Quantitation of PAH in Engine Oils Using GCxGC-TOFMS

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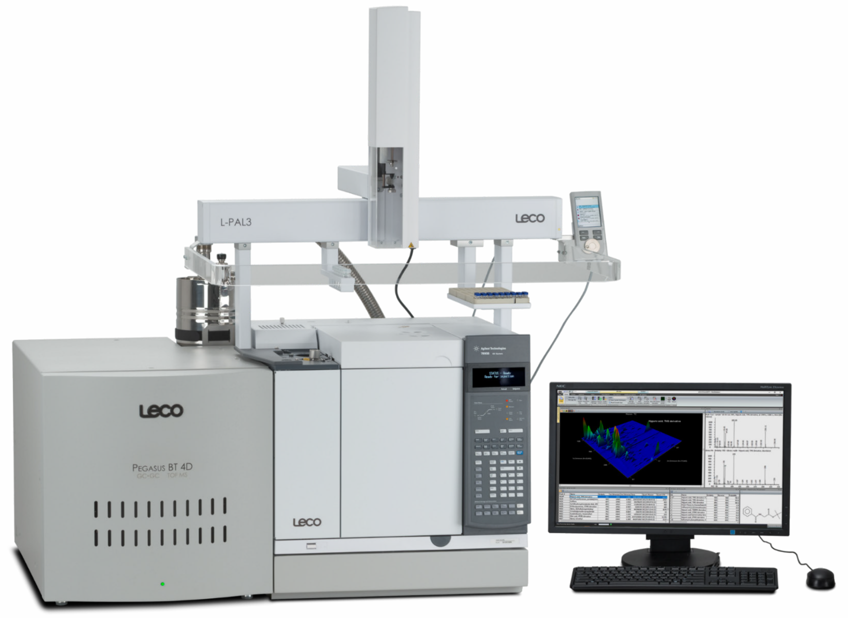
Overview

Calibration curves were built for a standard set of polycyclic aromatic hydrocarbons (PAH) and applied to engine oil samples containing various levels of PAHs and alkylated PAHs. Following expectations for combustion efficiencies, larger levels of each PAH correlated with engines driven shorter distances routinely. With mass precision better than traditional nominal mass instruments, the Pegasus® BT 4D provided the ability to accurately quantitate targeted, regulated compounds, as well as identify other components of interest by separating them in the 2nd dimension of GCxGC from the complex matrix of used engine oil.

Sample Key	
Unused Oil	Commercially available, unused SAE 30 engine oil
Used Oil (L)	Used engine oil from car routinely driven Long distances (average >100 miles/trip)
Used Oil (M)	Used engine oil from car routinely driven Medium distances (average <50 miles/trip)
New Oil (S)	New engine oil from car routinely driven Short distances (average <5 miles/trip)
Used Oil (S)	Used engine oil from car routinely driven Short distances (average <5 miles/trip)



