Comprehensive Analysis of Microplastics and Their Adsorbed Environmental Matrix Constituents Using a Combination of Thermal Desorption and Pyrolysis with GCxGC-HRTOFMS

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LECO EMPOWERING RESULTS

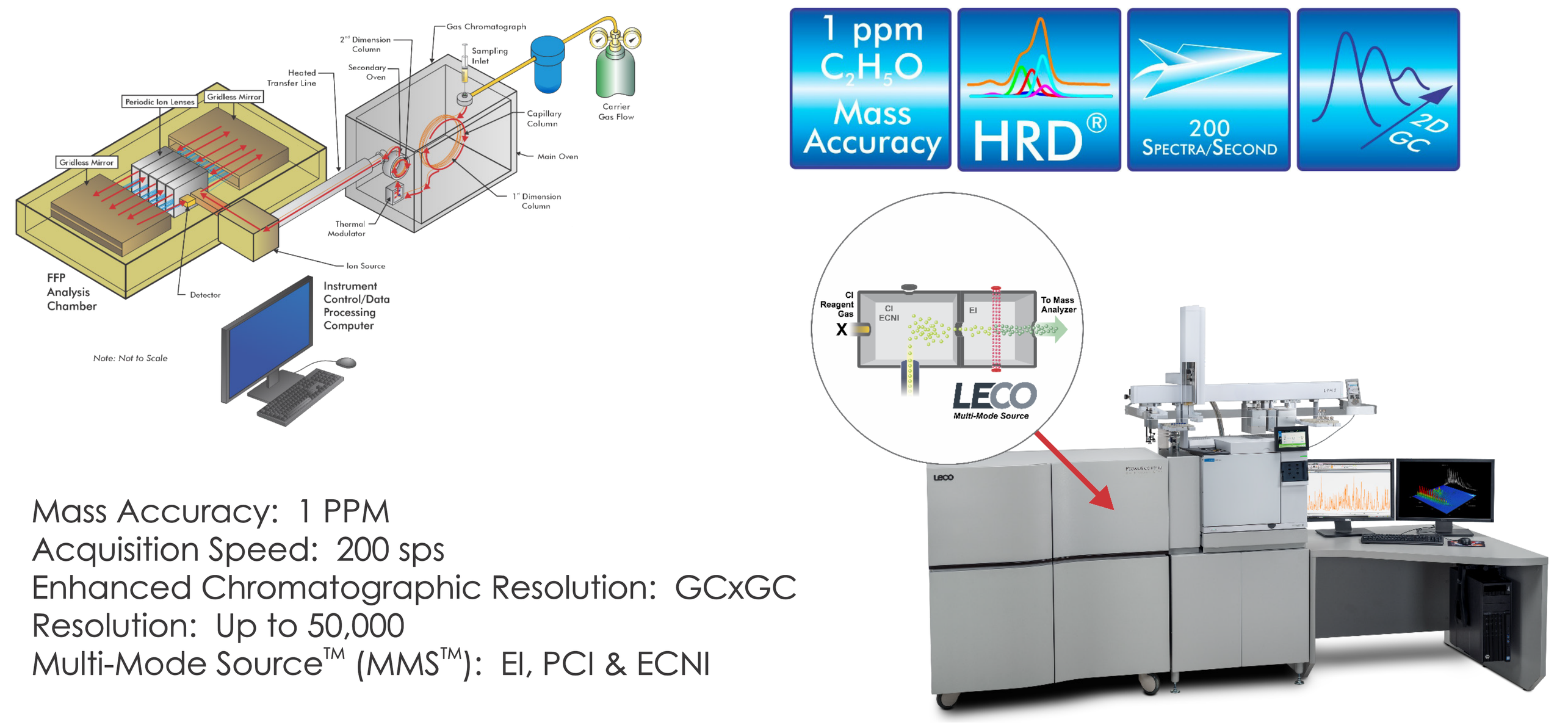
Introduction

- Plastic production began in the early 20th century
- Plastic waste is expected to grow to a total of 26 billion tons by 2050
- Plastic materials are very useful materials, but there are major issues:
  - Breakdown products (e.g., microplastics) can be detrimental to life
  - Additional harmful substances in the environment are often adsorbed by microplastics, creating a difficult matrix to analyze

Study Objective

To characterize air filter samples for microplastics and associated chemicals using thermal desorption and pyrolysis with multi-dimensional gas chromatography-high resolution time-of-flight mass spectrometry (TD/Py-GCxGC-HRTOFMS)

Analytical Platform



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

Figure 1. Pegasus® HRT+ 4D and Multi-Mode Source (MMS)

Instrument Parameters

Gas Chromatograph	Agilent 7890B with LECO Dual Stage QuadJet™ Modulator
Sample Introduction A	TD, Split 10:1 (3 min) → Splitless, 50 °C to 300 °C at 10 °C/s
Sample Introduction B	Pyr, 10:1 → Splitless (3 min), 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 205 °C, then ramp to 300 °C at 20 °C/min to 300 °C (hold 15 min). 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 spectra/s

