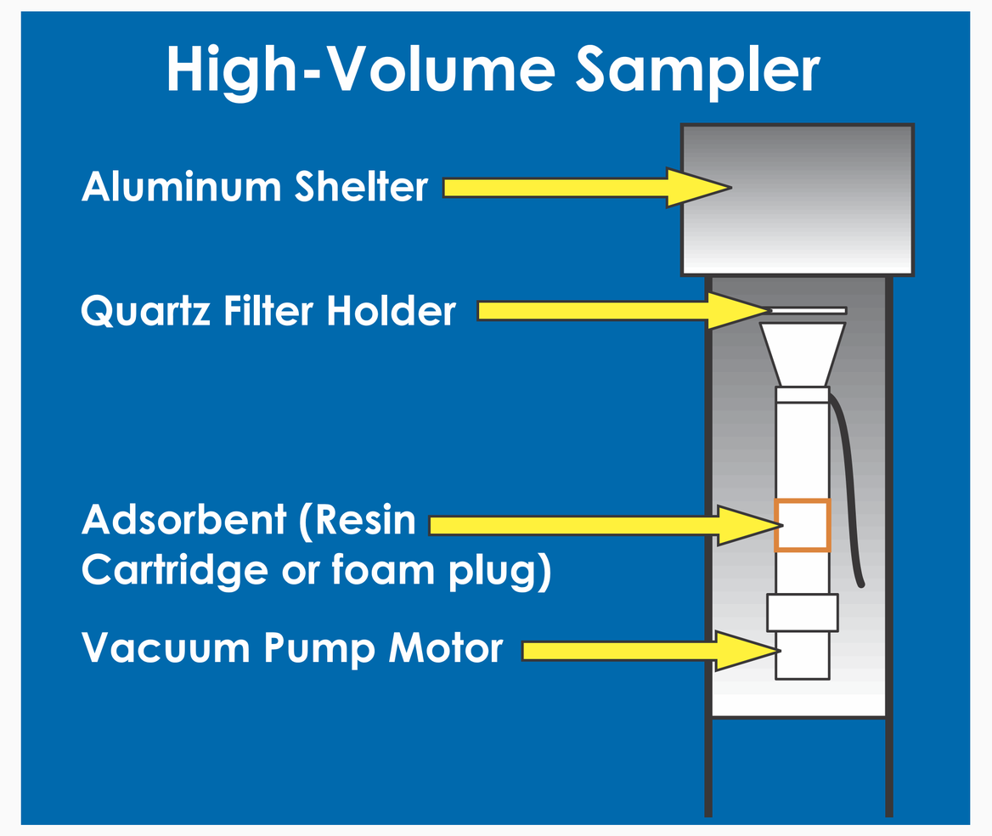
Name	R.T. (s)	Formula	PPM	Similarity
Benzene, hexachloro-	1595, 2.860	C_6Cl_6	0.87	928
Phenol, 2-chloro-4-methoxy-	1600, 1.900	$C_7H_7ClO_2$	1.37	932
2,2',3-Trichloro-1,1'-biphenyl	1915, 2.285	$C_{12}H_7Cl_3$	0.32	787
1,1'-Biphenyl, 2,4,4'-trichloro-	1970, 2.399	$C_{12}H_7Cl_3$	1.55	795
1,1'-Biphenyl, 2,4,4',6-tetrachloro-	1995, 2.552	$C_{12}H_6Cl_4$	1.06	679
1,1'-Biphenyl, 2,4,4'-trichloro-	2030, 2.320	$C_{12}H_7Cl_3$	0.76	886
1,1'-Biphenyl, 2,2',4,4'-tetrachloro-	2045, 2.440	$C_{12}H_6Cl_4$	0.39	942
1,1'-Biphenyl, 2,3',4,4',5-pentachloro-	2045, 2.620	$C_{12}H_5Cl_5$	-0.57	733
1,1'-Biphenyl, 3,3',4,4'-tetrachloro-	2120, 2.525	$C_{12}H_6Cl_4$	-0.09	726
1,1'-Biphenyl, 2,3',5,5'-tetrachloro-	2155, 2.470	$C_{12}H_6Cl_4$	-0.99	780
1,1'-Biphenyl, 2,2',3',4,6-Pentachloro-	2155, 2.620	$C_{12}H_5Cl_5$	0.68	879
1,1'-Biphenyl, 2,2',3,3'-tetrachloro-	2165, 2.320	$C_{12}H_6Cl_4$	0.75	931
Biphenyl, 2,4,4',5-tetrachloro-	2175, 2.336	$C_{12}H_6Cl_4$	0.08	905
Biphenyl, 2,4,4',5-tetrachloro-	2175, 2.456	$C_{12}H_6Cl_4$	0.08	908
1,1'-Biphenyl, 2,2',4,5,5'-pentachloro-	2175, 2.605	$C_{12}H_5Cl_5$	0.61	911
1,1'-Biphenyl, 2,2',4,4',5-pentachloro-	2185, 2.595	$C_{12}H_5Cl_5$	0.81	922
2,2',3,4',5-Pentachloro-1,1'-biphenyl	2215, 2.375	$C_{12}H_5Cl_5$	0.18	921
2,3,3',4,5'-Pentachloro-1,1'-biphenyl	2260, 2.520	$C_{12}H_5Cl_5$	1.17	901
1,1'-Biphenyl, 2,2',3,5,5',6-hexachloro-	2265, 2.840	$C_{12}H_4Cl_6$	1.32	780
1,1'-Biphenyl, 2,2',3,3',4-pentachloro-	2275, 2.480	$C_{12}H_5Cl_5$	-0.79	873
1,1'-Biphenyl, 2,2',3,3',4,4'-hexachloro-	2275, 2.585	$C_{12}H_4Cl_6$	0.43	889
1,1'-Biphenyl, 2,2',3,4',5',6-hexachloro-	2290, 2.786	$C_{12}H_4Cl_6$	0.49	920
2,2',3,3',5,6-Hexachloro-1,1'-biphenyl	2305, 2.558	$C_{12}H_4Cl_6$	N/A	780
1,1'-Biphenyl, 2,2',4,4',5,5'-hexachloro-	2310, 2.760	$C_{12}H_4Cl_6$	0.5	942
DDMU	2320, 2.285	$C_{14}H_9Cl_3$	-0.32	820
1,1'-Biphenyl, 2,2',3,4',5,5'-hexachloro-	2325, 2.555	$C_{12}H_4Cl_6$	0.58	916
1,1'-Biphenyl, 2,2',3',4,6-Pentachloro-	2340, 2.240	$C_{12}H_5Cl_5$	0.12	703
1,1'-Biphenyl, 2,3,3',4'-tetrachloro-	2340, 2.295	$C_{12}H_6Cl_4$	0.35	903