LECO Pegasus BT 4D

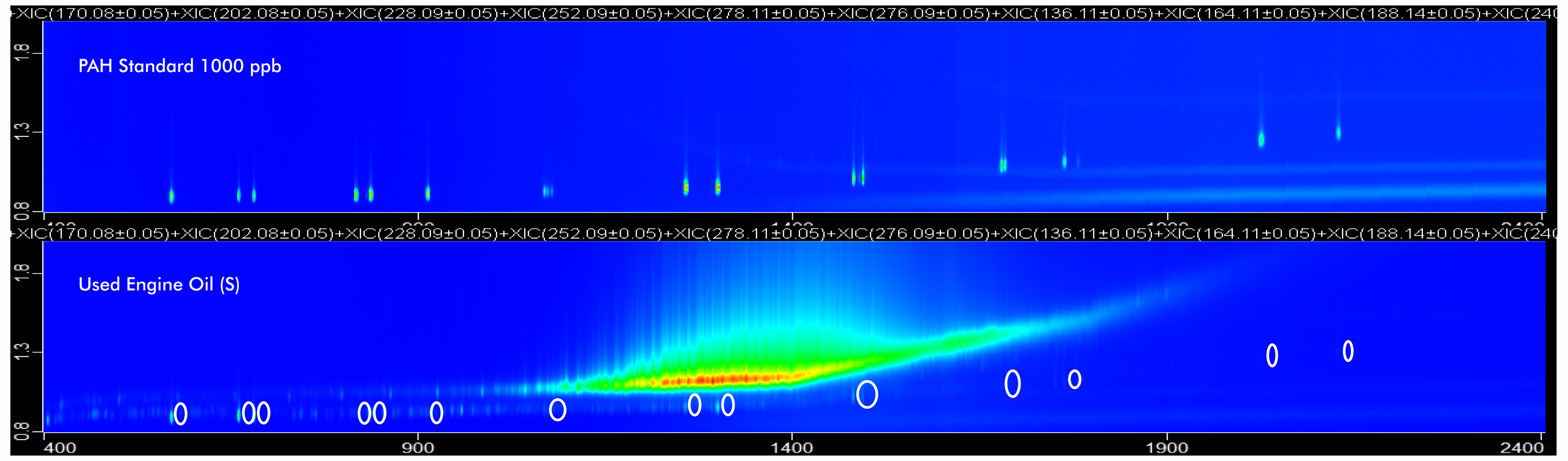


Figure 1. Chromatographic contour plots displaying characteristic masses for PAHs are shown for the PAH Standard at 1000 ppb concentration level and a sample of used engine oil from a car routinely driven short distances. GCxGC provides a clear separation of the PAH band, which elutes before the large mass of hydrocarbon interferences in the 2nd dimension.

Gas Chromatograph	Agilent 7890 with Dual Stage Quad Jet Modulator and LECO LPAL-3 Autosampler
Injection	Liquid injection, split 20:1 @ 320 °C
Carrier Gas	He @ 1.4 mL/min, Corrected Constant Flow
Primary Column	Rxi-PAH, 60 m x 0.25 mm i.d. x 0.10 μm coating (Restek, Bellefonte, PA, USA)
Secondary Column	Rxi-1HT, 0.6 m x 0.25 mm x 0.10 μm coating (Restek, Bellefonte, PA, USA)
Temperature Program	1.5 min at 80 °C, ramped 10 °C/min to 300 °C, then ramped 3 °C/min to 320 °C and held 10 min Secondary oven maintained +10 °C relative to primary oven
Modulation	2.5 s with temperature maintained +10 °C relative to 2nd oven
Transfer Line	350 °C
Mass Spectrometer	**LECO Pegasus BT 4D**
Ion Source Temperature	300 °C
Mass Range	45-500 m/z
Acquisition Rate	200 spectra/s

