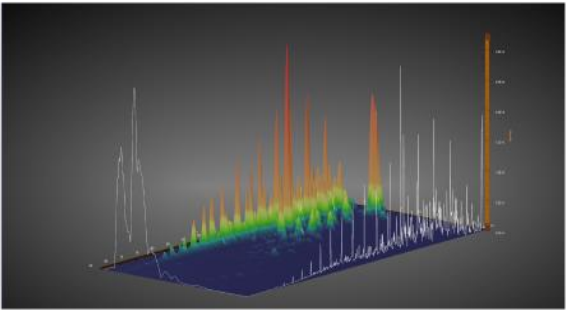
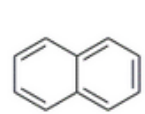
Improved Environmental Characterization of Polycyclic Aromatic Hydrocarbons by Two-Dimensional Gas Chromatography

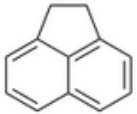


AGAT Laboratories

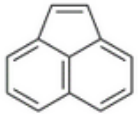
Polycyclic Aromatic Hydrocarbons (PAH)



naphthalene



acenaphthene



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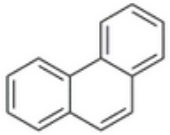

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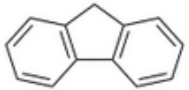

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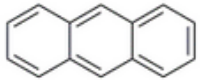

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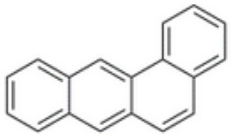
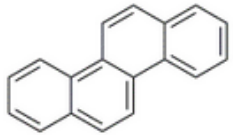


benzo[*a*]anthracene



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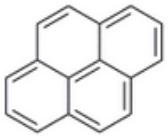
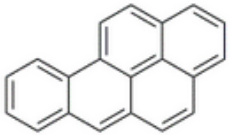


pyrene



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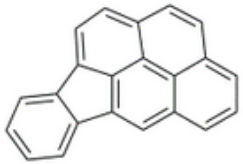
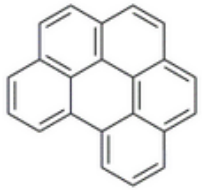


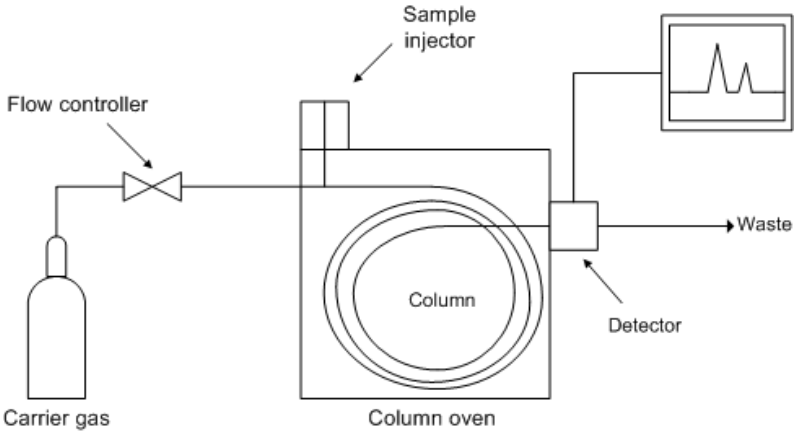
indeno[*1,2,3-cd*]pyrene

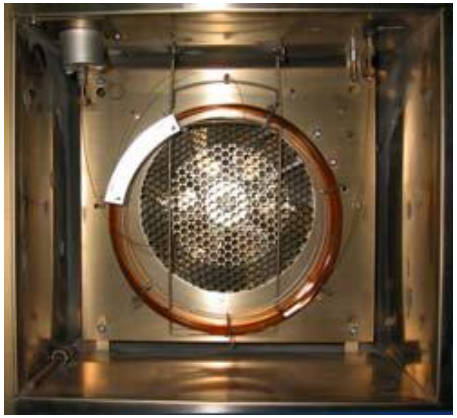


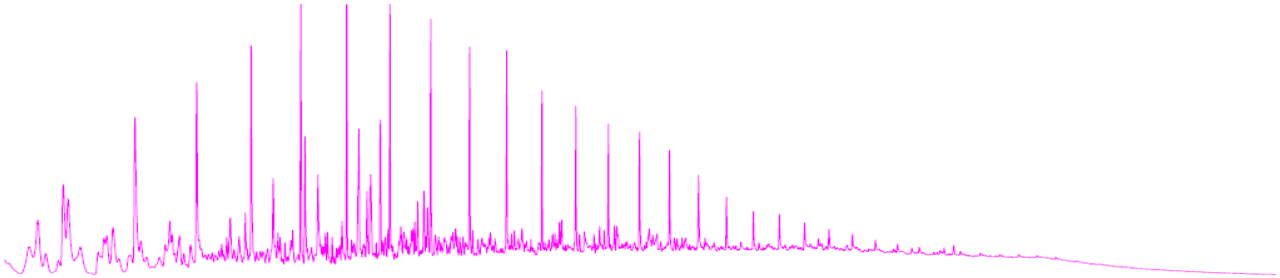
benzo[*ghi*]perylene

- Ubiquitous in crude oil, and generated in trace quantities by combustion of organic materials.
- Highly toxic.
- Subject to strict regulatory requirements (tier 1 soil remediation guideline down to 4.60 ppb).
- Analysis must therefore be highly accurate, with little background signal.
- Even trace background signal could put Alberta tier 1 compliant soils above guideline.

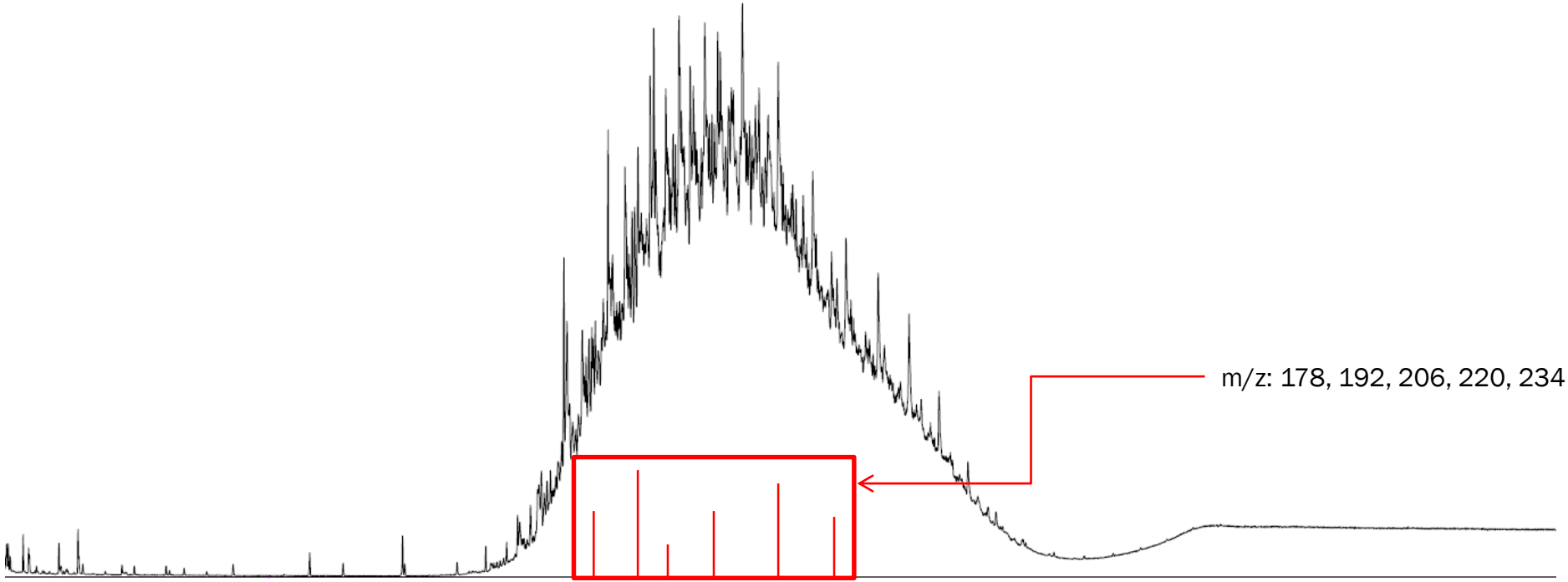
Gas Chromatography: What is it?