Name	R.T. (s)	Formula	PPM	Similarity
1,1'-Biphenyl, 2,3',4,4',5-pentachloro-	2340, 2.400	$C_{12}H_5Cl_5$	0.12	717
1,1'-Biphenyl, 2,2',4,5,6'-pentachloro-	2345, 2.357	$C_{12}H_5Cl_5$	0.33	807
2,3,3',4,5'-Pentachloro-1,1'-biphenyl	2345, 2.562	$C_{12}H_5Cl_5$	0.33	872
p,p'-DDE	2355, 2.350	$C_{14}H_8Cl_4$	0.02	935
1,1'-Biphenyl, 2,2',3,3',5,5',6-heptachloro-	2355, 2.795	$C_{12}H_3Cl_7$	0	897
1,1'-Biphenyl, 2,3,3',4',6-pentachloro-	2365, 2.401	$C_{12}H_5Cl_5$	0.35	931
1,1'-Biphenyl, 2,2',3,3',5,5',6-heptachloro-	2365, 2.745	$C_{12}H_3Cl_7$	0.34	832
2,3,3',5,5'-Pentachloro-1,1'-biphenyl	2370, 2.528	$C_{12}H_5Cl_5$	0.44	927
o,p'-DDE	2375, 2.410	$C_{14}H_8Cl_4$	-1.14	794
1,1'-Biphenyl, 2,2',3,3',4,5,6'-heptachloro-	2380, 2.780	$C_{12}H_3Cl_7$	0.8	914
1,1'-Biphenyl, 2,2',3,3',5,5',6-heptachloro-	2390, 2.770	$C_{12}H_3Cl_7$	1.23	850
1,1'-Biphenyl, 2,2',3,4',5',6-hexachloro-	2395, 2.602	$C_{12}H_4Cl_6$	0.61	913
1,1'-Biphenyl, 2,2',3,5,5',6-hexachloro-	2410, 2.594	$C_{12}H_4Cl_6$	0.01	844
1,1'-Biphenyl, 2,2',3,3',4,5,6,6'-octachloro-	2415, 2.780	$C_{12}H_2Cl_8$	-0.42	825
2,3,3',4',5,5'-Hexachloro-1,1'-biphenyl	2440, 2.595	$C_{12}H_4Cl_6$	0.57	893
1,1'-Biphenyl, 2,2',3,4',5',6-hexachloro-	2475, 2.520	$C_{12}H_4Cl_6$	-0.03	917
2,2',3,4',5,6-Hexachloro-1,1'-biphenyl	2495, 2.345	$C_{12}H_4Cl_6$	0.79	908
1,1'-Biphenyl, 2,2',3,3',5,5',6-heptachloro-	2495, 2.765	$C_{12}H_3Cl_7$	-0.39	890
1,1'-Biphenyl, 2,2',3,3',4,4',5-heptachloro-	2505, 2.740	$C_{12}H_3Cl_7$	0.14	849
1,1'-Biphenyl, 2,2',3,3',5,5',6-heptachloro-	2515, 2.580	$C_{12}H_3Cl_7$	0.27	926
1,1'-Biphenyl, 2,2',3,3',5,5',6-heptachloro-	2525, 2.745	$C_{12}H_3Cl_7$	0.83	924
2,3,3',4,5'-Pentachloro-1,1'-biphenyl	2535, 2.345	$C_{12}H_5Cl_5$	0.5	924
1,1'-Biphenyl, 2,2',3,3',5,5',6-heptachloro-	2545, 2.535	$C_{12}H_3Cl_7$	0.46	926
1,1'-Biphenyl, 2,2',3,3',4,4',5,5'-octachloro-	2565, 2.799	$C_{12}H_2Cl_8$	0.18	885
1,1'-Biphenyl, 2,2',3,3',4,4',5,5'-octachloro-	2575, 2.760	$C_{12}H_2Cl_8$	-0.13	884
1,1'-Biphenyl, 2,2',3,4',5',6-hexachloro-	2635, 2.340	$C_{12}H_4Cl_6$	-0.22	925
1,1'-Biphenyl, 2,2',3,3',5,5',6-heptachloro-	2690, 2.500	$C_{12}H_3Cl_7$	-0.51	852