Air Sample Collection Locations

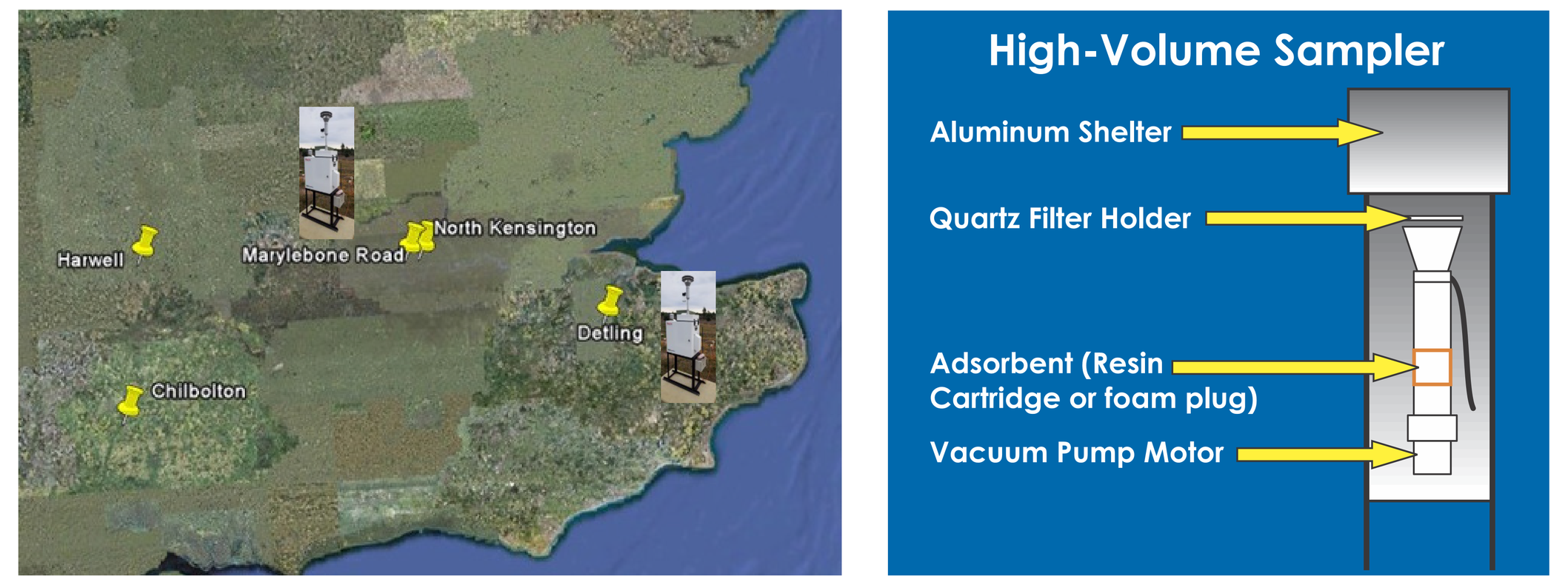


Figure 2. High volume samplers with PM10 Quartz filters (Right) were used to collect samples for 24 hour periods. Samples were collected by Imperial College researchers at Detling (Rural) and Marylebone (Urban) sites in the UK (Left).

Sample Preparation and Introduction

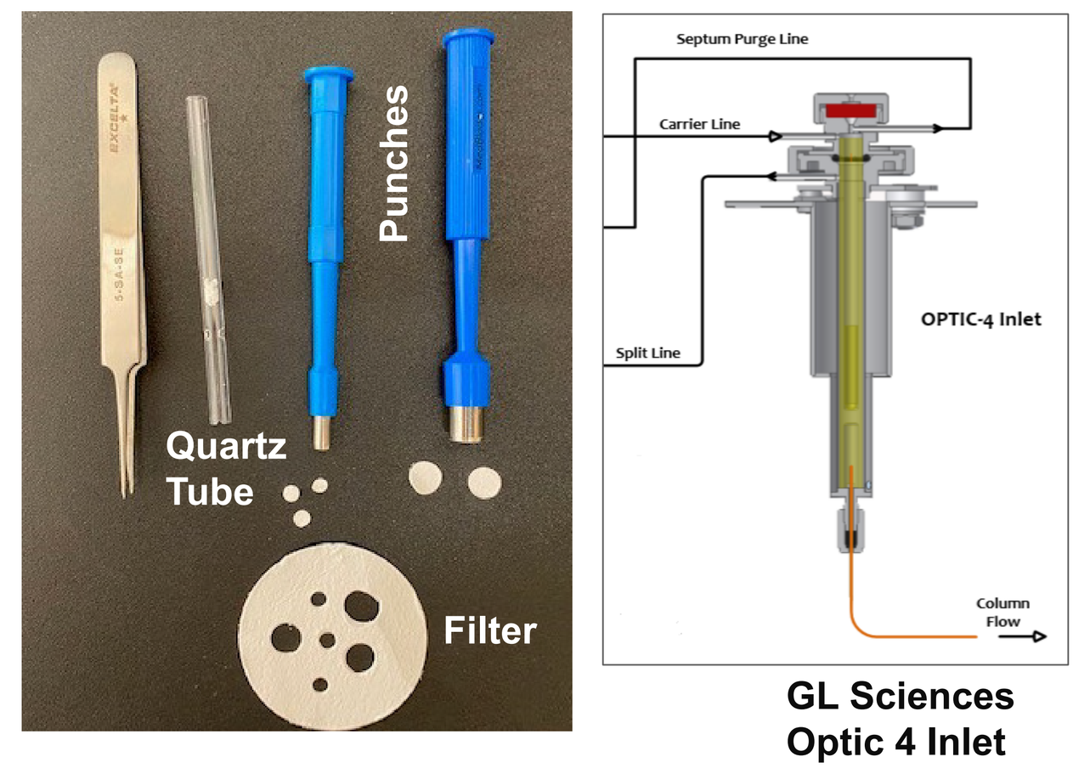


Figure 3. Two 4 mm or 8 mm diameter sample(s) were transferred to quartz tubes (Left). Tube was placed in a GL Sciences Optic-4 Inlet (Right) for thermal desorption and pyrolysis.

