QUANTITATION OF PAHS IN USED ENGINE OIL USING GCXGC AND TIME OF FLIGHT MASS SPECTROMETRY

Peak tailing due to interactions with GC columns and MS sources and reproducibility of internal standard injections often make the quantitative analysis of polycyclic aromatic hydrocarbons (PAHs) particularly challenging. The addition of a complex matrix, often found in petroleum products that have thousands of distinct components, only makes experiments even more problematic. These difficulties are inherent to characterizing PAH levels in samples of used engine oils, which not only gives insight into engine combustion efficiencies but also helps ensure proper environmentally-conscious waste disposal.

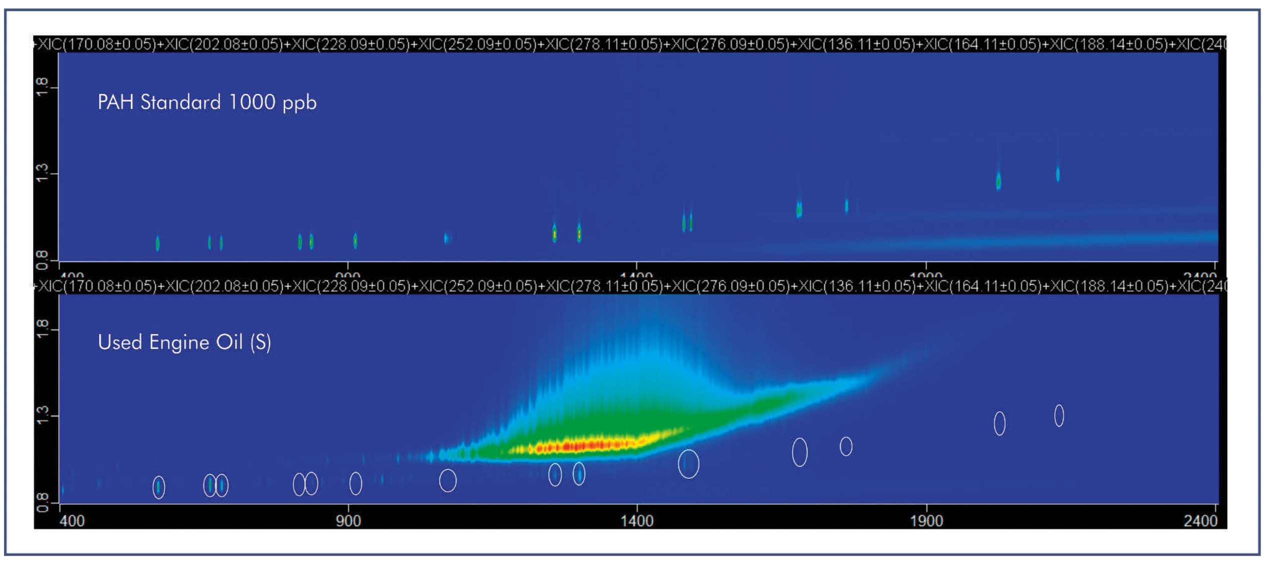

Figure 1. Chromatographic contour plots displaying characteristic masses for PAHs are shown for the PAH Standard at 1000 ppb concentration level and a sample of used engine oil from a car routinely driven short distances. GCxGC provides a clear separation of the PAH band, which elutes before the large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

Using a combination of comprehensive two-dimensional gas chromatography (GCxGC) and high performance time-of-flight mass spectrometry (TOFMS) found in the LECO Pegasus BT 4D, PAHs are separated from matrix interferences using both orthogonal column phase selectivity and additional extracted ion mass precision. Identification of specific compounds is accomplished by retention time correlation with standard mixes and full-mass range spectral matching with commercial libraries. With common quantitation challenges overcome, PAH levels in used engine oils are compared between gasoline-powered engines in cars that routinely travel short vs. long distances, providing insight into the nature of combustion by-products that occur when engines are routinely operated under different conditions.

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)

Figure 2: Sample key showing icons representing various samples of engine oil.

Experimental

Samples and Standards

PAH Calibration Standards (Restek #31874 EPA Method 8310 PAH Mixture) were made at concentrations of 5, 10, 25, 50, 100, 250, 500, 1000, and 2500 pg/µL in toluene and spiked with 100 pg/µL of PAH Internal Standard (Restek #31206 SV Internal Standard Mix).

Samples of used engine oil were collected from the dipsticks of various cars: one car routinely driven short distances with an average of 5 miles/trip before and after an oil change, labelled Used Oil (S) and New Oil (S); one car routinely driven medium distances with an average of less than 50 miles/trip labelled Used Oil (M); and one car routinely driven long distances with an average of greater than 100 miles per trip labelled Used Oil (L). A sample of unused oil was also collected from a newly opened bottle of commercially available SAE 30 engine oil. Figure 2 shows the icons and description for each sample type.