Monitoring the air we breathe

3) Air Particulate Matter

Air Samples: Collection and Introduction



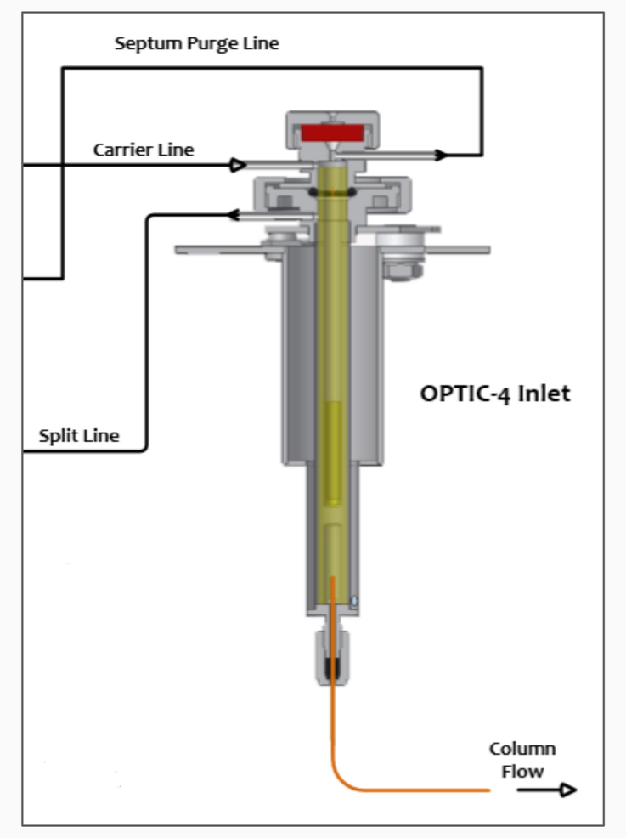


Figure 6. Active air sampler (left). Placed in urban and rural sites (24-hour Sampling). GL Sciences Optic-4 Inlet (Right) used for Thermal Desorption (TD) and Pyrolysis (Pyr).

Air Sample A (TD)

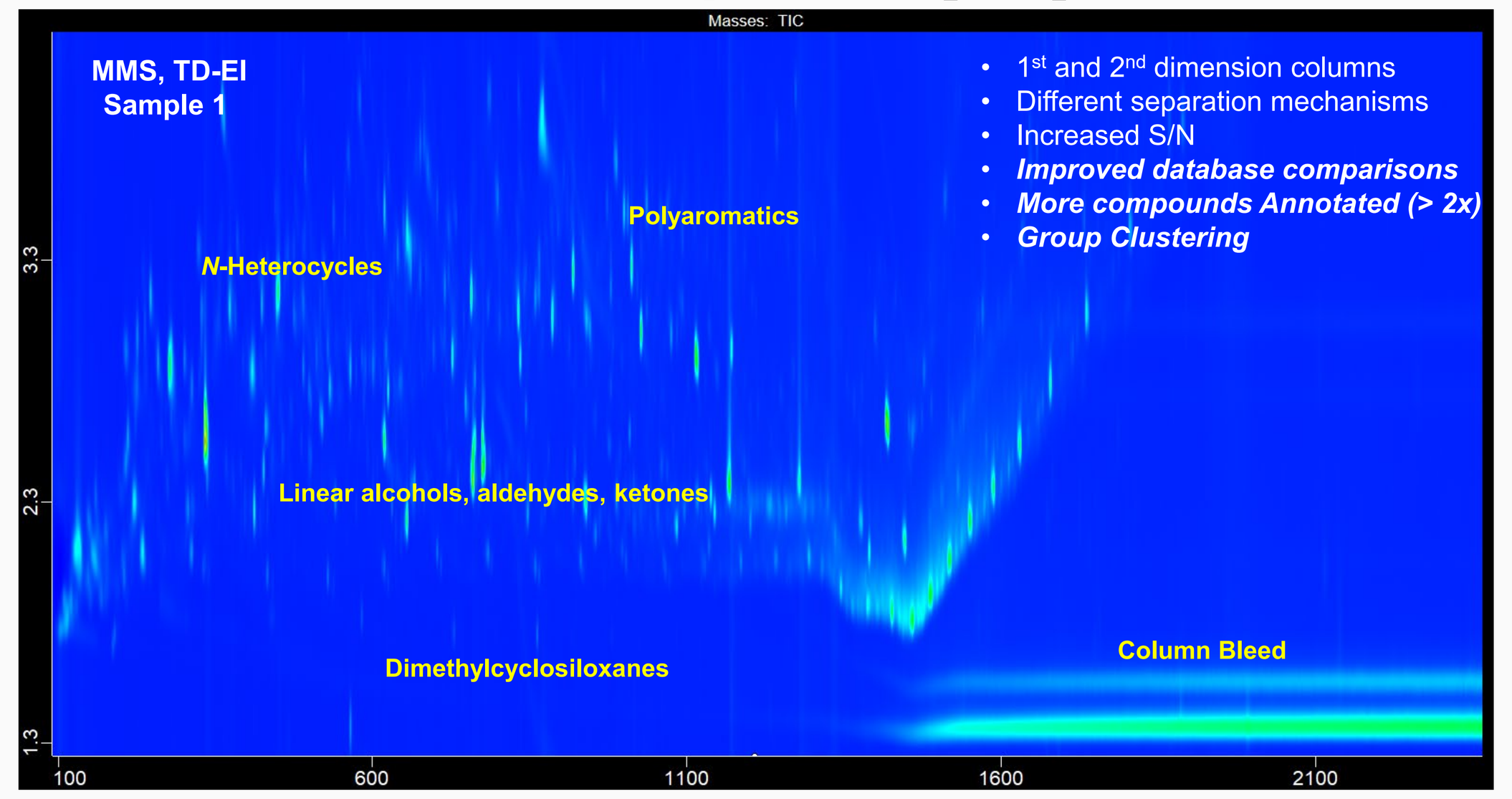


Figure 7. Contour plot displaying areas of group clustering for an air sample.