Sample 1, Thermal Desorption (TD): Methods and Results

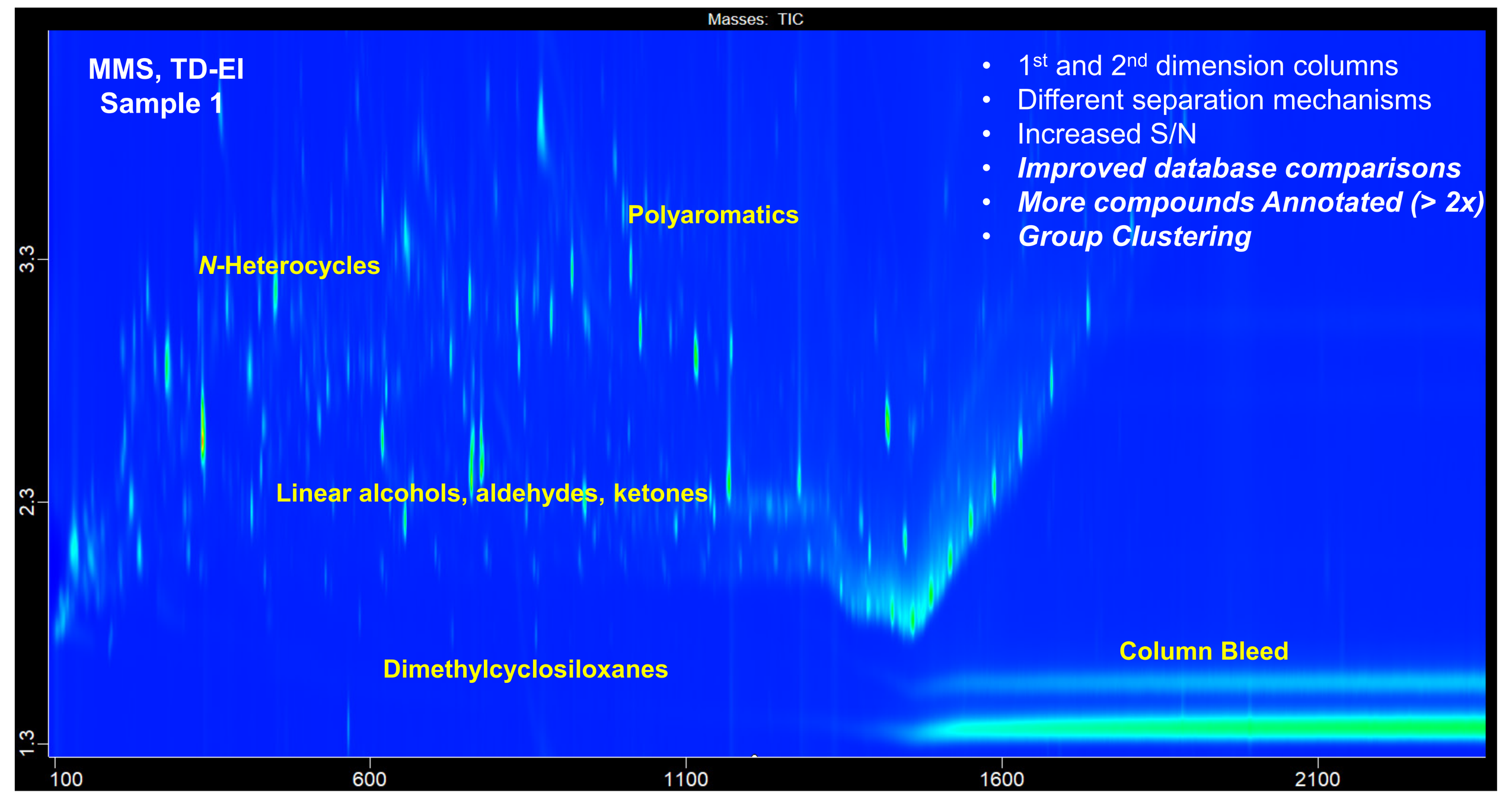


Figure 4. TD-EI contour plot displaying the location of different classes of compounds.

Table 2. TD-EI Sample 1, non-targeted processing results – representative compounds.

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

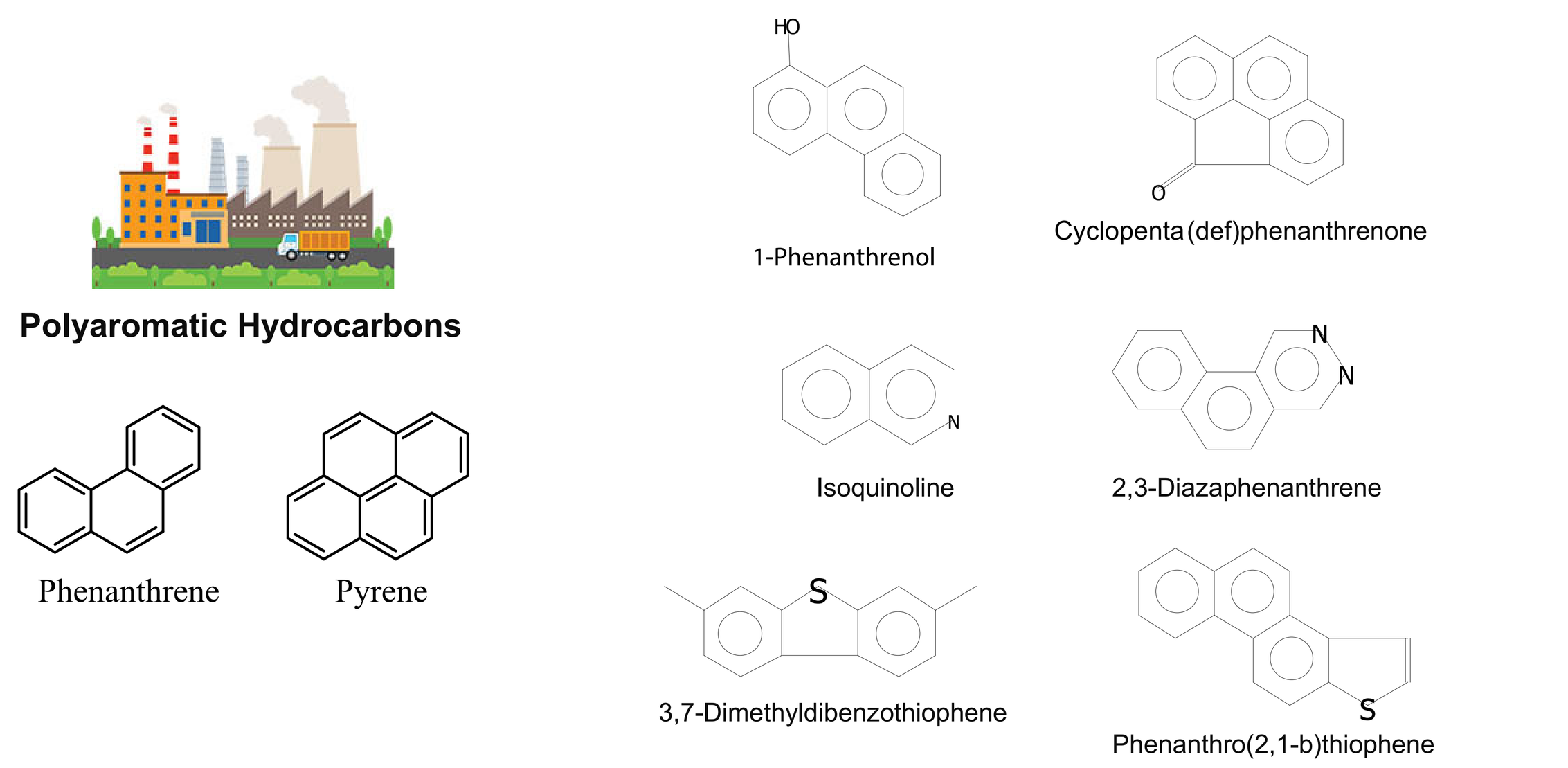


Figure 5. TD-EI Sample 1 pollutants: PAHs and hetero-PAHs.