Quantitation Using GCxGC

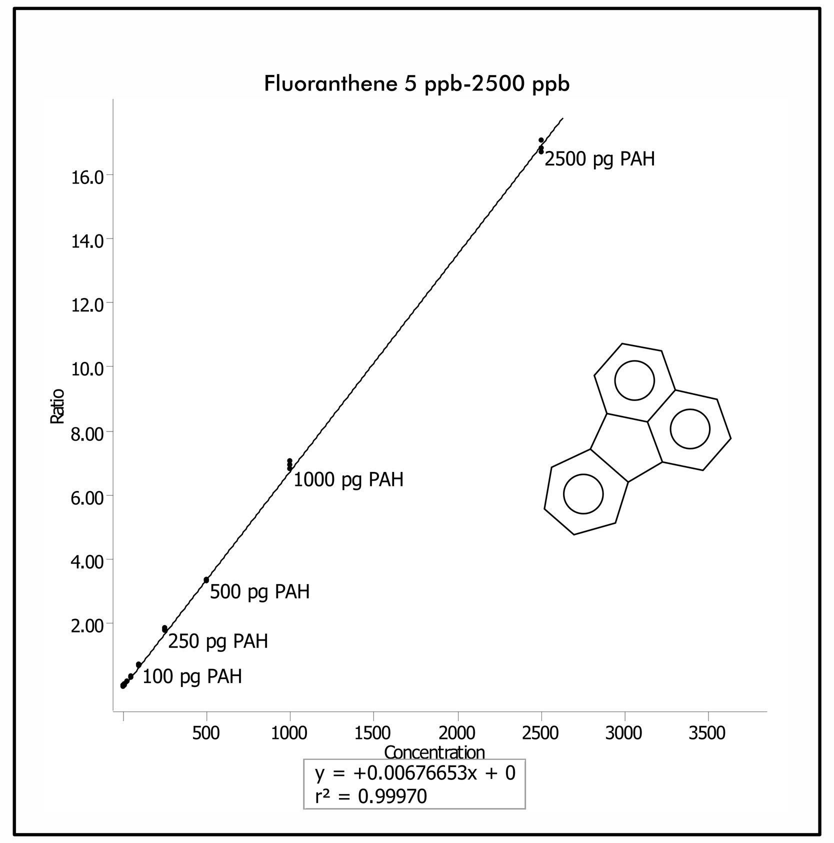


Figure 2. Calibration curve for fluoranthene standard above shows linearity from 5 to 2500 ppb, with R^2 =0.999.

Table 1. Correlation coefficient R^2>0.995 shown for each analyte in the calibration standard demonstrates excellent linearity for PAHs.

Analyte	R^2
Naphthalene	0.998
Acenaphthylene	0.999
Acenaphthene	0.998
Fluorene	0.998
Phenanthrene	0.998
Anthracene	0.999
Fluoranthene	0.999
Pyrene	0.999
Benz[a]anthracene	0.998
Chrysene	0.999
Benzo[b]fluoranthene	0.996
Benzo[k]fluoranthene	0.996
Benzo[a]pyrene	0.998
Indeno[1,2,3-cd]pyrene	0.998
Benzo[ghi]perylene	0.998

PAH Levels in Engine Oils (ppm)