Table 3: Representative Compounds in Sample A

Name	Formula	R.T. (s)	Similarity	PPM
Furan, 2-methyl-	C_5H_6O	141, 1.944	893	1.77
1,4-Dioxin, 2,3-dihydro-	$C_4H_6O_2$	195, 2.120	824	-0.26
Pyrazine	$C_4H_4N_2$	213, 2.408	820	0.77
Pyrazine	$C_4H_4N_2$	228, 2.596	793	0.25
Cyclopentane, 1,2,4-trimethyl-	C_8H_{16}	243, 2.016	791	0.99
1H-Pyrrole, 2-methyl-	C_5H_7N	306, 2.392	871	0.4
Maleic anhydride	$C_4H_2O_3$	309, 3.064	938	-0.24
4-Cyclopentene-1,3-dione	$C_5H_4O_2$	333, 3.328	892	-0.88
2-Heptanone	$C_7H_{14}O$	336, 2.336	847	1.33
4-Cyclopentene-1,3-dione	$C_5H_4O_2$	339, 3.061	901	-0.11
2(5H)-Furanone	$C_4H_4O_2$	366, 3.776	926	0.1
1,2-Cyclopentanedione	$C_5H_6O_2$	378, 2.928	918	0.33
Pyridine, 2-ethenyl-	C_7H_7N	381, 2.760	893	0.84
Benzaldehyde	C_7H_6O	405, 2.768	932	0.26
Furan, 2-pentyl-	$C_9H_{14}O$	432, 2.184	905	0.84
Pyridine, 2,4,6-trimethyl-	$C_8H_{11}N$	435, 2.504	861	0.68
Octanal	$C_8H_{16}O$	441, 2.327	932	N/A
Benzyl chloride	C_7H_7Cl	456, 2.872	832	0.95
2-Aminocyanoacetamide	$C_3H_5N_3O$	465, 1.320	885	N/A
1-Hexanol, 2-ethyl-	$C_8H_{18}O$	465, 2.344	935	N/A
p-Cymene	$C_{10}H_{14}$	465, 2.410	813	0.37
2H-Pyran-2-one	$C_5H_4O_2$	474, 3.877	864	1.07
Benzeneacetaldehyde	C_8H_8O	483, 3.136	909	0.73
2-Pyrrolidinone, 1-methyl-	C_5H_9NO	483, 3.520	934	-0.48
2-Cyclohexen-1-one, 3-methyl-	$C_7H_{10}O$	495, 3.072	820	0.64
1-Octanol	$C_8H_{18}O$	504, 2.272	829	N/A
2-Pyrrolidinone	C_4H_7NO	513, 3.416	951	-0.4
2,5-Furandicarboxaldehyde	$C_6H_4O_3$	519, 3.264	829	1.16
1-Heptanol, 6-methyl-	$C_8H_{18}O$	522, 1.961	812	N/A
2,5-Pyrrolidinedione, 1-methyl-	$C_5H_7NO_2$	525, 3.531	888	1.11
(S)-(+)-6-Methyl-1-octanol	$C_9H_{20}O$	570, 2.351	792	N/A
Succinimide	$C_4H_5NO_2$	570, 3.952	931	0.36