Each sample was diluted to 10 mg/mL in toluene and spiked with the PAH internal standard.

Acquisition Parameters

Table 1. GC×GC-TOFMS (Pegasus® BT 4D) Conditions

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

Data Processing

Sample files were processed using the Target Analyte Find (TAF) and Non-Target Deconvolution Peak Find (PF) features of ChromaTOF. Calibration curves for a quantitation method were created using peaks from the TAF processing within the Quantitation section of the ChromaTOF software. Identifications of peaks were confirmed by matching spectra from the NIST 17 commercial libraries to the deconvoluted peaks returned by PF processing.

Results and Discussion

Linear calibration curves were built using peak areas of each standard analyte with concentrations of 5-2500 pg/µL. Figure 3 shows an example of the calibration curve generated for fluoranthene, with excellent linearity demonstrated. Table 2 shows the linear least-squares correlation coefficients for each calibrated analyte, with values of greater than 0.995 for each.

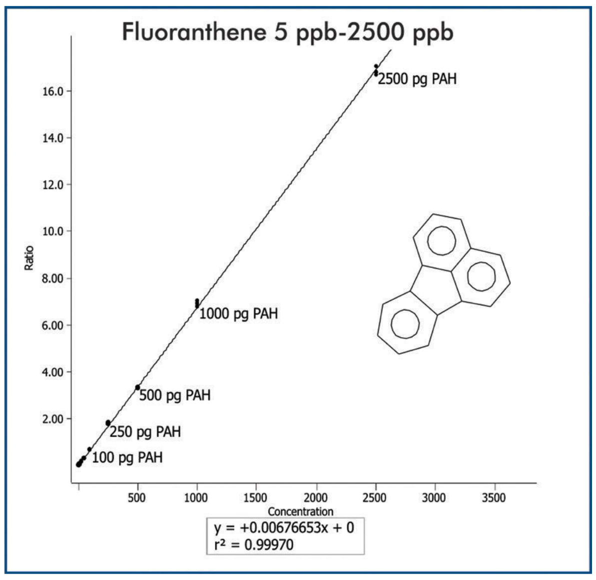

Figure 3: Calibration curve for fluoranthene standard above shows linearity from 5 to 2500 ppb, with R^2 =0.999.

Analyte	R^2
Naphthalene	0.998
1-Methylnaphthalene	0.998
2-Methylnaphthalene	0.997
Acenaphthylene	0.999
Acenaphthene	0.998
Fluorene	0.998
Phenanthrene	0.998
Anthracene	0.999
Fluoranthene	1.000
Pyrene	1.000
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

Table 2: PAH Standard Calibration Linearity

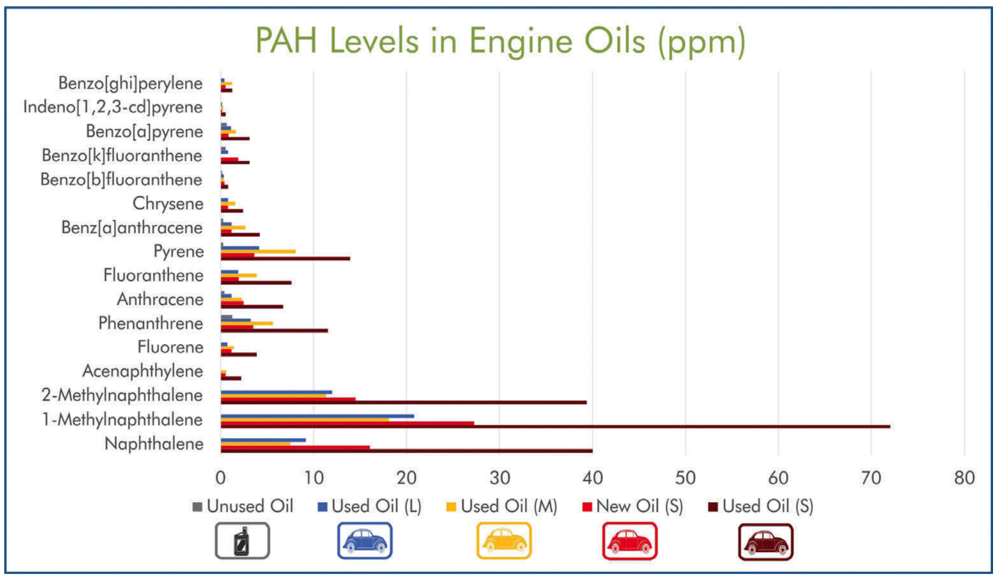

Figure 4: Summary of PAH and alkyl PAH levels found in engine oil sample, reported in ppm, as determined by the Pegasus BT 4D.

As shown in Figure 4, the Used Oil (S) showed the highest levels of any quantitated PAH, with significantly higher levels of the smaller PAHs, naphthalene and methylnaphthalenes. Especially interesting was the fact that even after an oil change, engine oil from the car routinely driven short distances still showed significantly higher levels of these smaller PAHs than the used oils from other cars.