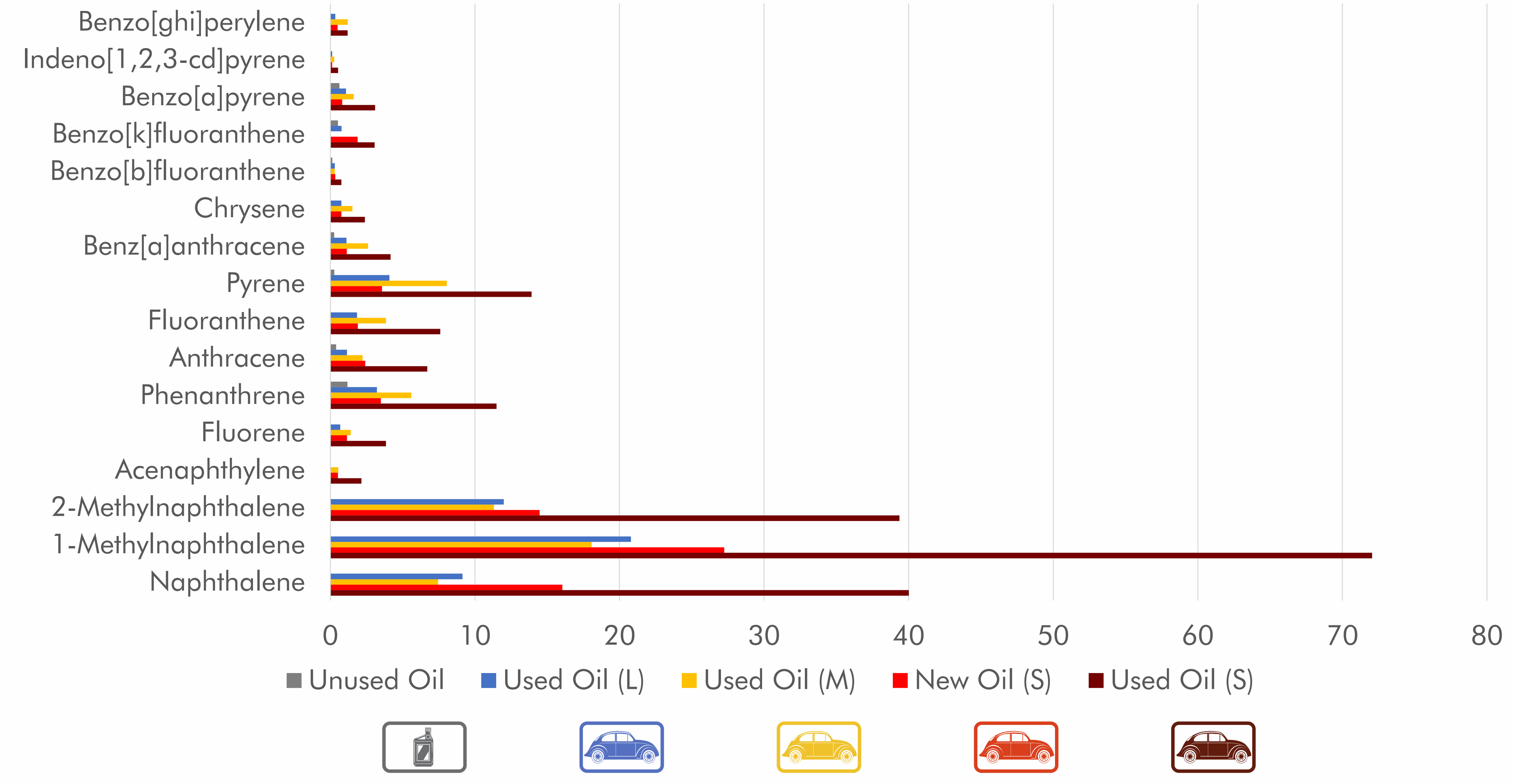


Figure 3. Calculated concentrations of each calibrated PAH in each engine oil sample are shown above, taking into account dilution and split ratios. Results match expectation for used engine oils based on predicted combustion efficiencies.