Name	Formula	R.T. (s)	Similarity	PPM
Benzonitrile, 2-methyl-	C_8H_7N	573, 3.449	843	0.8
Pyranone	$C_6H_8O_4$	579, 3.112	828	0.73
2-Propen-1-one, 1-phenyl-	C_9H_8O	588, 3.136	847	1.29
p-Menthan-1-ol	$C_{10}H_{20}O$	600, 2.460	919	N/A
Ethanone, 1-(4-methylphenyl)-	$C_9H_{10}O$	615, 2.888	843	1.38
Decanal	$C_{10}H_{20}O$	627, 2.271	942	N/A
1-Heptanol, 2-propyl-	$C_{10}H_{22}O$	633, 2.192	918	N/A
1,4:3,6-Dianhydro-α-d-glucopyranose	$C_6H_8O_4$	636, 3.296	873	-0.54
Ethanol, 2-phenoxy-	$C_8H_{10}O_2$	645, 2.928	827	0.46
Piperidine, 2-propyl-, (S)-	$C_8H_{17}N$	678, 2.040	831	0.74
Formamide, N-cyclohexyl-	$C_7H_{13}NO$	678, 3.456	815	0.57
Undecanal	$C_{11}H_{22}O$	711, 2.344	937	N/A
Formamide, N,N-dibutyl-	$C_9H_{19}NO$	711, 2.656	909	0.2
Indole	C_8H_7N	711, 3.448	896	0.77
1,2-Benzenedicarboxylic acid	$C_8H_6O_4$	726, 3.504	958	N/A
2-Pyrrolidinecarbonitrile, 5-oxo	$C_5H_6N_2O$	747, 3.984	844	0.99
Nicotine	$C_{10}H_{14}N_2$	786, 2.768	917	0.4
Vanillin	$C_8H_8O_3$	795, 3.536	844	-0.26
trans-Isoeugenol	$C_{10}H_{12}O_2$	831, 2.880	847	0.73
1-Dodecanol	$C_{12}H_{26}O$	840, 2.248	920	N/A
Phthalimide	$C_8H_5NO_2$	843, 3.608	912	0.31
2-Ethyl-1-dodecanol	$C_{14}H_{30}O$	864, 2.216	902	N/A
1-Dodecanamine, N,N-dimethyl-	$C_{14}H_{31}N$	894, 2.120	909	0.16
n-Tridecan-1-ol	$C_{13}H_{28}O$	915, 2.304	912	N/A
2,2-Dimethylindene, 2,3-dihydro-	$C_{11}H_{14}$	918, 2.784	791	0.24
1,3-Isobenzofurandione, 4,5-dimethyl-	$C_{10}H_8O_3$	921, 3.456	806	1.38
Cedrol	$C_{15}H_{26}O$	948, 2.656	913	0.82
2-Methyl-1-undecanol	$C_{12}H_{26}O$	957, 2.206	879	N/A
Octane, 1,1'-oxybis-	$C_{16}H_{34}O$	975, 2.112	938	N/A
1-Tetradecanol	$C_{14}H_{30}O$	984, 2.289	913	N/A
n-Hexyl salicylate	$C_{13}H_{18}O_3$	990, 2.659	817	1.53
γ-Dodecalactone	$C_{12}H_{22}O_2$	990, 2.880	890	N/A

Name	Formula	R.T. (s)	Similarity	PPM
2-Ethyl-1-dodecanol	$C_{14}H_{30}O$	999, 2.271	833	N/A
(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol	$C_{11}H_{14}O_3$	1008, 3.240	879	0.25
1-Dodecanol, 2-methyl-, (S)-	$C_{13}H_{28}O$	1011, 2.196	802	N/A
Benzoic acid, 2-ethylhexyl ester	$C_{15}H_{22}O_2$	1011, 2.608	907	N/A
Methyl tetradecanoate	$C_{15}H_{30}O_2$	1014, 2.296	792	0.65
Cotinine	$C_{10}H_{12}N_2O$	1023, 3.912	859	1.42
α-Hexylcinnamaldehyde	$C_{15}H_{20}O$	1038, 2.744	850	-0.6
Syringylacetone	$C_{11}H_{14}O_4$	1053, 3.448	843	0.8
Isopropyl myristate	$C_{17}H_{34}O_2$	1077, 2.188	944	-0.15
Ethanedione, diphenyl-	$C_{14}H_{10}O_2$	1083, 3.552	937	0.58
2-Pentadecanone, 6,10,14-trimethyl-	$C_{18}H_{36}O$	1092, 2.223	900	0.94
β-Phenylpropiophenone	$C_{15}H_{14}O$	1107, 3.416	919	0.33
Caffeine	$C_8H_{10}N_4O_2$	1107, 4.136	914	0.82
1-Hexadecanol	$C_{16}H_{34}O$	1113, 2.292	941	N/A
Dimethyl palmitamine	$C_{18}H_{39}N$	1131, 2.096	908	0.03
Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	1140, 2.240	925	-0.49
4-(2-Phenylvinyl)pyridine, trans-	$C_{13}H_{11}N$	1149, 3.681	792	-0.81
trans-Sinapaldehyde	$C_{11}H_{12}O_4$	1185, 3.656	812	1.02
Chalcone	$C_{15}H_{12}O$	1191, 3.548	818	-1.01
m-Aminophenylacetylene	C_8H_7N	1227, 1.344	828	1.04
Benzene, 1,1'-(1,3-butadiyne-1,4-diyl)bis-	$C_{16}H_{10}$	1269, 3.952	853	0.07
Methyl dehydroabietate	$C_{21}H_{30}O_2$	1374, 2.528	869	0.21
Cyclohexane, 1,3,5-triphenyl-	$C_{24}H_{24}$	1416, 2.592	853	1.44
Squalene	$C_{30}H_{50}$	1530, 2.345	841	-0.68
Cholesta-3,5-diene	$C_{27}H_{44}$	1569, 3.036	821	-0.22
Pyridine, 2,4,6-triphenyl-	$C_{23}H_{17}N$	1617, 2.088	858	-0.37
19-Norcholesta-1,3,5(10)-trien-6-one	$C_{26}H_{38}O$	1686, 1.944	829	1.12
Stearyl palmitate	$C_{34}H_{68}O_2$	1962, 1.736	788	0.86

