Piecing Together Pollutant Profiles: Combining High-Resolution MS From Multiple Ionization Modes With Multidimensional GC for Petroleum Forensics and Environmental Analyses

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Introduction

Complex mixtures create challenges for calculating risk exposure and determining environmental remediation, necessitating streamlined analytical workflows for detailed compositional identification.

Analysis of heavy fuel oil (HFO) and a mixture of common persistent organic pollutants (POP) was performed by comprehensive two-dimensional gas chromatography (GCxGC) combined with high-resolution time-of-flight mass spectrometry (HRTOFMS) in multiple ionization modes: electron ionization (EI), positive chemical ionization (PCI), and electron capture negative chemical ionization (ECNI). Deconvoluted EI spectra from individual chromatographic peaks were matched to commercial libraries, with hits ranked by an identification grading system based on criteria including mass accuracy of both molecular ions when present and chemically possible fragment ions. Complementary information from PCI and ECNI were used to further confirm molecular formula of individual compounds and leverage scaled mass defect plots to target chromatographic areas of interest.

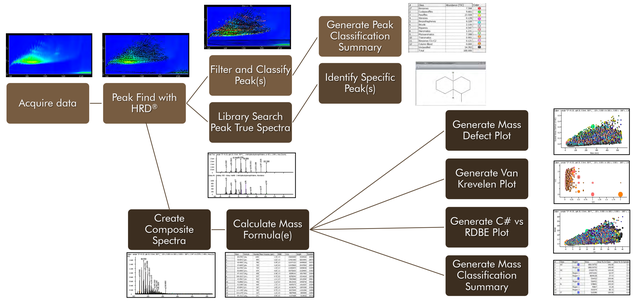


Figure 1: Generalized workflow for working through GCxGC High-Resolution Data.

1) Primary ion formation: $CH_4 + e^- \rightarrow CH_4^{+\bullet} + CH_3^{+\bullet} + CH_2^{+\bullet} + CH^+ + C^{+\bullet} + H_2^{+\bullet} + H^+$

2) Reagent ion formation: $CH_4^{+\bullet} + CH_4 \rightarrow CH_5^+ + CH_3^\bullet$; $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$; $CH_5^+ + C_2H_5^+ \rightarrow C_3H_7^+ + H_2$

3) Adduct Formation: $M + CH_5^+ \rightarrow [M+H]^+ + CH_4$; $M + C_2H_5^+ \rightarrow [M+C_2H_5]^+$; $M + C_3H_7^+ \rightarrow [M+C_3H_7]^+$; $AH + CH_5^+ \rightarrow A^+ + CH_4 + H_2$

Formation of Thermal Electrons ('e⁻'): CH_4(Buffer gas)+ $e^- \rightarrow e^- + CH_3^+ + {}^\bullet H + e^-$; CH_4(Buffer gas)+ $e^- \rightarrow e^- + CH_3^+ + H^+ + {}^\bullet H + e^-$

1) Associative Resonance Capture: $M + {}^\bullet X \rightarrow M^-$

2) Dissociative Resonance Capture: $M\text{-}X + {}^\bullet X \rightarrow M + X^-$

3) Ion Pair Formation: $M\text{-}X + {}^\bullet X \rightarrow M^+ + X^- + e^-$

Figure 2: Pegasus® HRT⁺4D with Multi-Mode Ionization source, which provides ability to analyze samples in EI, PCI, and ECNI modes without venting or other manual hardware changes, preserving chromatographic correlation between modes.

Petroleum Forensics

Goals: Identify biomarkers and thermal maturity markers such as hopanes, steranes, and dibenzothiophenes, whose ratios assist in tracing source of heavy fuel oils.

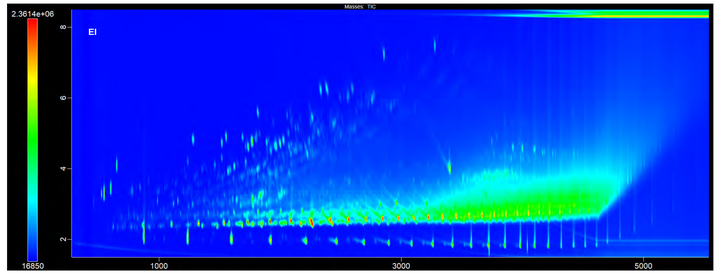


Figure 3: Total Ion Chromatogram of heavy fuel oil illustrates the complexity of the matrix and the benefits of multidimensional chromatography for class separation of peaks.