Sample 1 (TD-EI): Methods and Results, Continued

Table 3. TD-EI Sample 1, Polyaromatic Hydrocarbons

Name	Formula	Obs RI	Lib. RI	R.T. (s)	Similarity	PPM
Naphthalene, 2-methyl-	$C_{11}H_{10}$	1309	1297 ± 10(53)	711, 2.984	830	0.47
Naphthalene, 1-methyl-	$C_{11}H_{10}$	1327	1307 ± 10(54)	726, 2.960	823	1.23
2,6-Diisopropylnaphthalene	$C_{16}H_{20}$	1736	1728 ± 4(16)	1020, 2.720	794	1.62
Phenanthrene	$C_{14}H_{10}$	1810	1776 ± 13(63)	1068, 3.552	935	0.79
Anthracene	$C_{14}H_{10}$	1820	1786 ± 15(49)	1074, 3.539	750	0.72
Anthracene, 9-ethenyl-	$C_{16}H_{12}$	1885		1113, 3.504	872	0.06
Phenanthrene, 2-methyl-	$C_{15}H_{12}$	1925	1898 ± 11(4)	1137, 3.464	869	0.3
Phenanthrene, 1-methyl-	$C_{15}H_{12}$	1935	1910 ± 24(7)	1143, 3.464	885	0.55
Anthracene, 1-methyl-	$C_{15}H_{12}$	1955	1959 ± 17(6)	1155, 3.528	889	0.39
Naphthalene, 2-phenyl-	$C_{16}H_{12}$	2000	1978 ± 9(3)	1182, 3.528	862	0.05
Phenanthrene, 2,5-dimethyl-	$C_{16}H_{14}$	2038		1203, 3.416	793	-0.01
Phenanthrene, 2,7-dimethyl-	$C_{16}H_{14}$	2049	2028 ± 0(1)	1209, 3.424	816	1.06
Anthracene, 1,4-dimethyl-	$C_{16}H_{14}$	2065		1218, 3.480	838	0.62
Phenanthrene, 2,3-dimethyl-	$C_{16}H_{14}$	2076	2056 ± 2(2)	1224, 3.480	861	0.98
Phenanthrene, 4,5-dimethyl-	$C_{16}H_{14}$	2081		1227, 3.520	861	0.82
Phenanthrene, 1,7-dimethyl-	$C_{16}H_{14}$	2092	2053 ± 1(2)	1233, 3.540	784	0.68
Fluoranthene	$C_{16}H_{10}$	2097	2059 ± 17(42)	1236, 3.805	942	0.17
5,6-Dihydro-4H-benz[de]anthracene	$C_{17}H_{14}$	2114		1245, 3.416	765	0.97
Phenanthrene, 9,10-dimethyl-	$C_{16}H_{14}$	2124	2093 ± 2(2)	1251, 3.576	723	1.08
Pyrene	$C_{16}H_{10}$	2124	2103 ± 20(40)	1251, 3.848	887	0.79
1-Ethyl-2-methylphenanthrene	$C_{17}H_{16}$	2157		1269, 3.352	752	1.27
Phenanthrene, 2,3,5-trimethyl-	$C_{17}H_{16}$	2189	2142 ± 0(1)	1287, 3.384	816	1.07

Name	Formula	Obs RI	Lib. RI	R.T. (s)	Similarity	PPM
9-Ethyl-10-methylanthracene	$C_{17}H_{16}$	2207		1296, 3.448	769	0.6
11H-Benzo[b]fluorene	$C_{17}H_{12}$	2226		1305, 3.696	860	-0.39
1-Methyl-4-p-tolylnaphthalene	$C_{18}H_{16}$	2232		1308, 3.368	748	0.67
9-Ethyl-10-methylanthracene	$C_{17}H_{16}$	2239		1311, 3.504	760	0.96
Retene	$C_{18}H_{18}$	2252	2221 ± 28(3)	1317, 3.272	790	1.05
1-Methylpyrene	$C_{17}H_{12}$	2252	2215 ± 3(3)	1317, 3.744	911	-0.93
1,4-Dimethyl-2-phenyl-naphthalene	$C_{18}H_{16}$	2277		1329, 3.280	717	0.98
4-Methylpyrene	$C_{17}H_{12}$	2284		1332, 3.586	874	-0.11
Pyrene, 2-methyl-	$C_{17}H_{12}$	2310		1344, 3.432	854	-0.15
1,3,6,8-Tetramethylanthracene	$C_{18}H_{18}$	2348		1362, 2.792	705	0.47
Benzo[ghi]fluoranthene	$C_{18}H_{10}$	2452		1404, 3.224	897	0.44
Benzo[ghi]fluoranthene	$C_{18}H_{10}$	2513		1425, 3.216	819	0.95
Benzo[c]phenanthrene	$C_{18}H_{12}$	2522		1428, 3.130	889	0.66
1,2-Dihydrobenzo[b]fluoranthene	$C_{20}H_{14}$	2557		1440, 2.848	719	0.32
2-Methylchrysene	$C_{19}H_{14}$	2650		1470, 2.992	882	0.37
1-Methylchrysene	$C_{19}H_{14}$	2660		1473, 3.072	849	0.38
Benz[a]anthracene, 7-methyl-	$C_{19}H_{14}$	2670		1476, 3.144	733	0.92
7-Methylbenz[a]anthracene	$C_{19}H_{14}$	2690		1482, 3.256	797	0.55
Phenanthrene, 2-phenyl-	$C_{20}H_{14}$	2720		1491, 3.336	768	0.93
Pyrene, 1-phenyl-	$C_{22}H_{14}$	2983		1581, 1.984	738	0.22
Indeno[1,2,3-cd]fluoranthene	$C_{22}H_{12}$	3344		1770, 3.691	743	0.63