1D GC: Background Interference is a Problem



PAH by 1D-GC: Gulf of Mexico Oil Spill

Figure 1: Gulf of Mexico Oil Spill Total Ion:

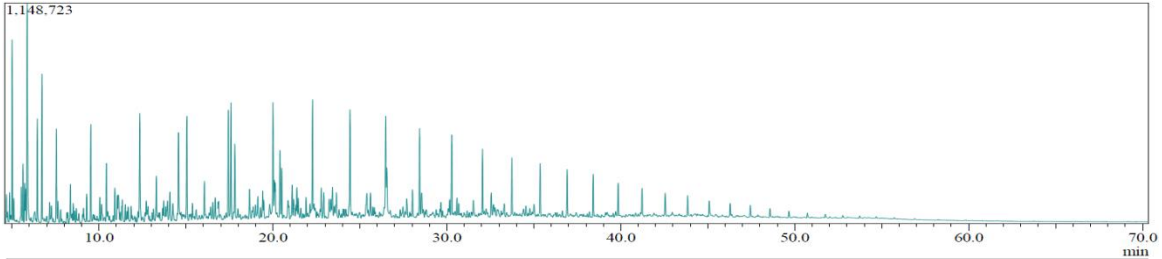
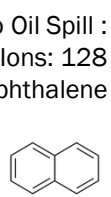


Figure 2: Gulf of Mexico Oil Spill :
Ions: 128
Naphthalene



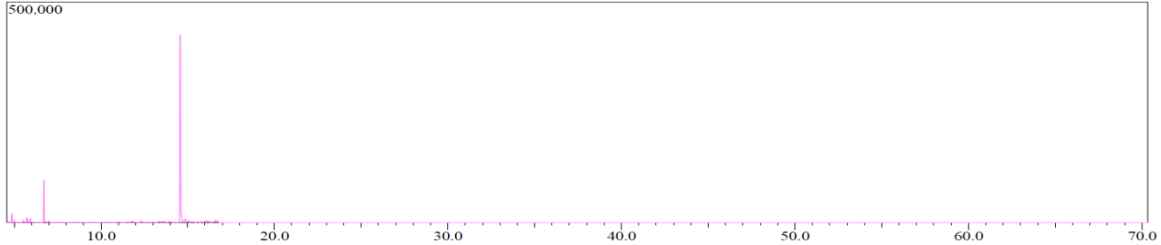
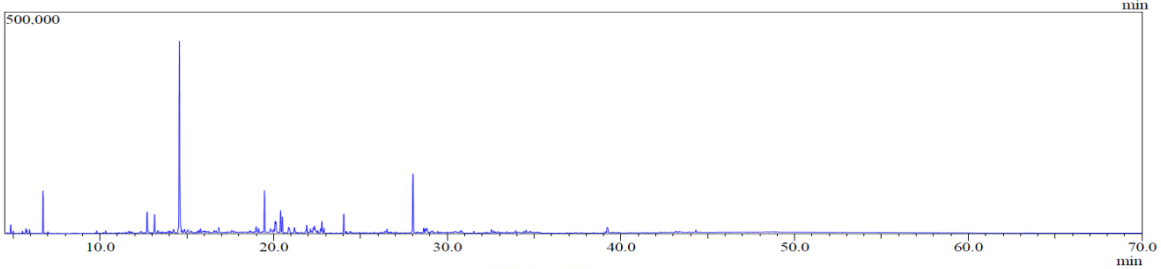


Figure 3: Gulf of Mexico Oil Spill :
128, 152, 154, 166, 178, 202, 228, 252, 276, 278
Parent PAH



PAH by 1D-GC: Gulf of Mexico Oil Spill (Zoomed)

Figure 1: Gulf of Mexico Oil Spill Total Ion:

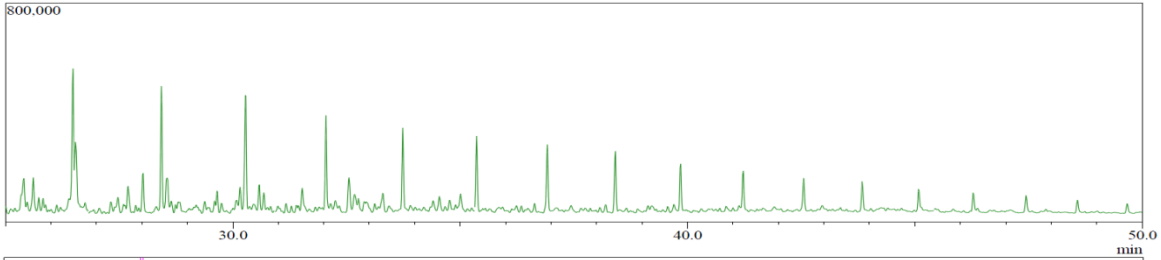
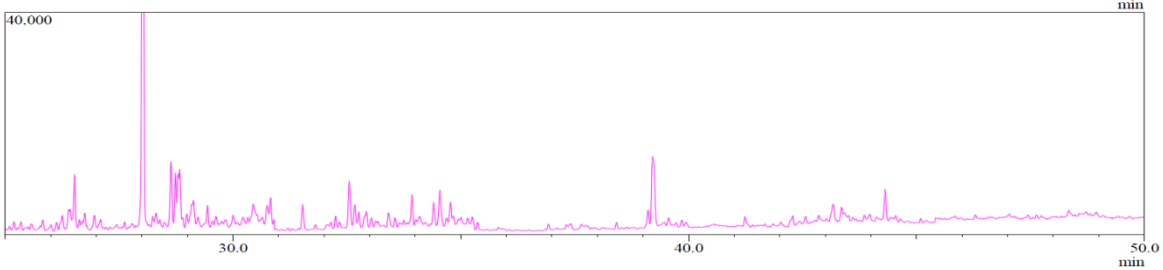
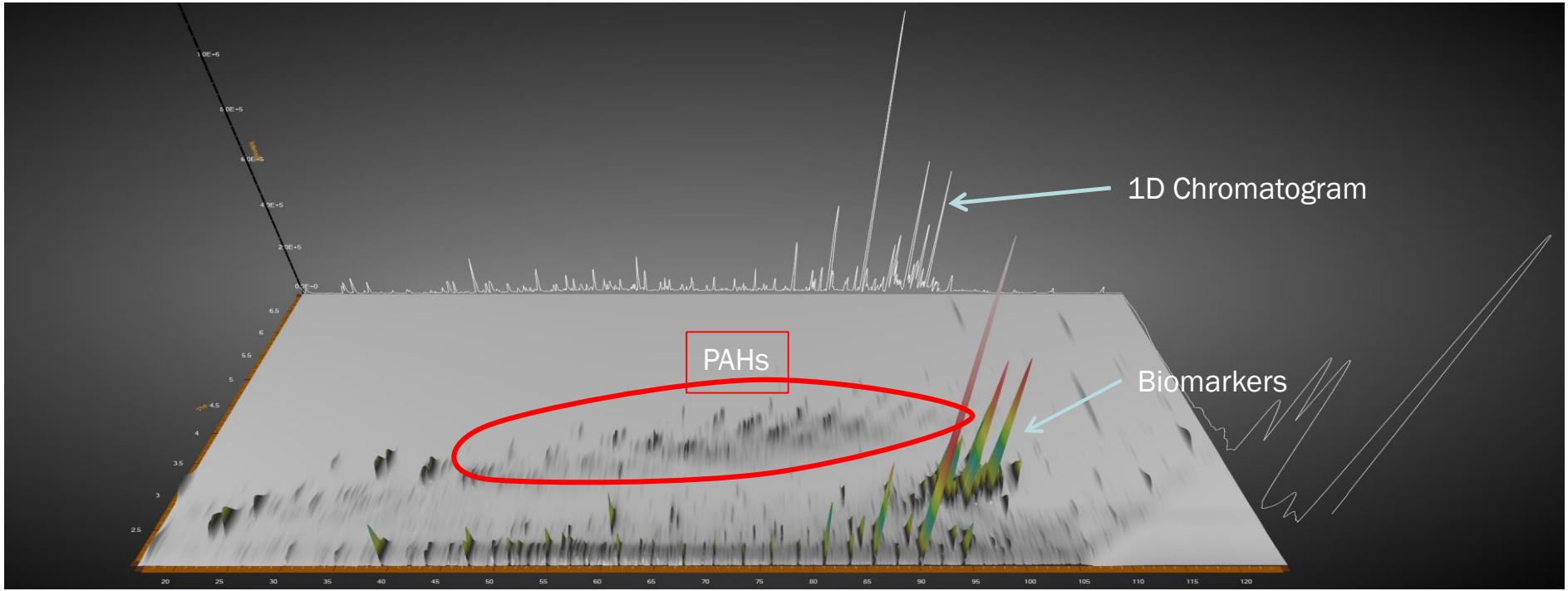


Figure 2: Gulf of Mexico Oil Spill :
Ions: 128, 152, 154, 166, 178, 202, 228, 252, 276, 278
Parent PAH