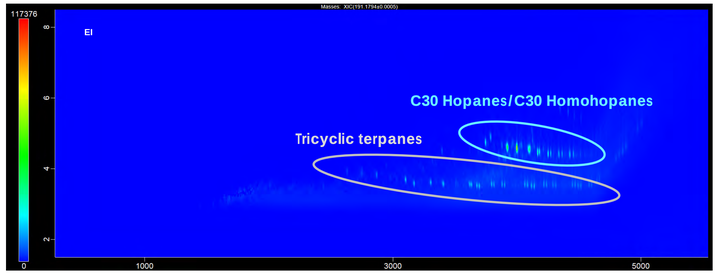
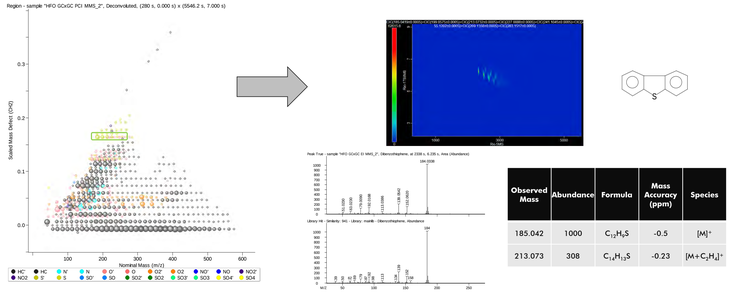


Figure 4: Extracted Ion Chromatogram of heavy fuel oil plotting characteristic mass fragment for hopanes and steranes reveals regions of interest for these biomarkers.



Observed Mass	Abundance	Formula	Mass Accuracy (ppm)	Species
185.042	1000	$C_{12}H_9S$	-0.5	$[M]^+$
213.073	308	$C_{14}H_{13}S$	-0.23	$[M+C_2H_4]^+$

Figure 5: Colorized mass defect plot of the PCI data from heavy fuel oil allows for quick identification of peaks with heteroatomic species of interest, such as S-containing compounds. Plotting the masses of interest (in the green box) onto the contour plot allowed for identification of C0-C5 series of dibenzothiophenes.

Environmental Analyses

Goals: Leverage ECNI to identify and created targeted methods for organic pollutants of interest.

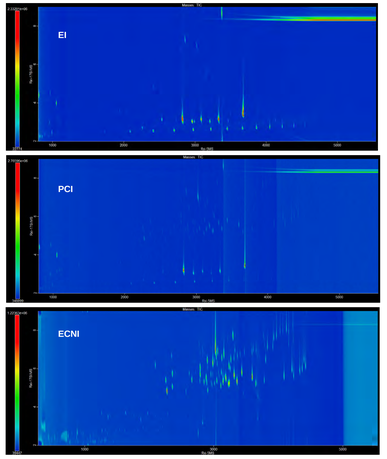


Figure 6: Total Ion Chromatograms of environmental mixture shows the power of the complementary modes of ionization, especially with the high selectivity of ECNI for the low-level halogenated species that could be missed by EI analysis alone.

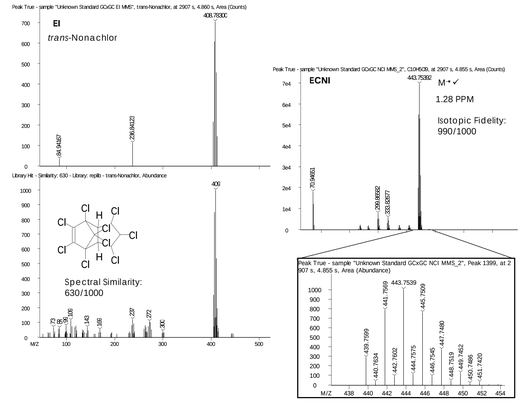
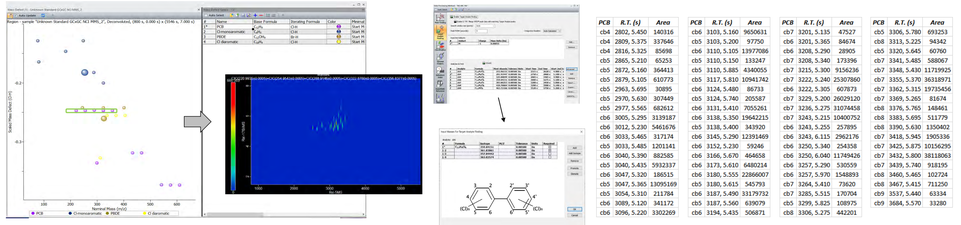


Figure 7: Confirming identity of trans-nonachlor using combination of EI fragmentation and ECNI molecular ion with high isotopic fidelity; where EI match to library did not provide either molecular ion or high enough confidence in spectral similarity score, the corresponding ECNI peak shows a clear molecular ion with excellent isotopic fidelity for the putative formula.