Similarity Ave. 871/1000

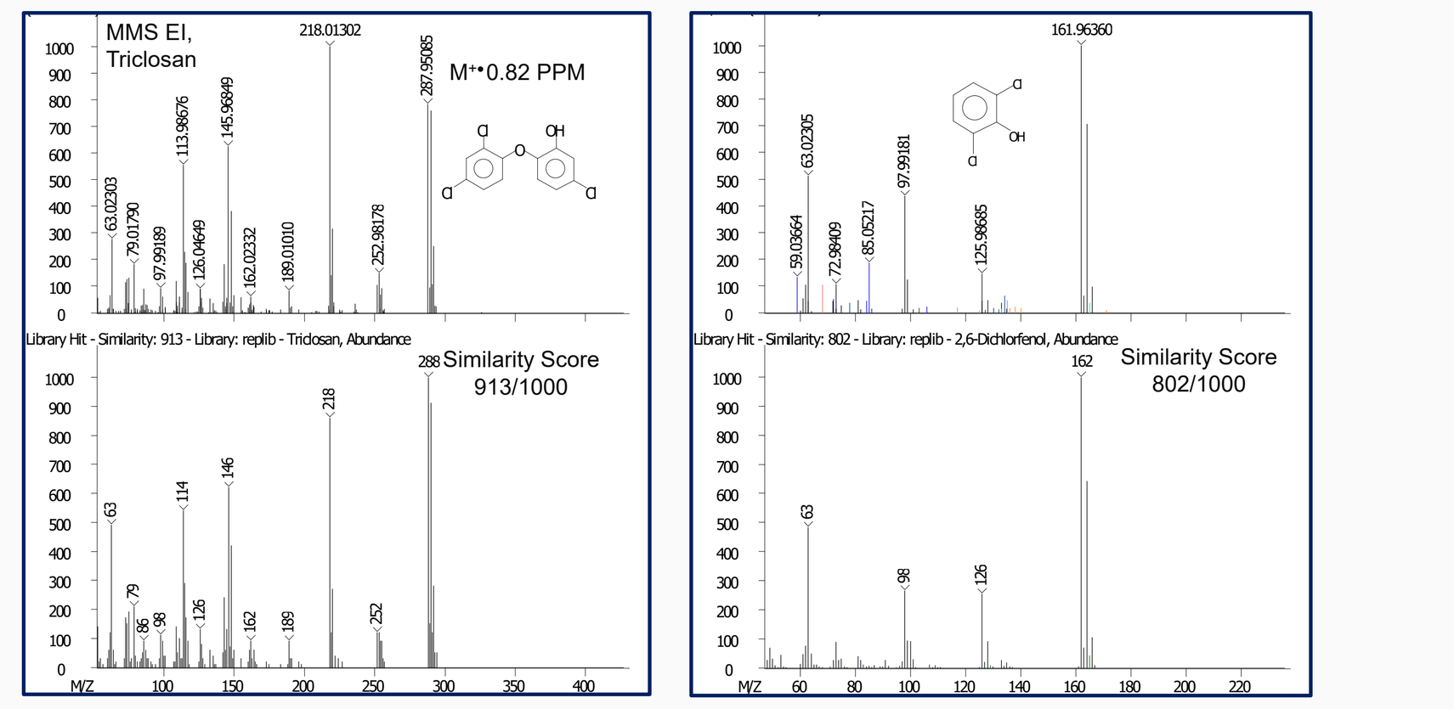


Figure 8. Peak True and library EI mass spectra for triclosan (Left) and 2,6-dichlorophenol (Right).

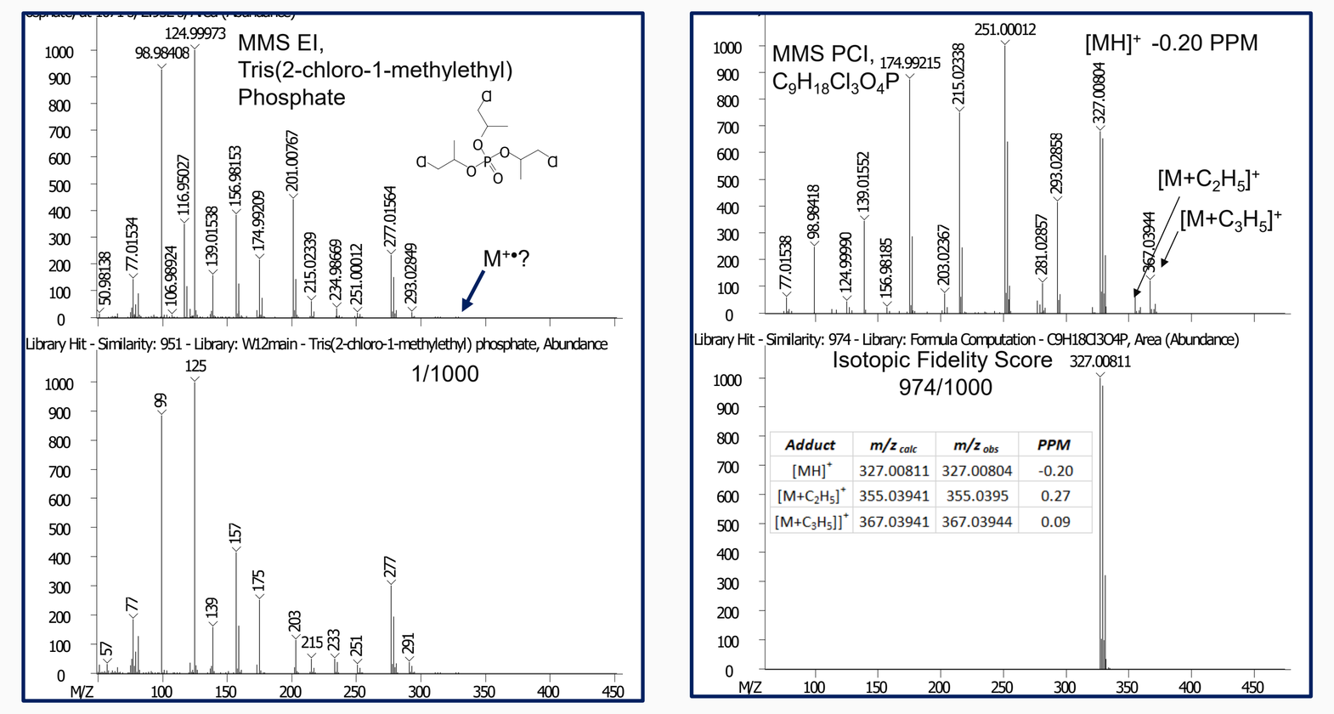


Figure 9. Peak True and library EI mass spectra for a phosphorus flame retardant (Left) and complementary PCI spectrum (Right).