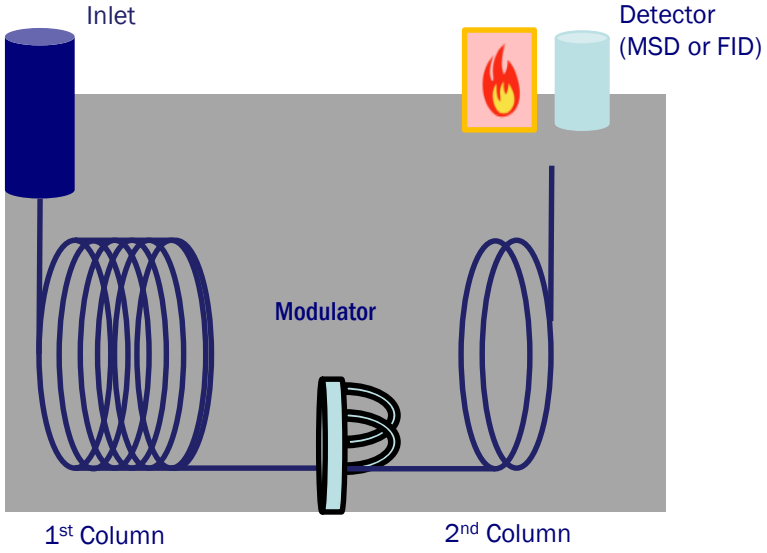


What is Two-Dimensional Gas Chromatography (2D-GC)?

Boreal soil spiked with crude oil

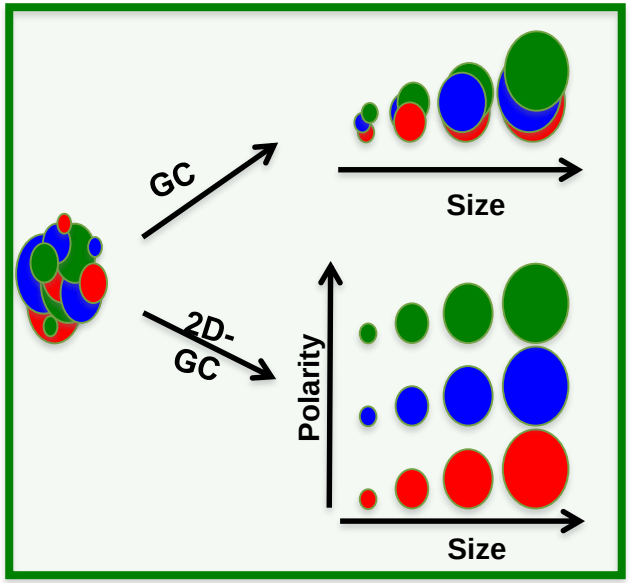


How does Two-Dimensional Gas Chromatography work?

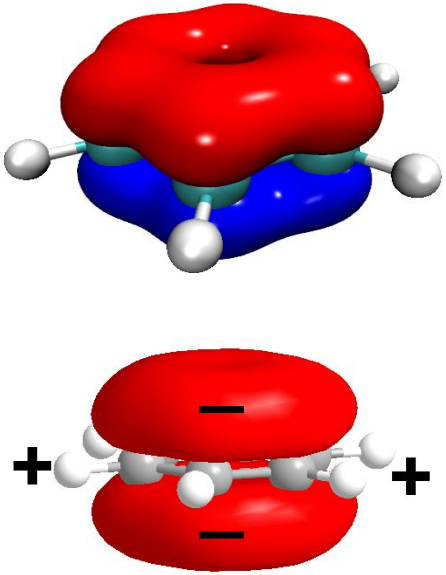


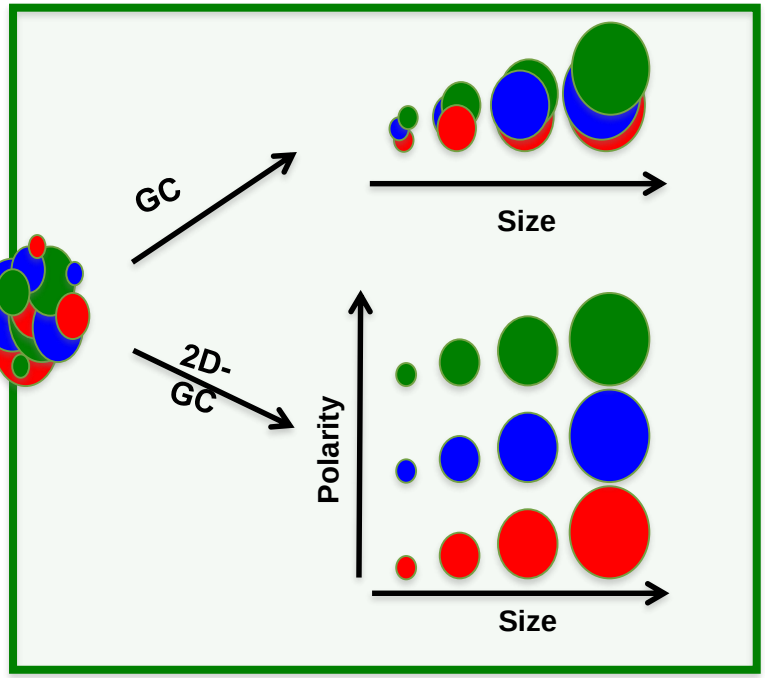
1-3 hours

5-10 seconds

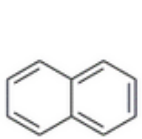


The Polarity of Aromatic Compounds

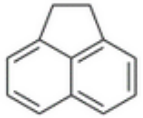




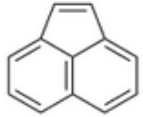
Polycyclic Aromatic Hydrocarbons (PAH)



naphthalene



acenaphthene



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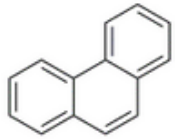
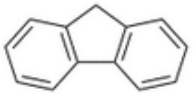


phenanthrene



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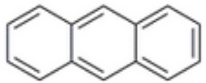

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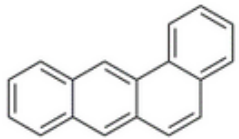
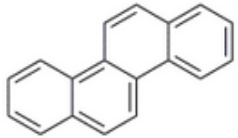


benzo[*a*]anthracene



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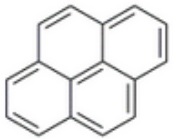
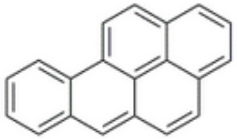
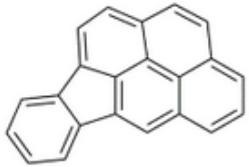