Similarity Ave. 818/1000
Ave. |PPM| 0.66

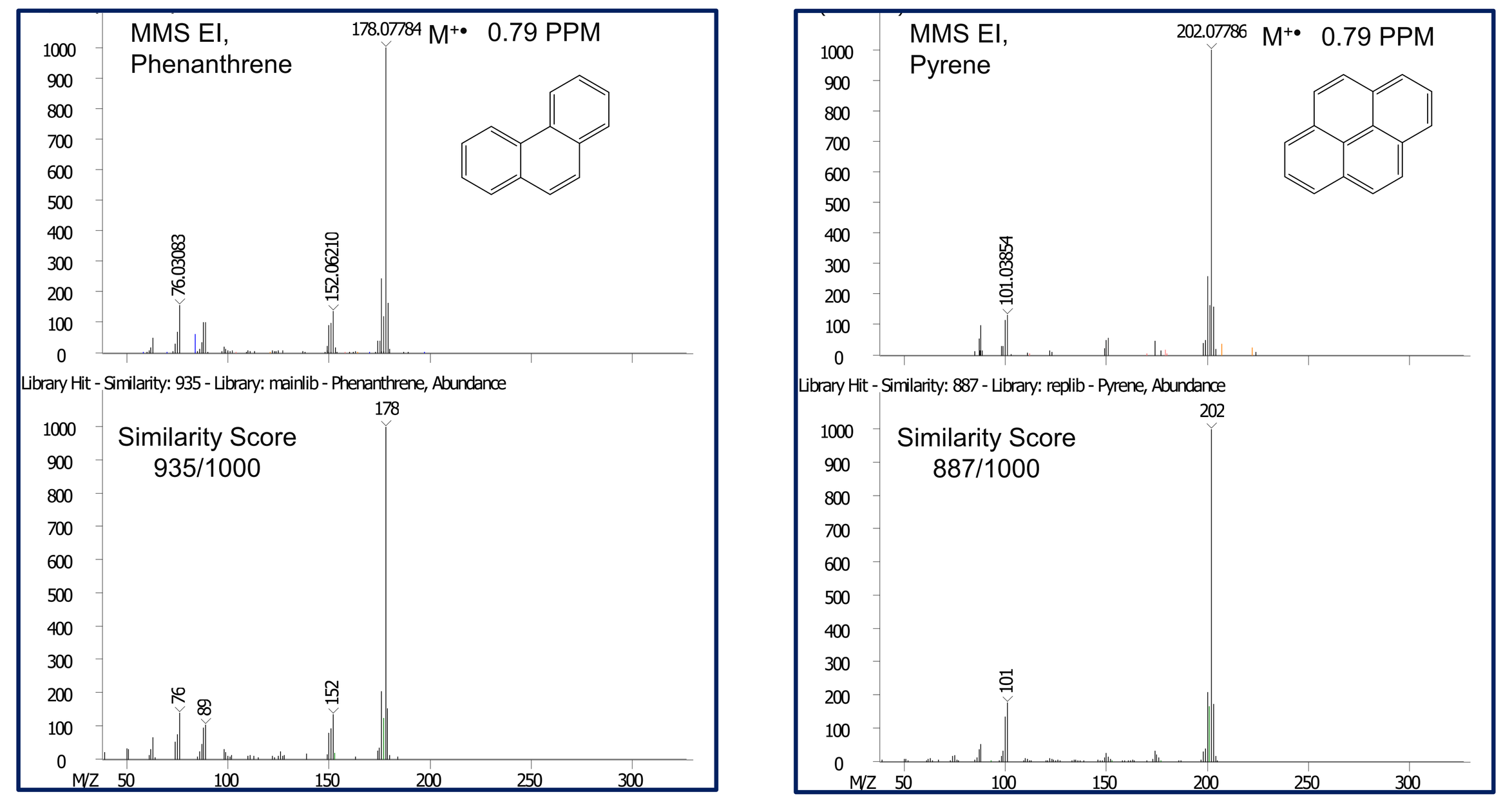


Figure 6. Peak True and library EI mass spectra for phenanthrene (Left) & pyrene (Right).

Table 4. TD-EI Sample 1, Hetero-Polyaromatic Hydrocarbons

Name	Formula	Obs. RI	Lib. RI	R.T. (s)	Similarity	PPM
Isoquinoline	C_9H_7N	1280	1261 ± 5(8)	687, 3.392	868	0.78
Isoquinoline, 1-methyl-	$C_{10}H_9N$	1360	1345 ± 0(1)	753, 3.088	837	0.58
Quinoline, 2,6-dimethyl-	$C_{11}H_{11}N$	1437.5	1412 ± 1(3)	813, 3.128	803	1.18
Quinoline, 2,4-dimethyl-	$C_{11}H_{11}N$	1462.5	1454 ± 1(7)	831, 3.104	840	0.81
1-Naphthalenamine, N-methyl-	$C_{11}H_{11}N$	1475		840, 3.005	725	1.08
6-Quinolinamine, 2-methyl-	$C_{10}H_{10}N_2$	1504.2		861, 3.280	816	0.36
Dibenzofuran	$C_{12}H_8O$	1537.5	1515 ± 10(27)	885, 3.272	732	0.95
2-Naphthalenol	$C_{10}H_8O$	1541.7	1521 ± 3(13)	888, 3.552	779	0.93
1(2H)-Acenaphthylenone	$C_{12}H_8O$	1686.4		987, 3.782	793	-0.09
9H-Fluoren-9-one	$C_{13}H_8O$	1768.2	1749 ± 3(4)	1041, 3.560	906	0.59
Anthrone	$C_{14}H_{10}O$	1855		1095, 3.544	727	0.95
2,3-Naphthalenedicarboxaldehyde	$C_{12}H_8O_2$	1860	1859 ± 0(1)	1098, 4.071	713	-0.29
Naphtho[1,2-c]furan-1,3-dione	$C_{12}H_6O_3$	1870		1104, 3.928	838	0.94
Anthrone	$C_{14}H_{10}O$	1890		1116, 3.584	838	1.09
Xanthone	$C_{13}H_8O_2$	1895	1855 ± 11(2)	1119, 3.736	756	1.48
1-Phenanthrenol	$C_{14}H_{10}O$	1905		1125, 3.552	837	0.81
Benzo[h]isoquinoline	$C_{13}H_9N$	1905		1125, 3.784	835	0.77
Anthrone	$C_{14}H_{10}O$	1920		1134, 3.660	826	1.19
Naphtho[1,2-c]furan-1,3-dione	$C_{12}H_6O_3$	1965		1161, 3.968	776	1.21
4-Hydroxy-9-fluorenone	$C_{13}H_8O_2$	1985		1173, 3.933	873	1.04
Anthracene, 9-methoxy-	$C_{15}H_{12}O$	1995		1179, 3.464	751	1.18
Anthrone	$C_{14}H_{10}O$	2000		1182, 3.920	802	0.71
3,7-Dimethyldibenzothiophene	$C_{14}H_{12}S$	2005.4		1185, 3.416	768	0.01
9,10-Phenanthrenedione	$C_{14}H_8O_2$	2005.4	2050 ± 61(2)	1185, 3.952	867	0.54
4-Hydroxy-9-fluorenone	$C_{13}H_8O_2$	2043.2		1206, 4.184	808	0.75
Phenanthrene, 9-methoxy-	$C_{15}H_{12}O$	2048.6		1209, 3.552	699	0.65
3,7-Dimethyldibenzothiophene	$C_{14}H_{12}S$	2054.1		1212, 3.522	715	-0.16
Naphtho[1,2-c]furan-1,3-dione	$C_{12}H_6O_3$	2081.1		1227, 1.440	819	0.82