Air Sample B (Pyr)

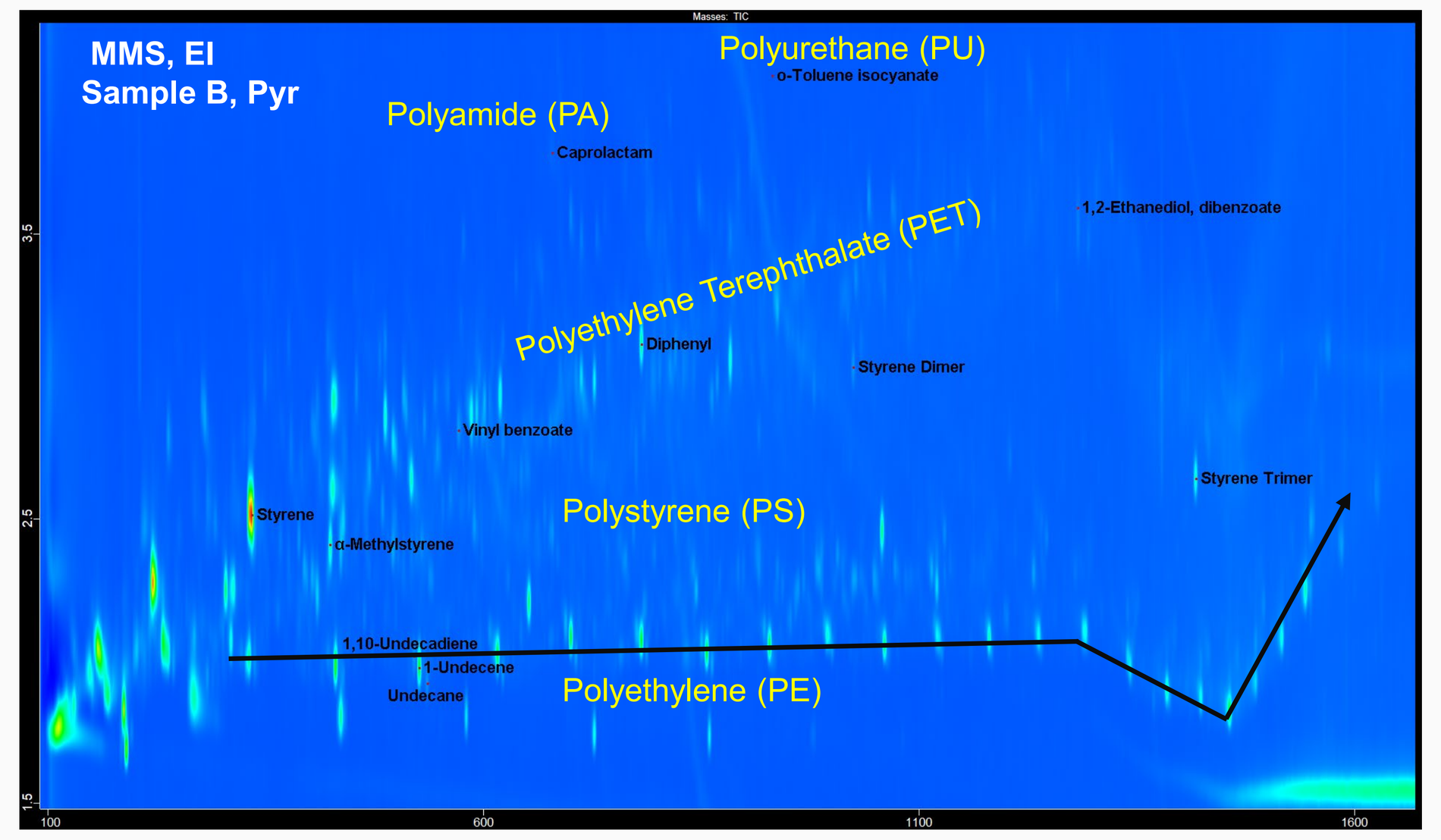


Figure 10. Contour plot displaying pyrolytic markers in Sample B.