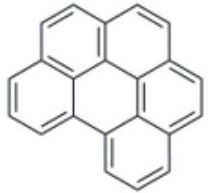
pyrene



benzo[*a*]pyrene

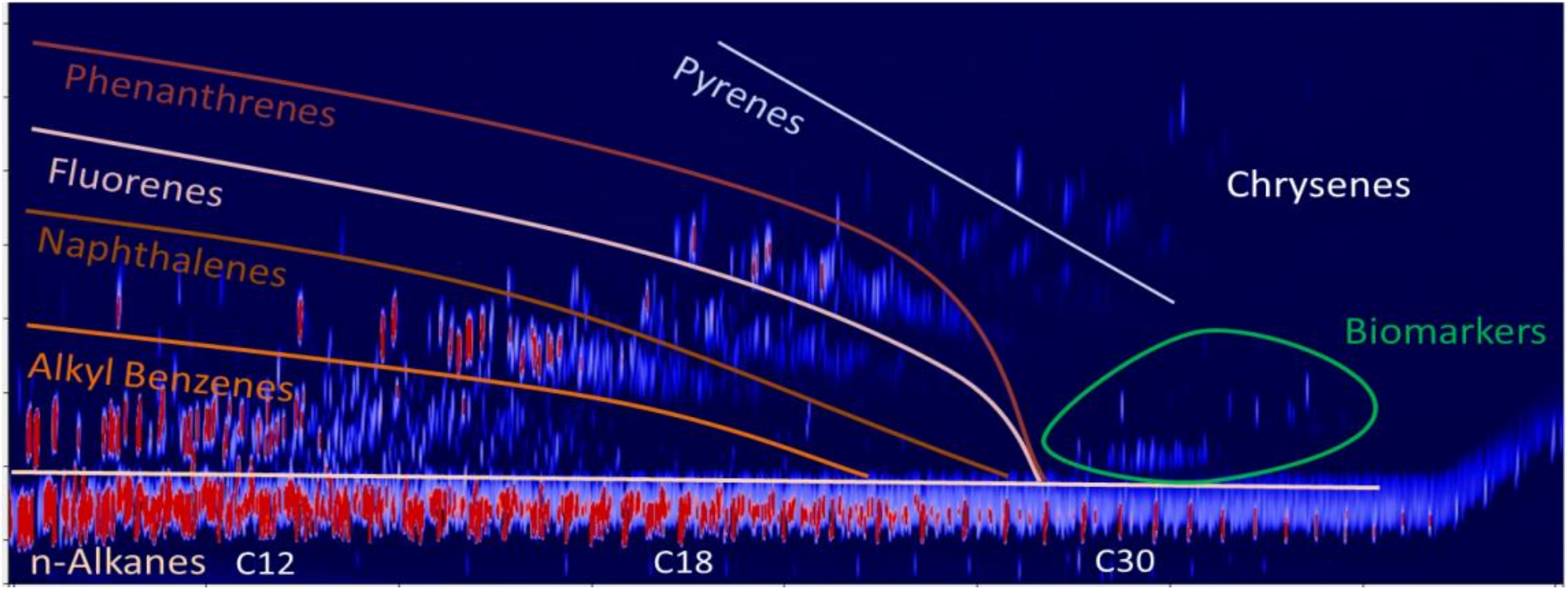


indeno[*1,2,3-cd*]pyrene



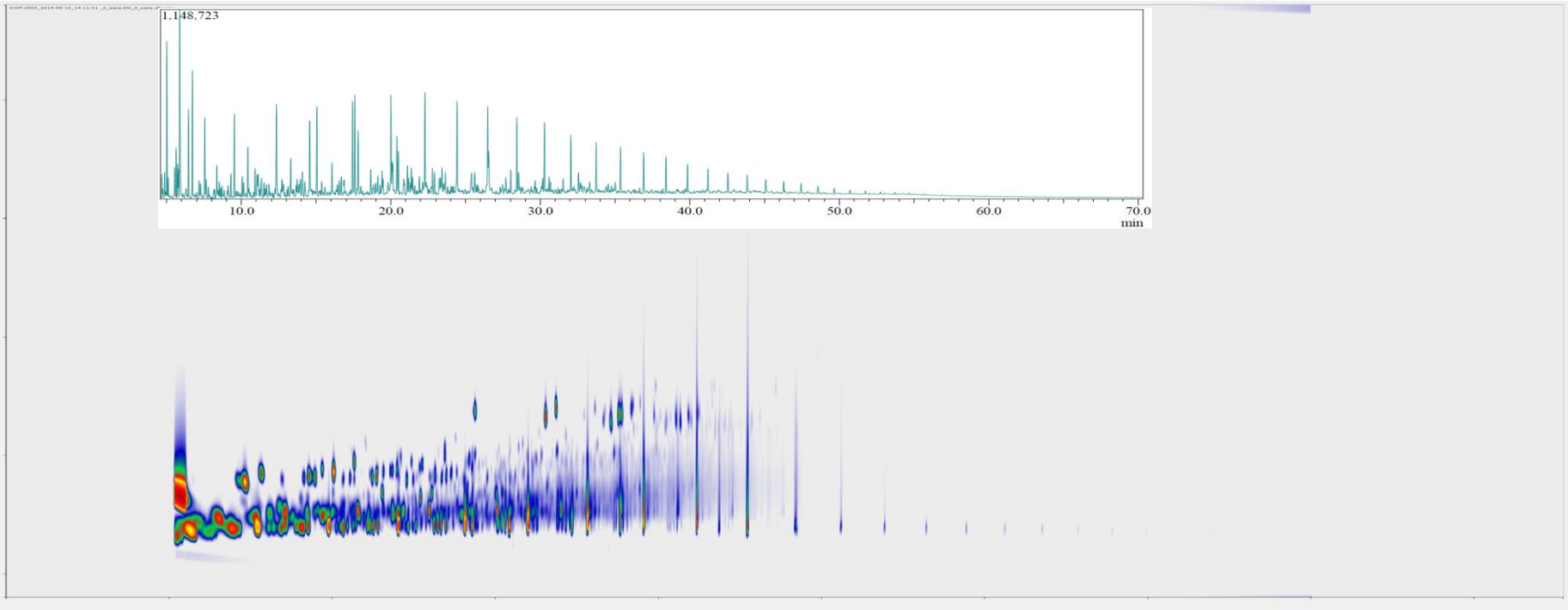
benzo[*ghi*]perylene

PAH by 2D-GC


Phenanthrenes
Pyrenes
Fluorenes
Chrysenes
Naphthalenes
Biomarkers
Alkyl Benzenes
n-Alkanes
C12
C18
C30

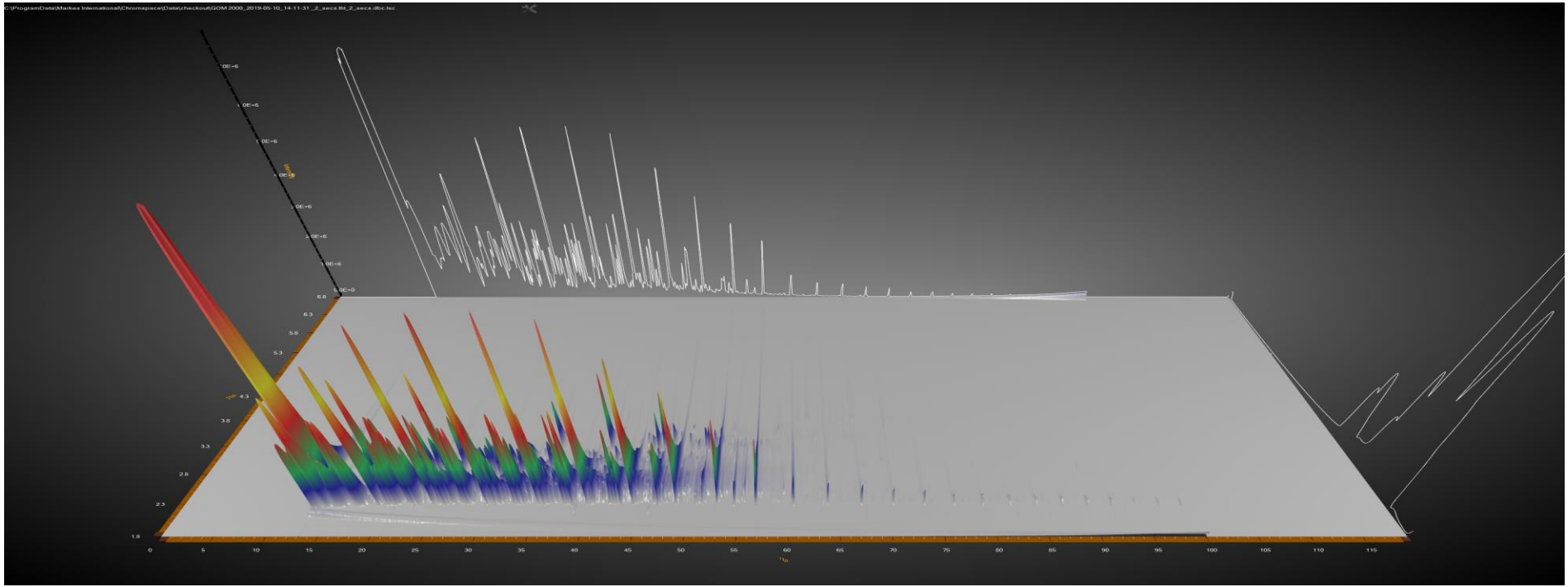
PAH by 2D-GC: Gulf of Mexico Oil Spill

Total Ion:



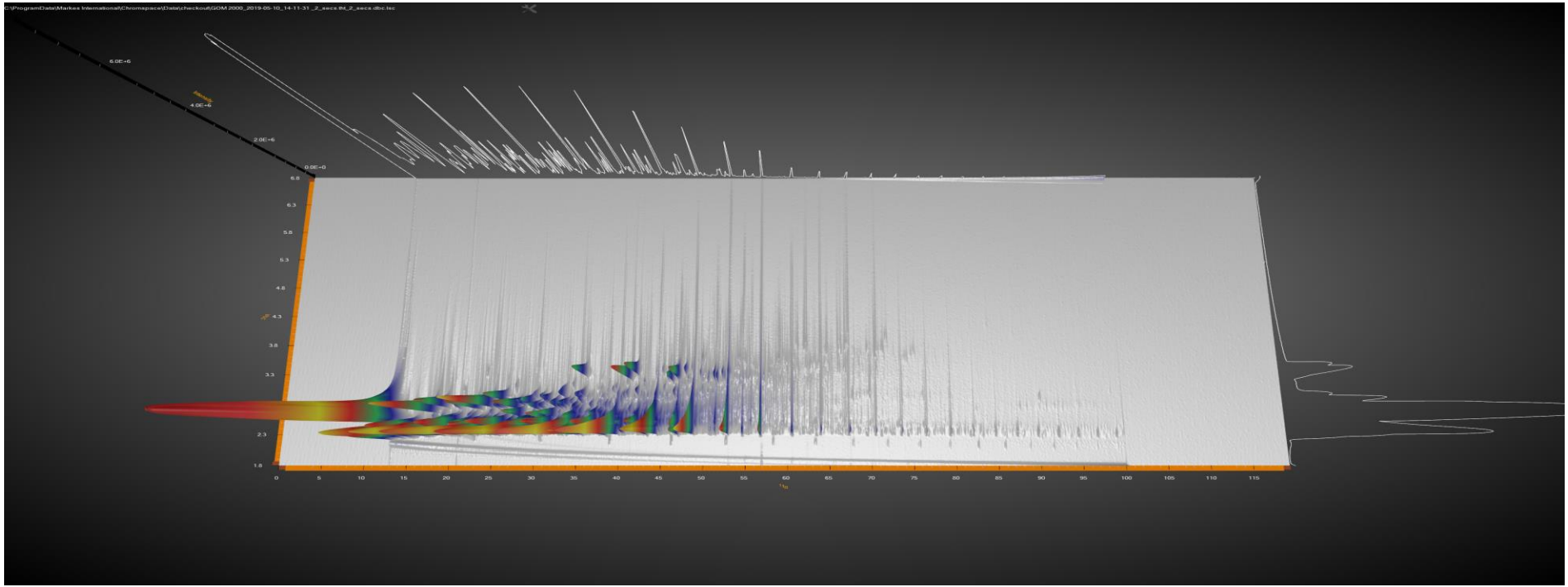
PAH by 2D-GC: Gulf of Mexico Oil Spill

Total Ion:



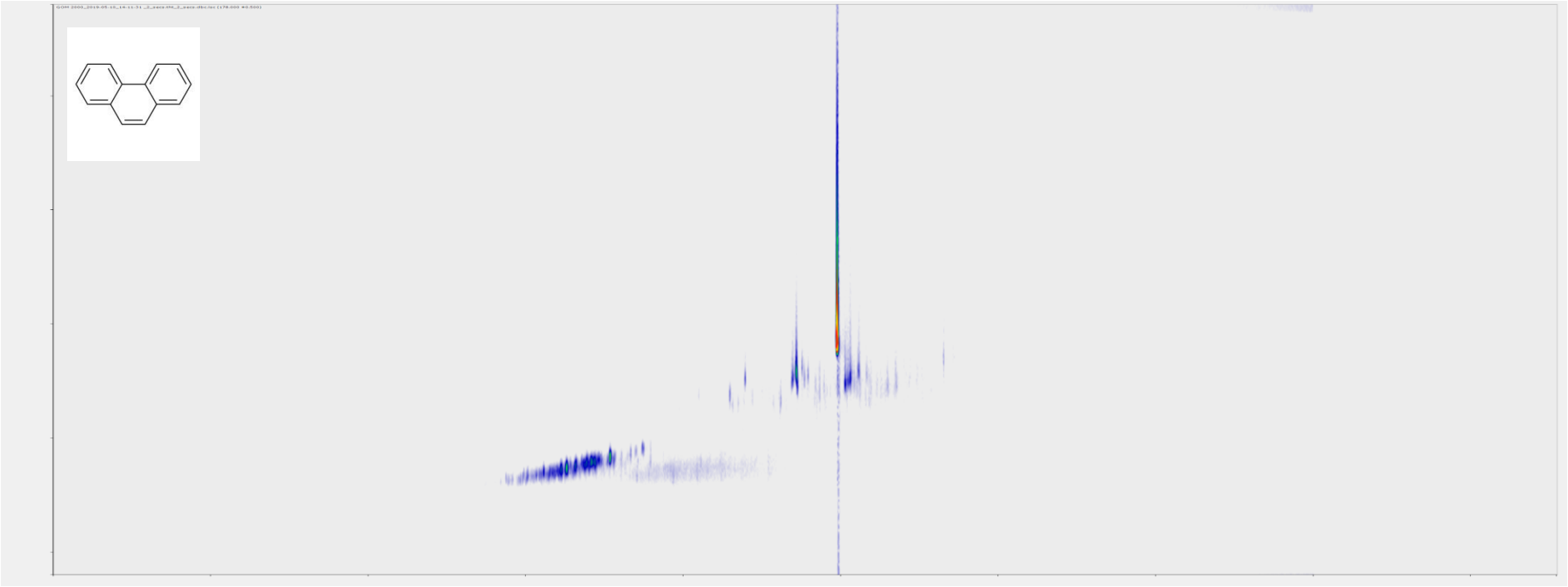
PAH by 2D-GC: Gulf of Mexico Oil Spill

Total Ion:



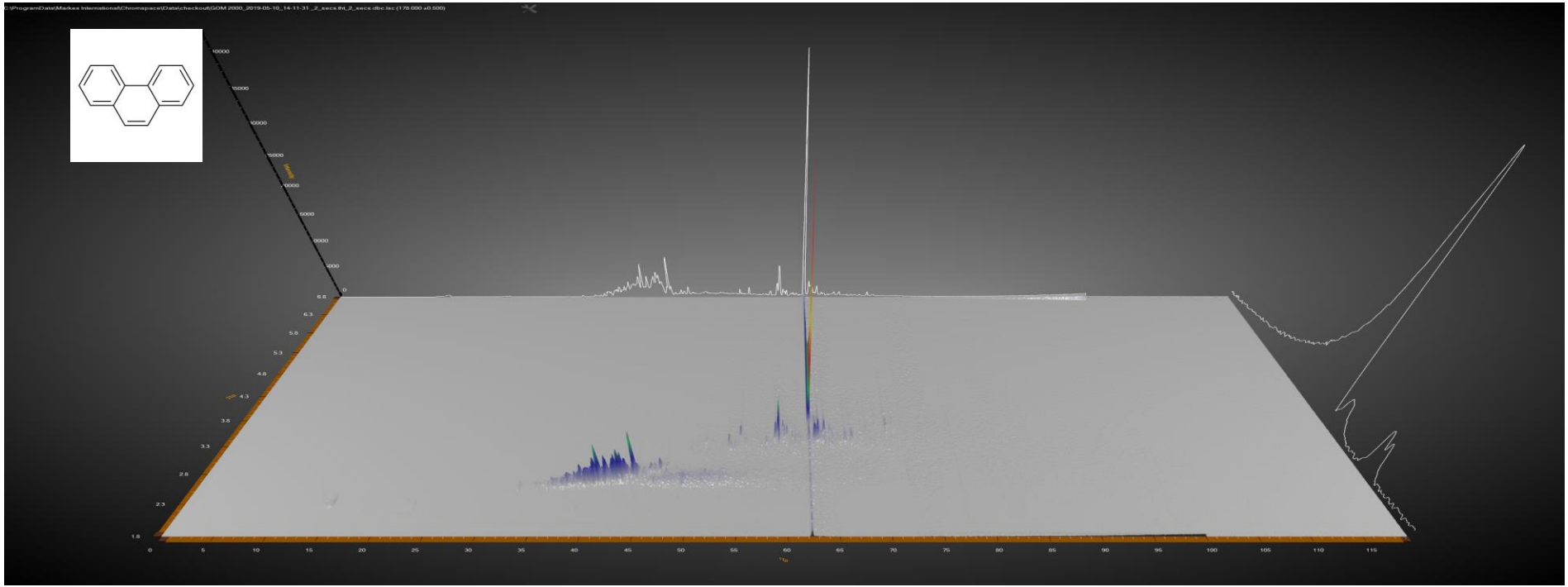
PAH by 2D-GC: Gulf of Mexico Oil Spill

Ions: 178 m/z



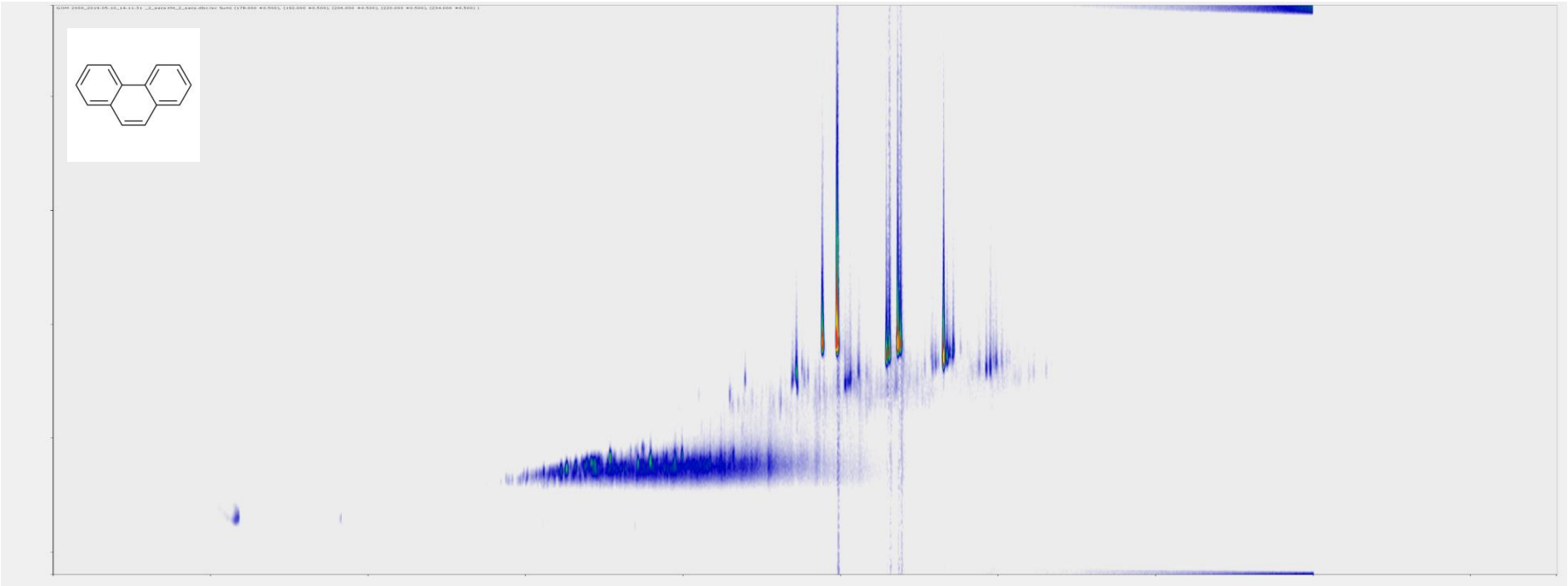
PAH by 2D-GC: Gulf of Mexico Oil Spill

Ions: 178 m/z



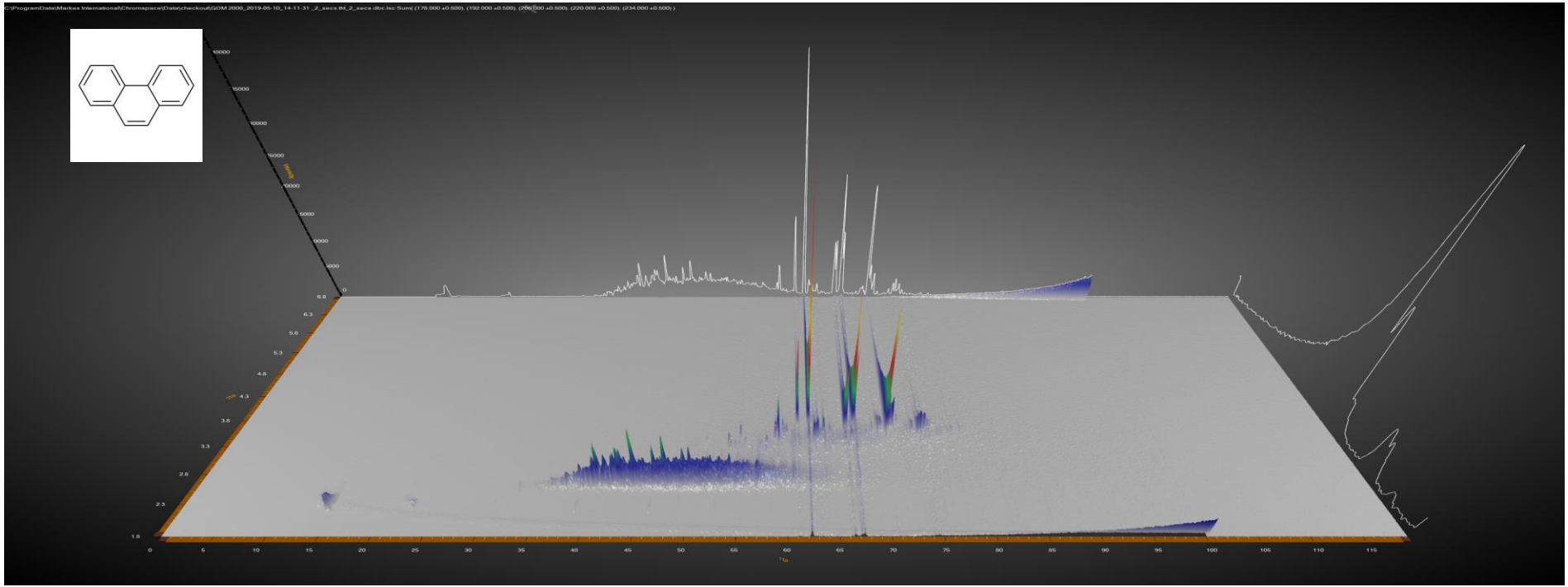
PAH by 2D-GC: Gulf of Mexico Oil Spill

Ions: 178, 192, 206, 220, 234 m/z



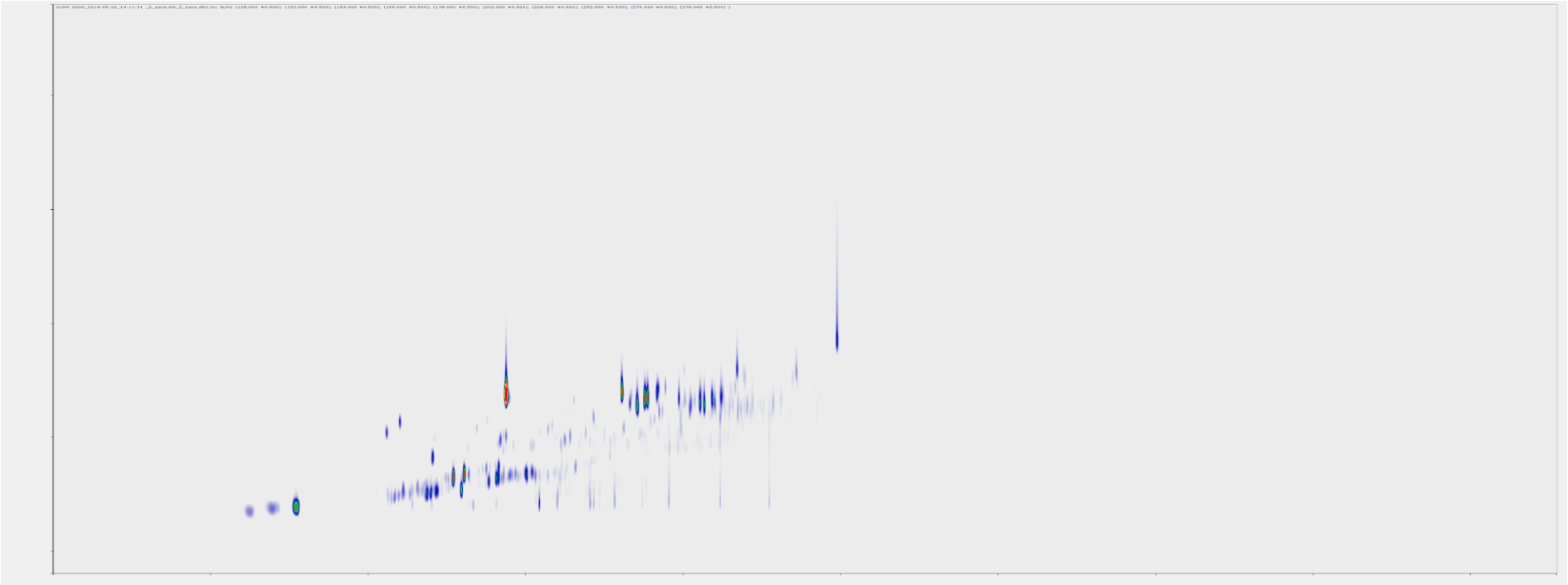
PAH by 2D-GC: Gulf of Mexico Oil Spill

Ions: 178, 192, 206, 220, 234 m/z



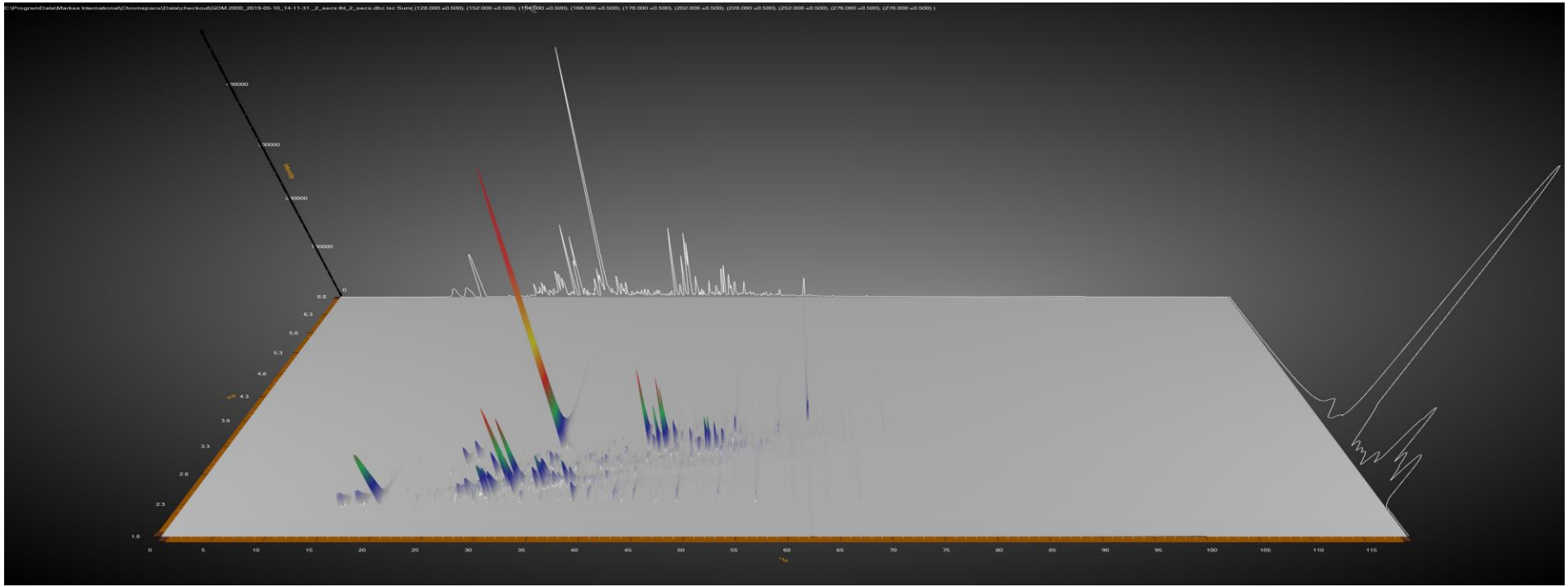
PAH by 2D-GC: Gulf of Mexico Oil Spill

Ions: 128, 152, 154, 166, 178, 202, 228, 252, 276, 278 m/z



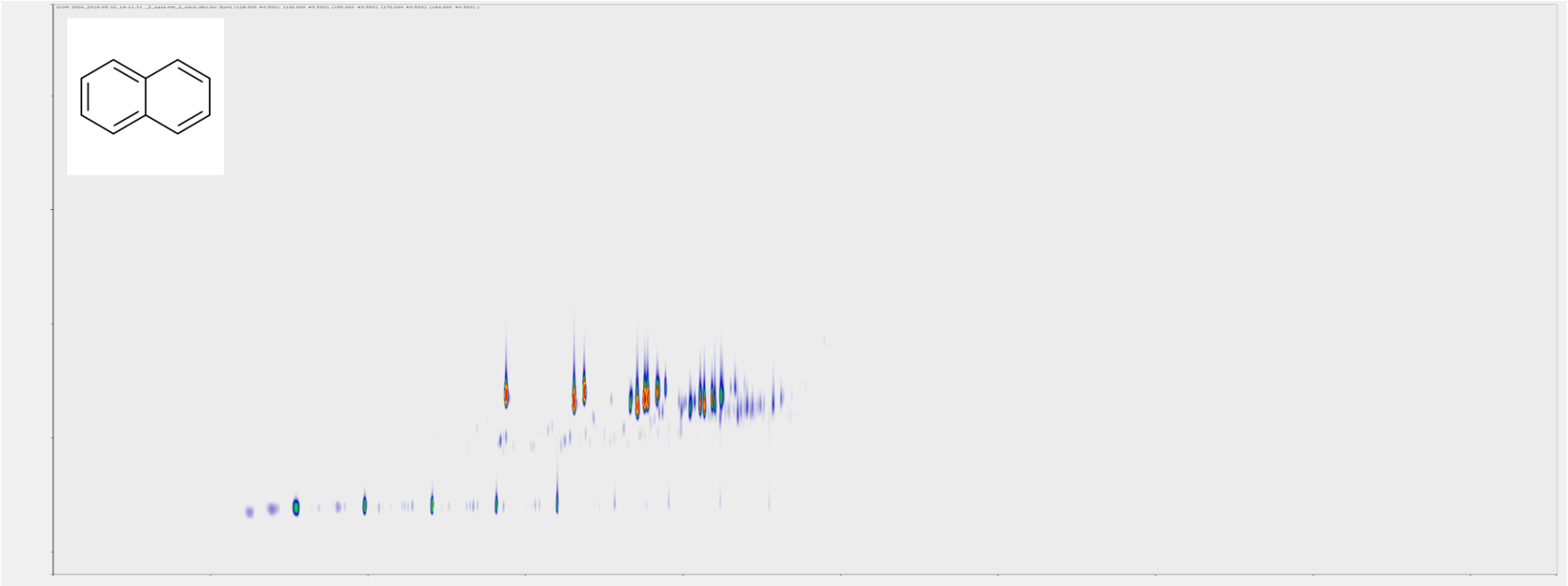
PAH by 2D-GC: Gulf of Mexico Oil Spill

Ions: 128, 152, 154, 166, 178, 202, 228, 252, 276, 278 m/z