GCxGC Improves Deconvolution

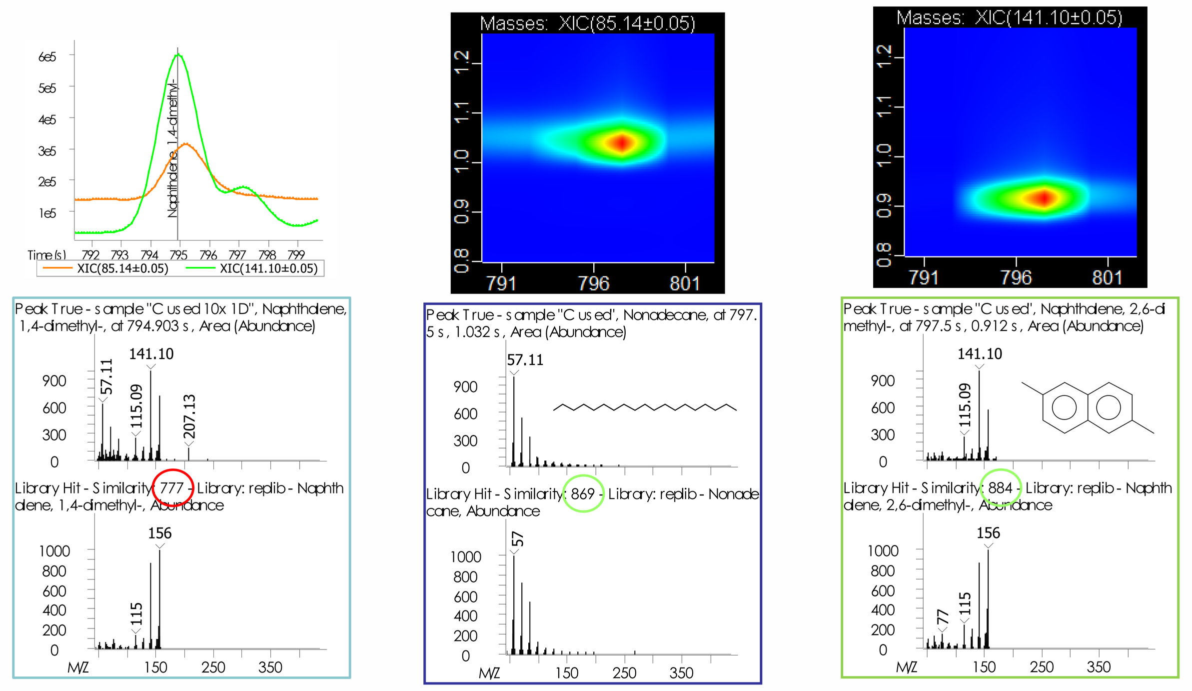


Figure 4. The deconvolution example shown here compares the results of 1D vs. GCxGC analysis. In the peak shown in the 1D chromatogram, the deconvoluted Peak True spectrum that contains m/z 57.11 and m/z 141.10 as major features yields a low library similarity score of 777/1000. Further investigation with GCxGC analysis yields two separate, chromatographically-resolved peaks in the same 1st dimension retention time, which can be identified as nonadecane with the characteristic m/z 57.11 and 2,6-dimethylnaphthalene with m/z 141.10, with respective library similarity scores of 869/1000 and 884/1000.

Sulfur and Oxygen Containing Species

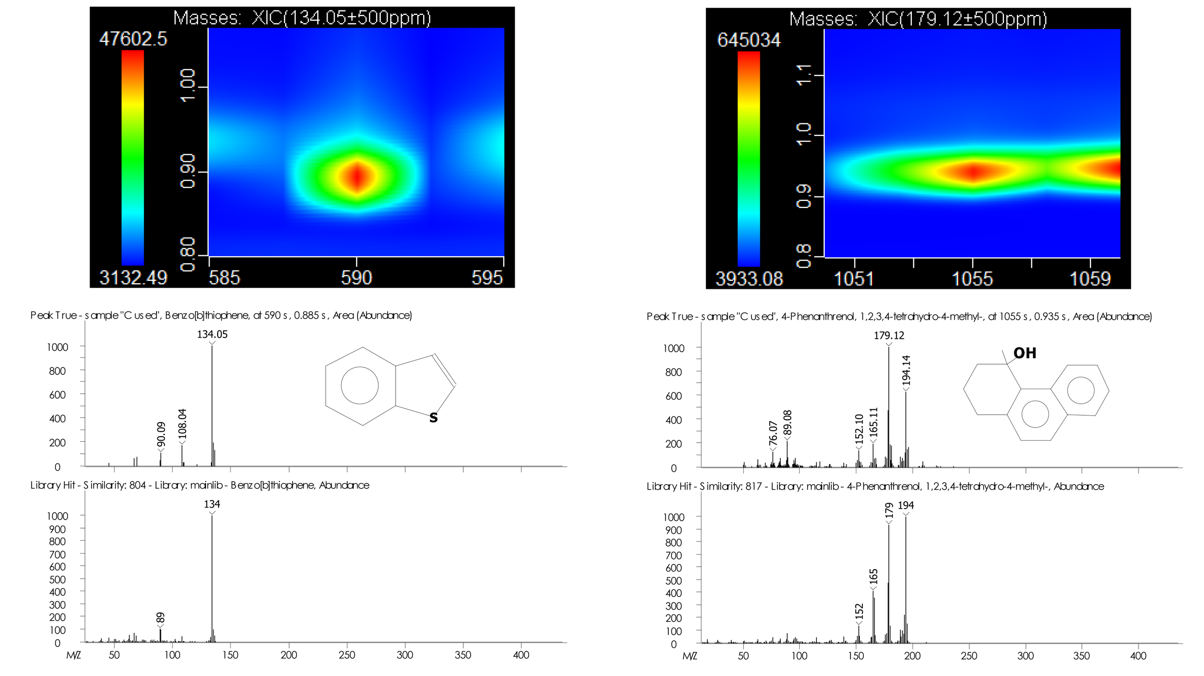


Figure 6. Nontargeted compounds containing oxygen and sulfer were identified in used engine oil. Two examples of compounds identified through automated Peak Find and library searching are shown above: benzo(b)thiophene and 1,2,3,4-tetrahydro-4-methyl-4-phenanthrol.