PCB	R.T. (s)	Area	PCB	R.T. (s)	Area	PCB	R.T. (s)	Area	PCB	R.T. (s)	Area
cb4	2802, 5.450	140116	cb6	3103, 5.160	9650631	cb7	3201, 5.335	47527	cb5	3306, 5.780	691253
cb4	2809, 5.375	337646	cb5	3103, 5.200	97750	cb6	3201, 5.365	84674	cb8	3313, 5.225	94342
cb4	2816, 5.325	85698	cb6	3110, 5.105	13977086	cb6	3208, 5.290	28905	cb5	3320, 5.645	60760
cb5	2865, 5.230	65253	cb5	3110, 5.150	133247	cb7	3208, 5.340	173396	cb7	3341, 5.485	588067
cb5	2872, 5.160	364413	cb5	3110, 5.885	4340055	cb7	3215, 5.300	9156236	cb7	3348, 5.430	11719925
cb5	2879, 5.105	610773	cb5	3117, 5.810	10941742	cb7	3222, 5.240	25307860	cb7	3355, 5.370	36318971
cb5	2963, 5.695	30895	cb6	3124, 5.480	86733	cb6	3222, 5.305	607879	cb7	3362, 5.315	19735456
cb5	2970, 5.630	307449	cb5	3124, 5.740	205587	cb7	3229, 5.200	26029120	cb7	3369, 5.265	81674
cb5	2977, 5.565	682612	cb6	3131, 5.410	7055261	cb7	3236, 5.275	31074458	cb8	3376, 5.765	148461
cb6	3005, 5.295	3139187	cb6	3138, 5.350	19642215	cb7	3243, 5.215	10400752	cb8	3383, 5.695	511779
cb6	3012, 5.230	5461676	cb5	3138, 5.400	343920	cb6	3243, 5.255	257895	cb8	3390, 5.630	1350402
cb6	3033, 5.465	317174	cb6	3145, 5.290	12931469	cb6	3243, 6.115	2962176	cb7	3418, 5.945	1905336
cb5	3033, 5.485	1201141	cb6	3152, 5.230	59246	cb6	3250, 5.340	254358	cb7	3425, 5.875	10156295
cb6	3040, 5.390	8823585	cb7	3166, 5.670	464658	cb6	3250, 6.040	11749426	cb7	3432, 5.800	38118063
cb5	3040, 5.435	5932337	cb6	3173, 5.610	6480214	cb6	3257, 5.290	530559	cb7	3439, 5.740	918195
cb6	3047, 5.320	186515	cb6	3180, 5.555	22866007	cb6	3257, 5.970	1548893	cb8	3460, 5.465	102724
cb5	3047, 5.365	13095169	cb5	3180, 5.615	545793	cb7	3264, 5.410	73620	cb8	3467, 5.415	713250
cb5	3054, 5.310	211784	cb6	3187, 5.490	33179732	cb7	3285, 5.515	170704	cb9	3537, 5.440	63334
cb6	3089, 5.120	341172	cb5	3187, 5.560	639079	cb5	3299, 5.825	108975	cb9	3684, 5.570	33280
cb6	3096, 5.220	3302269	cb6	3194, 5.435	506871	cb8	3306, 5.275	442201			

Figure 8: Mass defect plot generated from ECNI data allows for targeting groups of compounds like these PCB congeners displayed onto the contour plot. Regions of interest can then be targeted to find specific analytes using the highlighted masses; table reflects resulting PCB congeners identified with a S/N of greater than 20.

Conclusion

Many pieces of the identification puzzle were provided by the combination of GCxGC with multiple modes of HRTOFMS ionization—GCxGC offered not only enhanced chromatographic resolution and cleaner mass spectra for more accurate deconvolution, but also structural information based on regions of elution, while the HRTOFMS supplied full-mass range spectra and confident calculation of chemical formulae in addition to the ability to leverage scaled mass defect plots for heteroatom determination. This poster highlights the power of combining all these contributions into one workflow with streamlined tools within one software package that allows for more confident identification of both targeted and nontarget species of interest.