Name	Formula	Obs. RI	Lib. RI	R.T. (s)	Similarity	PPM
Cyclopenta(def)phenanthrenone	$C_{15}H_8O$	2086.5		1230, 3.960	916	0.89
Naphtho[1,2-c]furan-1,3-dione	$C_{12}H_6O_3$	2091.9		1233, 1.328	796	1.11
9-Phenanthrenol	$C_{14}H_{10}O$	2108.1	2124 ± 0(1)	1242, 4.184	728	1.45
9,10-Anthracenedione, 2-methyl-	$C_{15}H_{10}O_2$	2140.5	2146 ± 0(1)	1260, 3.832	844	0.82
Benzo[b]naphtho[2,3-d]furan	$C_{16}H_{10}O$	2156.8		1269, 3.656	892	0.71
Phenanthrene-9-carboxaldehyde	$C_{15}H_{10}O$	2162.2		1272, 4.024	868	0.45
Phenanthrene-9-carboxaldehyde	$C_{15}H_{10}O$	2167.6		1275, 4.088	816	0.21
Benzo[b]naphtho[2,3-d]furan	$C_{16}H_{10}O$	2178.4		1281, 3.752	859	0.71
Benzo[kl]xanthene	$C_{16}H_{10}O$	2189.2		1287, 3.744	836	1.48
4-Phenyl-2-naphthol	$C_{16}H_{12}O$	2232.3	2187 ± 0(1)	1308, 3.947	783	0.32
2H-Phenanthro[9,10-b]pyran	$C_{17}H_{12}O$	2238.7		1311, 3.872	701	0.9
9,10-Anthracenedione, 2,3-dimethyl-	$C_{16}H_{12}O_2$	2290.3		1335, 3.424	837	1.24
11H-Benzo[a]fluoren-11-one	$C_{17}H_{10}O$	2400		1386, 3.224	895	1.08
Phenanthro(2,1-b)thiophene	$C_{16}H_{10}S$	2434.8		1398, 3.216	797	1.2
1-(10-Methylanthracen-9-yl)ethanone	$C_{17}H_{14}O$	2443.5		1401, 3.108	732	0.72
11H-Benzo[a]fluoren-11-one	$C_{17}H_{10}O$	2443.5		1401, 3.240	765	0.93
11H-Benzo[a]fluoren-11-one	$C_{17}H_{10}O$	2469.6		1410, 3.232	809	1.15
1-Phenyldibenzofuran	$C_{18}H_{12}O$	2530.4		1431, 2.968	804	1.69
7H-Benz[de]anthracen-7-one	$C_{17}H_{10}O$	2565.2	2525 ± 0(1)	1443, 3.184	911	1.16
Naphtho[2,1,8,7-klmn]xanthene	$C_{18}H_{10}O$	2591.3		1452, 2.944	727	1.83
Benzo(c)carbazole	$C_{16}H_{11}N$	2600		1455, 3.192	793	0.33
1-Phenyldibenzofuran	$C_{18}H_{12}O$	2620		1461, 2.920	744	0.93
6H-Benz[de]anthracen-6-one	$C_{17}H_{10}O$	2650		1470, 3.360	807	1.3
6H-Benz[de]anthracen-6-one	$C_{17}H_{10}O$	2670		1476, 3.448	776	0.81
1-Phenyldibenzofuran	$C_{18}H_{12}O$	2700		1485, 3.448	737	0.49
1-Pyrenemethanol, α-phenyl-	$C_{23}H_{16}O$	2933.3		1563, 1.688	719	0.22