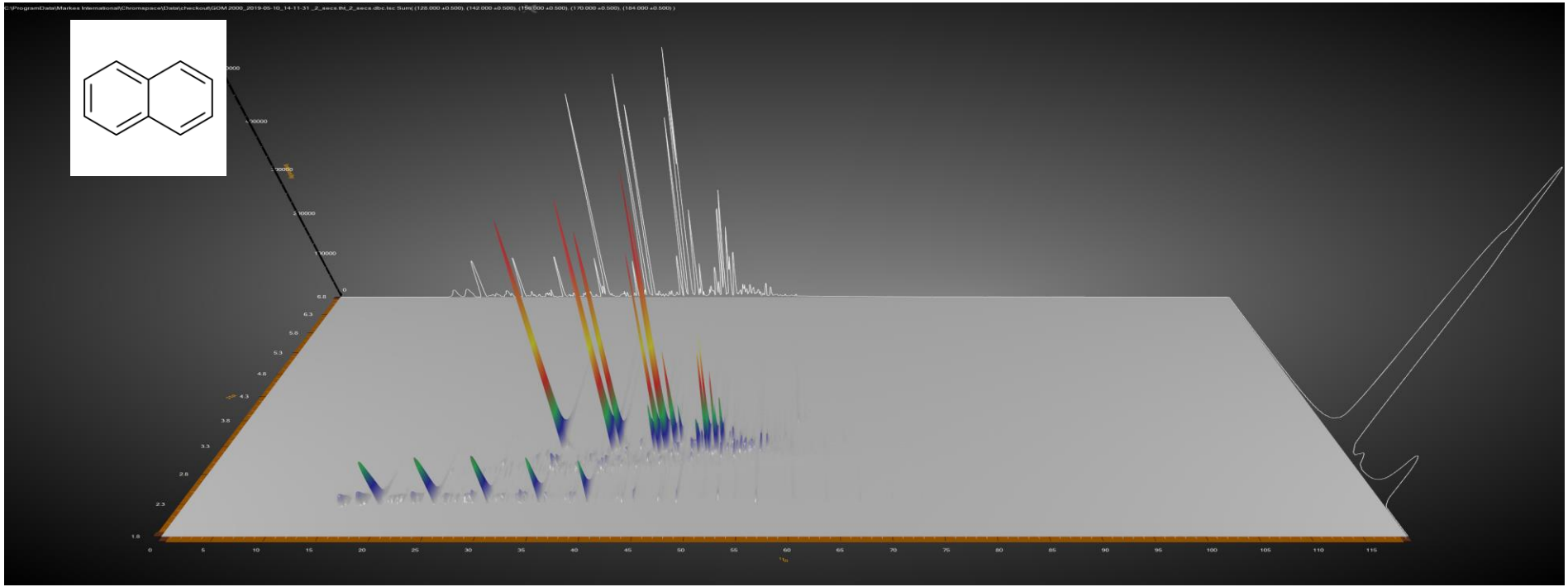
PAH by 2D-GC: Gulf of Mexico Oil Spill

Ions: 128, 142, 156, 170, 184 m/z



PAH by 2D-GC: Gulf of Mexico Oil Spill

Ions: 128, 142, 156, 170, 184 m/z



Quantitative Results: Gulf of Mexico Oil Spill (1D vs. 2D)

PAH	Concentration by 1D (ppb)	Concentration by 2D (ppb)
Naphthalene	1532	1311
Fluorene	491	464
Phenanthrene	1284	1235
Fluoranthrene	9.07	2.94
Pyrene	42.3	26.4
Chrysene	217	176
Benzo[e]pyrene	20.8	19.1
Benzo[b]fluoranthrene	7.98	5.19

Ions used for detection: Naphthalene 128; Fluorene 166; Fluoranthrene 202; Pyrene 202; Chrysene 228; Benzo[e]pyrene 252; Benzo[b]fluoranthrene 252. Data normalized to internal PAH standard.