Conclusion

GCxGC TOFMS was successfully used for quantitation of PAHs in used engine oils. The combination of increased chromatographic resolution with GCxGC and additional mass specificity of the Pegasus BT 4D provides a comprehensive solution for analysis of petroluem products, identifying many types of analytes of interest.

Delivering the Right Results

Identifying Alkyl PAHs

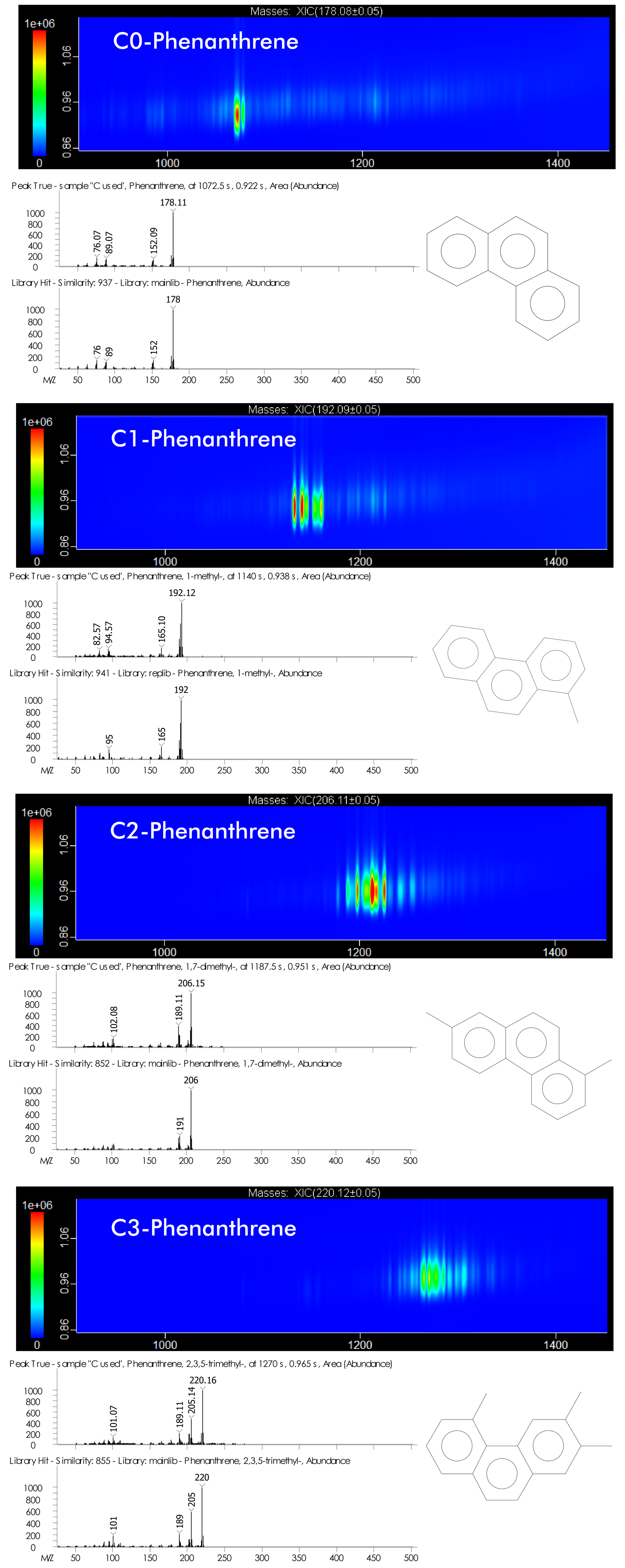


Figure 5. Representative masses for C0-C3 clusters of phenanthrene isomers are plotted in the chromatographic contour plots above. Two additional significant figures beyond the decimal available on the Pegasus BT 4D provides extra specificity. Deconvoluted Peak True spectra corresponding to the most intense peak of each cluster are compared to spectra from commercial libraries for tentative identification.