Table 4: Pyrolytic Markers

Polymer	Pyrolysis Markers	RI	Marker Ions m/z
PS	Styrene α-Methylstyrene Styrene Dimer Styrene Trimer	878 960 1761 2514	104.06205 118.07770, 117.06988, 103.05423 208.12465, 130.07770, 91.05423 312.18725, 207.11683, 91.05423
PE	Alkanes 1-Alkenes α,ω-Alkadienes	Series Series Series	85.10118, 71.08553, 57.06988 97.10118, 83.0883, 69.06988, 55.05423 95.08553, 81.06988, 67.05423, 55.05423
PU	Toluene Diisocyanate Isophorone Diisocyante Methylene Diphenyl Diisocyanate	1352 1584 2092	174.04238, 145.03964 123.11683, 110.06004 250.07368, 208.07569
PET	Diphenyl Vinyl Benzoate 1,2-Ethanediol, dibenzoate	1366 1132 2178	154.07770, 76.03075 105.03349, 77.03862, 51.02314 105.03349, 77.03862
N6	Caprolactam Caprolactam dimer	1255 2005	113.08352, 85.05222, 55.01784 226.16758, 198.17266

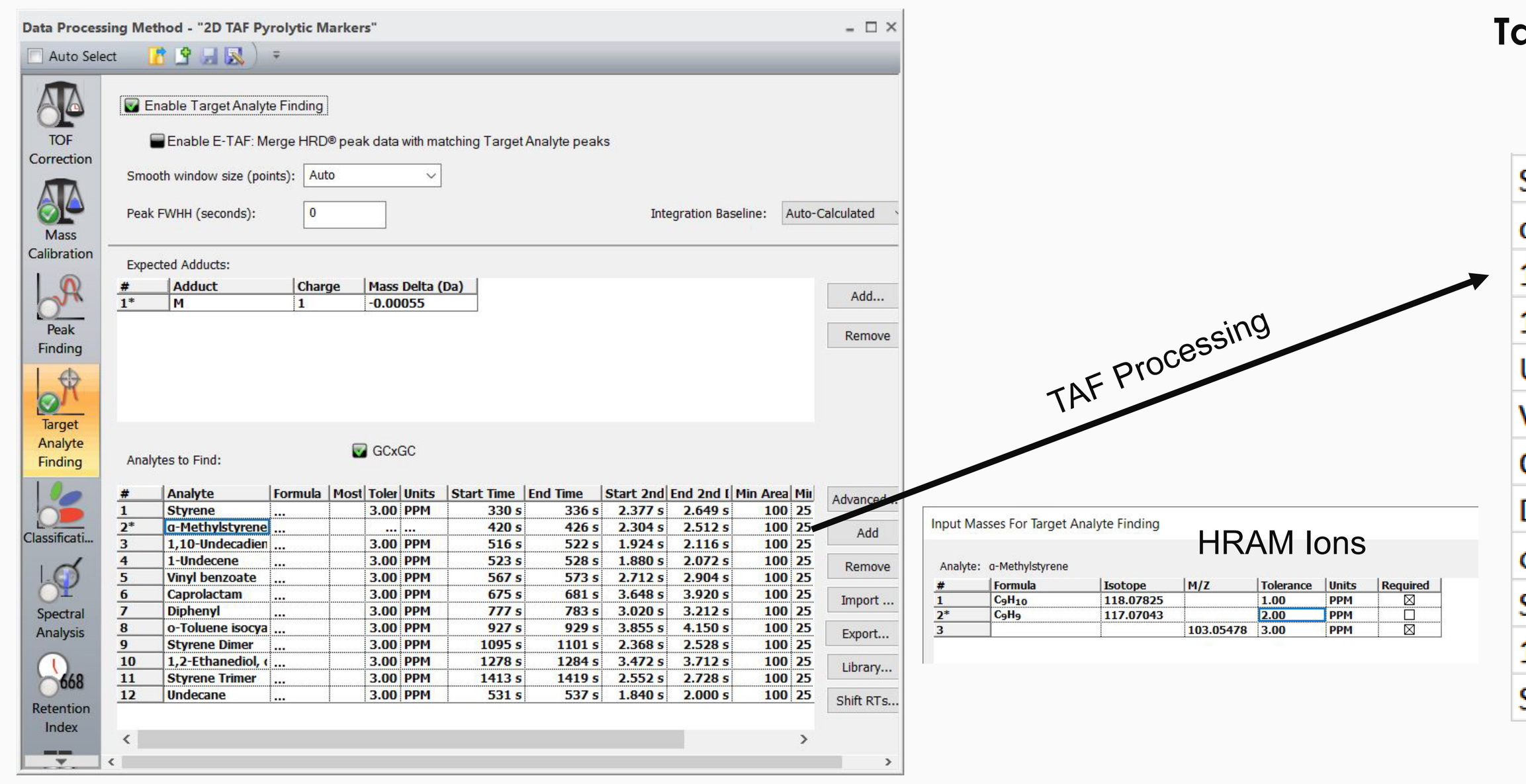


Figure 11. Target Analyte Finding (TAF) – pyrolytic markers.

Table 5: Sample B, TAF Results

Name	R.T. (s)	Area
Styrene	336, 2.560	12089563
α-Methylstyrene	426, 2.432	2233858
1,10-Undecadiene	522, 2.032	132298
1-Undecene	528, 1.992	713542
Undecane	537, 1.944	412998
Vinyl benzoate	573, 2.816	455352
Caprolactam	681, 3.784	1365928
Diphenyl	783, 3.104	1067612
o-Toluene isocyanate	927, 4.136	7767
Styrene Dimer	1101, 2.440	34938
1,2-Ethanediol, dibenzoate	1284, 3.552	266467
Styrene Trimer	1413, 2.600	58137

Summary

- HRT and MMS technology are powerful tools for the analysis of complex environmental samples (dust, food, air)
- Compounds were annotated using:
  - Database comparisons
  - Formula determinations using high-resolution accurate mass ions
  - Chemical ionization data resulted in increased confidence for compound annotation