Quantitative Results: Alida Beds (1D vs. 2D)

PAH	Concentration by 1D (ppb)	Concentration by 2D (ppb)
Naphthalene	560	454
Fluorene	159	91.0
Phenanthrene	181	109
Fluoranthrene	5.23	3.74
Chrysene	26.3	17.9
Pyrene	17.8	11.5
Benzo[b]fluoranthene	5.78	4.86
Benzo[e]pyrene	7.95	6.86

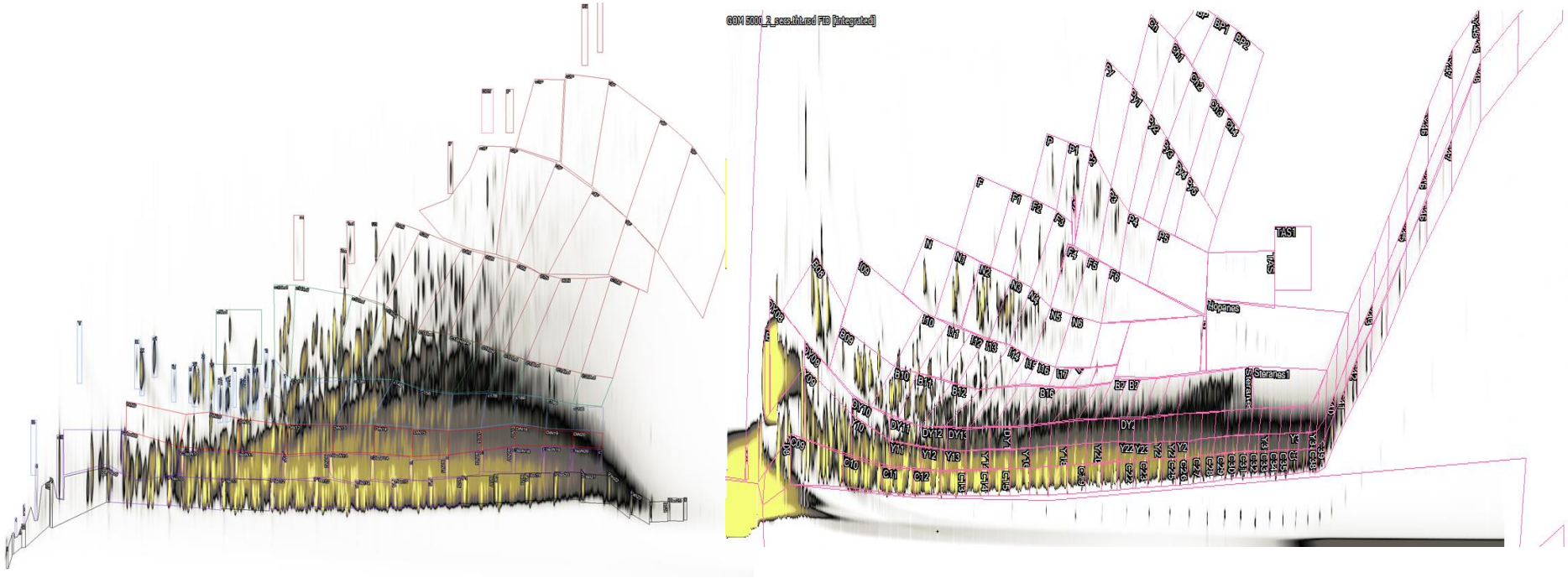
Ions used for detection: Naphthalene 128; Fluorene 166; Phenanthrene 178; Fluoranthrene 202; Pyrene 202; Chrysene 228; Benzo[e]pyrene 252; Benzo[b]fluoranthrene 252.

Quantitative Results: Duverney Formation (1D vs. 2D)

PAH	Concentration by 1D (ppb)	Concentration by 2D (ppb)
Naphthalene	538	429
Fluorene	80.4	50.7
Phenanthrene	122	80.6
Fluoranthrene	0.44	ND
Chrysene	7.50	11.3
Pyrene	4.76	3.06
Benzo[b]fluoranthene	0.19	ND
Benzo[e]pyrene	1.30	1.15

Ions used for detection: Naphthalene 128; Fluorene 166; Phenanthrene 178; Fluoranthrene 202; Pyrene 202; Chrysene 228; Benzo[e]pyrene 252; Benzo[b]fluoranthrene 252.

PAH by 2D-GC: Group Analysis



PAH by 2D-GC: Group Analysis

GCXGC group type analysis

C_{no}	n-P	iso-P	n-CC5/6	iso-N	DiN	mono-Ar	N mono Ar	di AR	N Di Ar	Tri Ar	N Tri Ar	
6	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	
7	0.00	0.00	0.00	0.00	0.14	0.47	0.25	0.52	0.00			
8	0.02	0.22	0.17	0.13	0.02	0.42	0.71	0.63	0.77	0.75	0.66	
9	2.65	0.95	0.90	0.60	0.76	0.72	0.50	0.42	0.65	0.43	0.84	
10	3.50	0.11	0.12	0.15	0.10	0.75	0.71	0.82	0.44	0.89	0.62	
11	5.64	0.11	0.12	0.15	0.10	0.32	0.38	0.57	0.96	0.18	0.59	
12	1.45	3.30	3.30	5.51	4.41	0.08	0.56	0.61	0.83	0.53	0.84	
13	0.91	0.63	0.41	0.30	0.07	0.92	0.55	0.02	0.27	0.81	0.89	
14	0.53	0.53	0.91	0.38	0.48	0.10	0.35	0.82	0.59	0.83	0.21	
15	0.32	0.93	0.50	0.45	0.22	0.13	0.60	0.28	0.81	0.52	0.23	
16	0.24	0.46	0.69	0.22	0.90	0.54	0.62	0.26	0.65	0.72	0.96	
17	0.90	0.30	0.75	0.50	0.32	0.06	0.81	0.25	0.12	0.13	0.15	
18	0.25	0.45	0.52	0.44	0.91	0.09	0.82	0.67	0.14	0.39	0.88	
19	0.05	0.14	0.51	0.13	0.16	0.03	0.11	0.86	0.91	0.06	0.43	
20	0.10	0.06	0.29	0.18	0.54	0.46	0.86	0.11	0.47	0.59	0.28	
21	0.05	0.25	0.41	0.32	0.03	0.04	0.87	0.14	0.22	0.23	0.97	
22	0.04	0.01	0.01	0.28	0.07	0.27	0.32	0.03	0.15	0.17	0.17	
23	0.00	0.04	0.06	0.02	0.09	0.03	0.02	0.03	0.01	0.02	0.04	
24	0.00	0.09	0.04	0.02	0.06	0.08	0.04	0.06	0.05	0.10	0.06	total
total	16.65	8.60	9.72	9.77	9.39	5.51	9.09	7.11	8.01	7.35	8.81	100.00

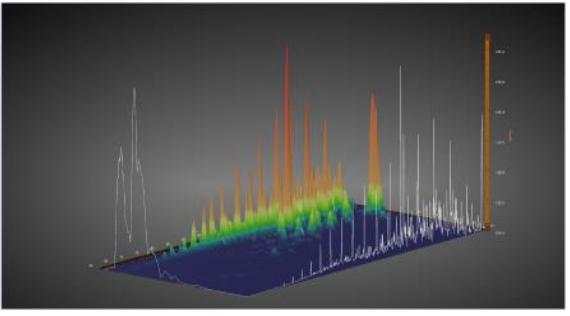
Fully Quantitative!!

Cno- Carbon Number, n-P: Normal Paraffins, isoP: Isoparrafins; n-C5/6: n-alkane, cyclopentane cyclohexane; isoN: Isonaphthenes; diN: diNapthenes; Mono Ar: monoaromatics; n-mono Ar: naphthenic mono aromatics; Di Ar: Diaromatics; N-DiAR: naphthenic diaromatics; TriAr: Triaromatics; N Tri Ar: naphthenic triaromatics.

PAH by 2D-GC: Conclusions

- PAH are highly toxic, and thus highly regulated.
- Analysis that reduces background signal avoids data being biased high.
- Even trace background signal could put tier 1 compliant soils above guideline.
- 2D GC is a unique platform for PAH speciation and resolution, as it separates compounds both on the basis of size and polarity.

Questions?



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