Similarity Ave. 871/1000
Ave. |PPM| 0.82

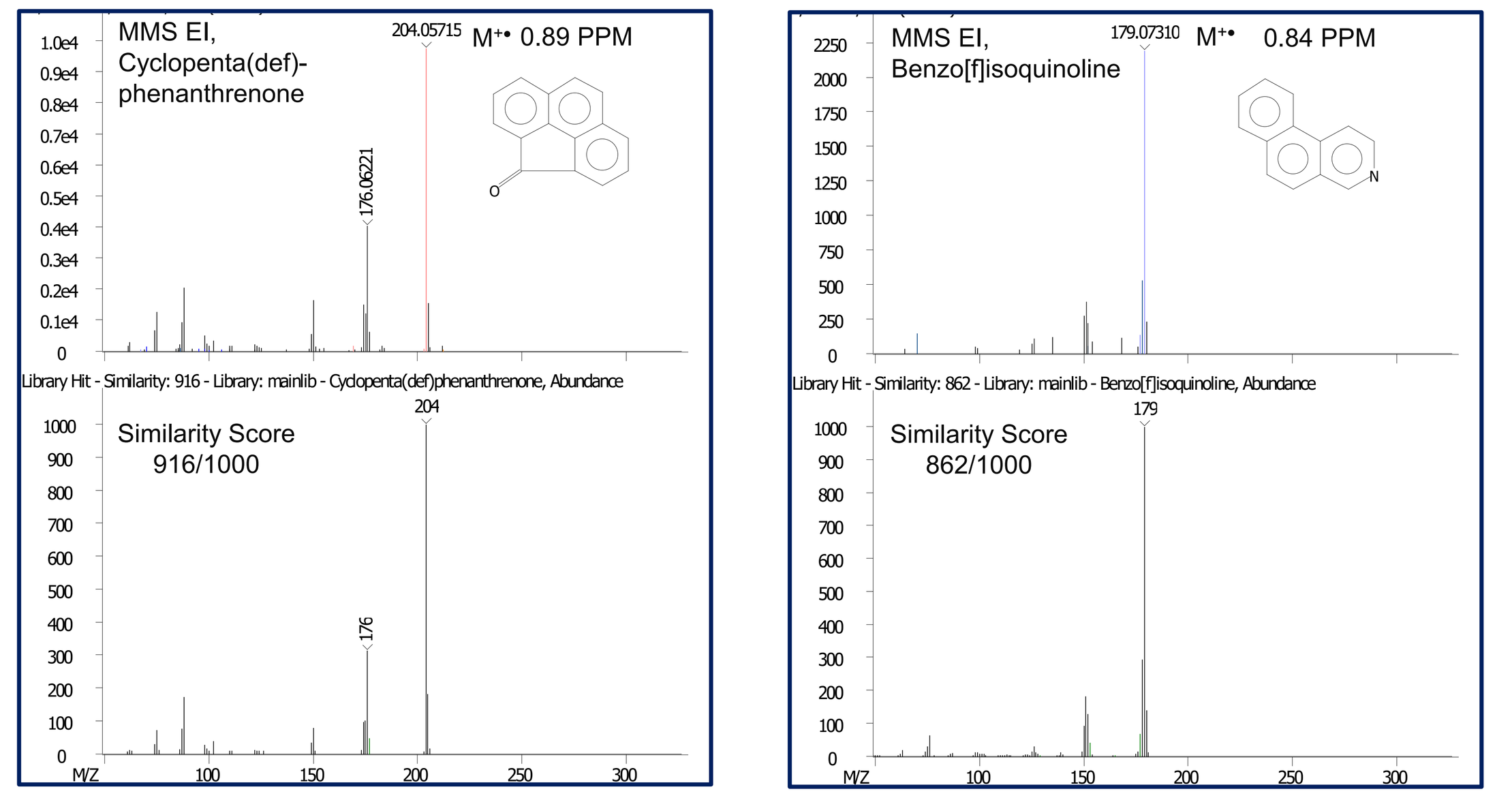


Figure 7. Peak True and library EI mass spectra for cyclopenta(def)phenanthrenone (Left) and benzo[f]isoquinoline (Right).

Sample 2, Pyrolysis (Pyr, EI): Targeting Pyrolytic Markers

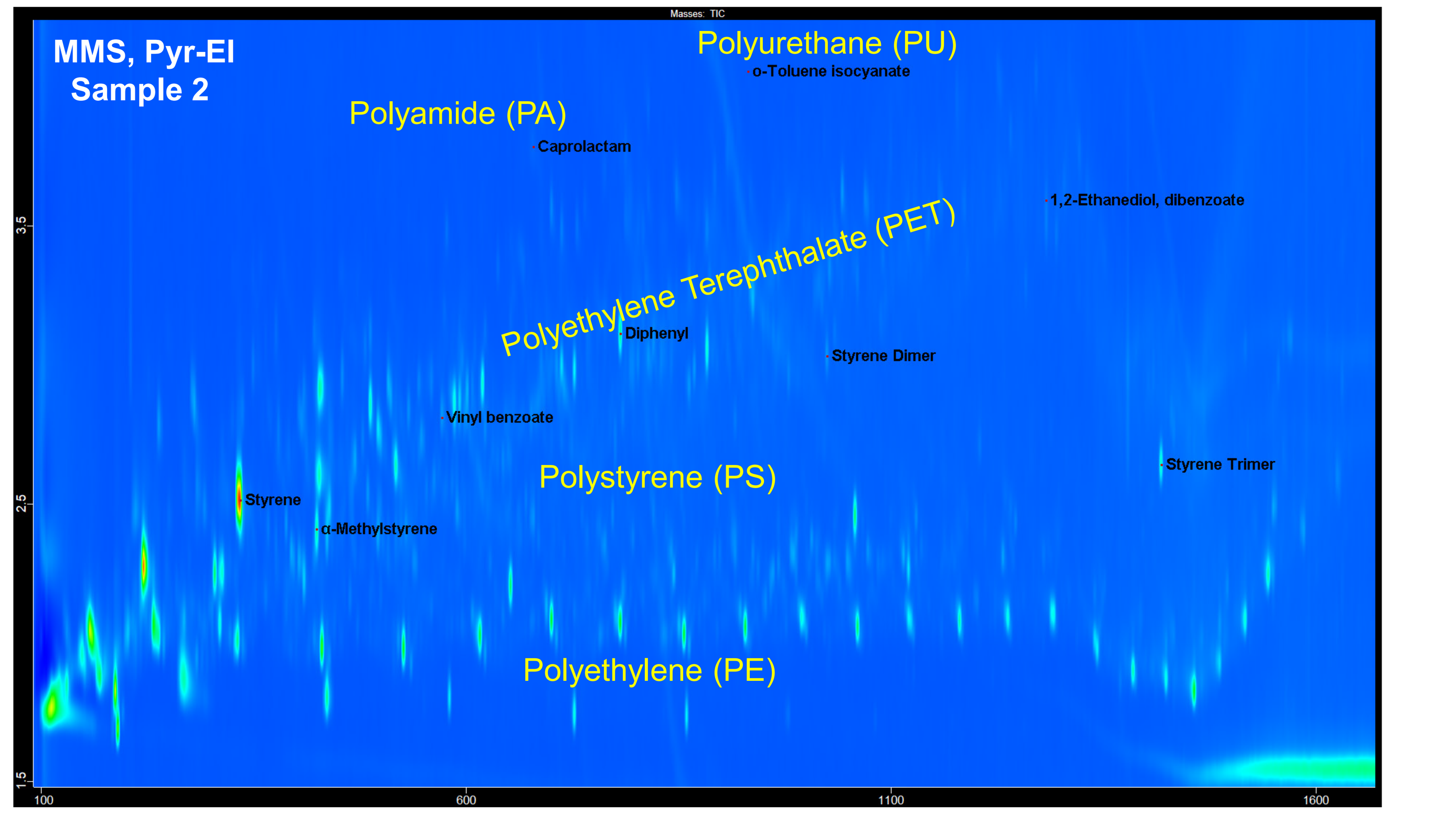
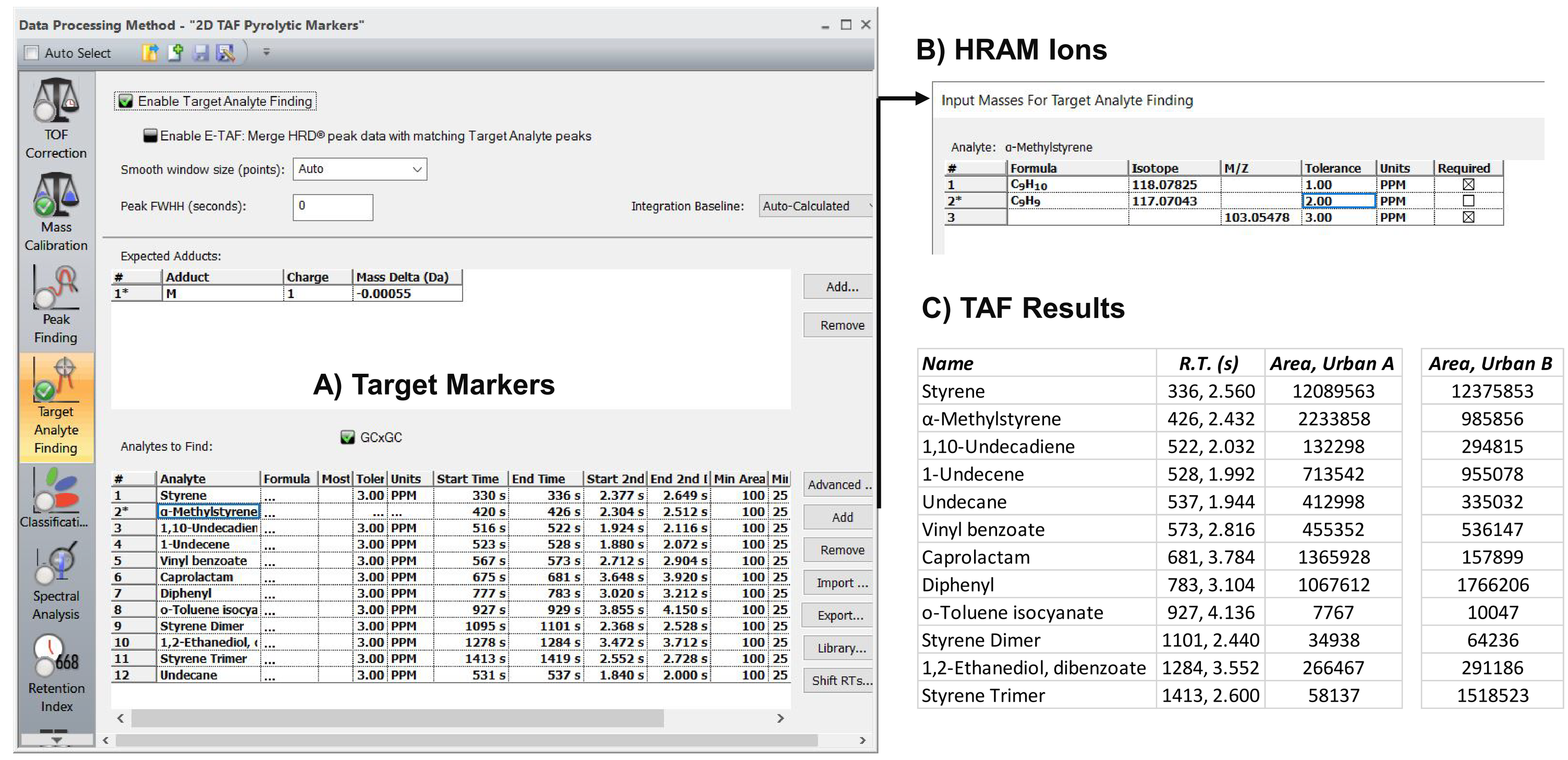


Figure 8. Contour plot displaying pyrolytic markers in Sample 2 after pyrolysis-GCxGC-EI-TOFMS.



C) TAF Results

Name	R.T. (s)	Area, Urban A	Area, Urban B
Styrene	336, 2.560	12089563	12375853
α-Methylstyrene	426, 2.432	2233858	985856
1,10-Undecadiene	522, 2.032	132298	294815
1-Undecene	528, 1.992	713542	955078
Undecane	537, 1.944	412998	335032
Vinyl benzoate	573, 2.816	455352	536147
Caprolactam	681, 3.784	1365928	157899
Diphenyl	783, 3.104	1067612	1766206
o-Toluene isocyanate	927, 4.136	7767	10047
Styrene Dimer	1101, 2.440	34938	64236
1,2-Ethanediol, dibenzoate	1284, 3.552	266467	291186
Styrene Trimer	1413, 2.600	58137	1518523

Figure 9. Targeting Pyrolytic Markers: TAF method) using 1st and 2nd dimension time windows (A) with HRAM ions (B). Markers in Sample 2 (C).

Summary

- HRT and MMS technology are powerful tools for the analysis of complex samples.
- The highly ordered, comprehensive contour plots can be used to screen for pollutants in air samples.
- Retrospective analysis using TAF facilitates quick identification of markers in the comprehensive data.