In addition to the quantified target components, alkylated PAHs, which may have higher environmental toxicity, were found in the used motor oils. Based on characteristic masses and position in the structured, two-dimensional chromatogram, various C0-C3-phenanthrene isomers were identified. In Figure 5 below, representative masses for C0-C3 clusters of phenanthrene isomers calculated from the chemical formula are plotted in the chromatographic contour plots. Two additional significant figures beyond the decimal available on the Pegasus BT 4D provide extra specificity. The deconvoluted Peak True spectra corresponding to the most intense peak of each cluster are compared to spectra from commercial libraries for tentative identification.

Besides the ability to separate the PAHs from hydrocarbon interferences, the second dimension in GCxGC allows for better deconvolution results due to enhanced chromatographic resolution of peaks. An example of this is shown in Figure 6 below, where two peaks clearly separated in the 2nd dimension had co-eluted in the first dimension, causing an incorrect analyte assignment in the 1D run. In the peak shown in the 1D chromatogram, the deconvoluted Peak True spectrum contains m/z 57.11 and m/z 141.10 as major features and 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. Their respective library similarity scores are 869/1000 and 884/1000.

With the combination of improved chromatographic resolution and extra mass precision beyond the decimal, identifying compounds with heteroatomic substitutions with more specificity is also possible using Peak Find with NonTarget deconvolution.

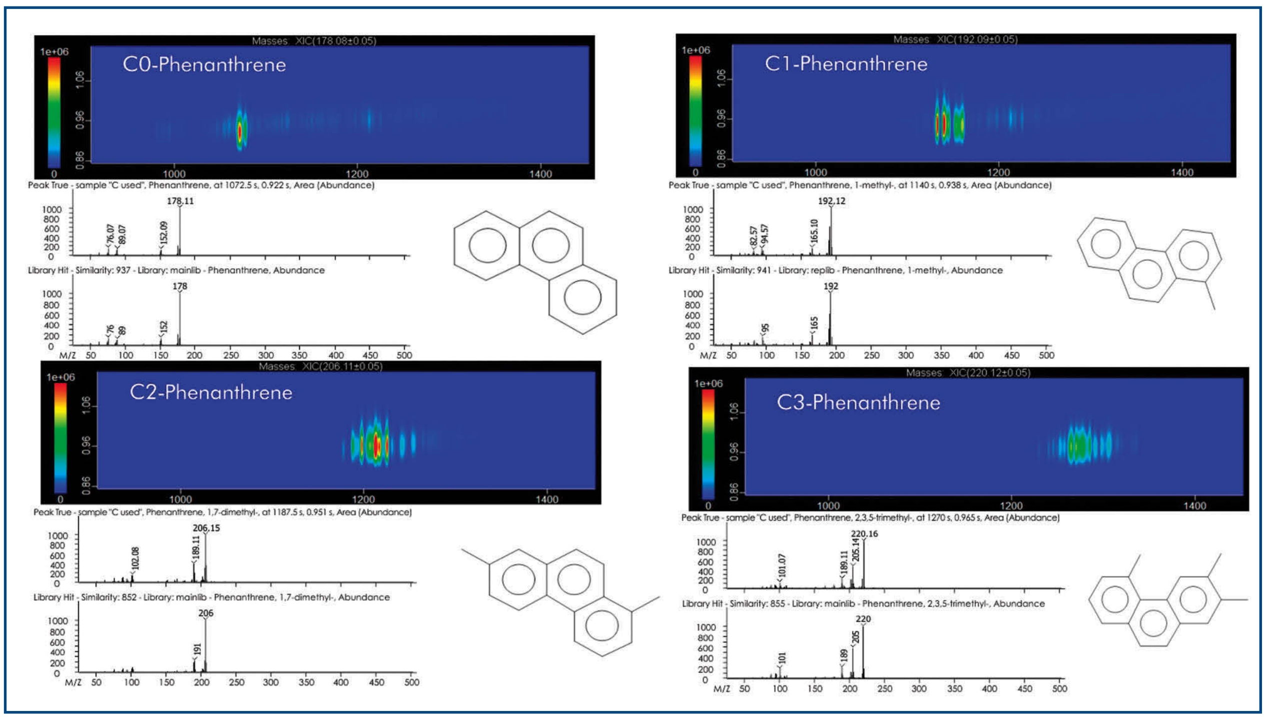

Figure 5: C0-C3-phenanthrene isomer clusters shown with corresponding library-matched spectra for the largest peak in each cluster.

In Figure 7 below, examples of a sulfur-containing and an oxygen-containing analyte are shown, with excellent library similarity scores: benzo(b)thiophene and 1,2,3,4-tetrahydro-4-methyl-4-phenanthrol.

Conclusion

In this article, calibration curves were built for a standard set of PAHs and applied to engine oil samples with 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 accuracies 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.

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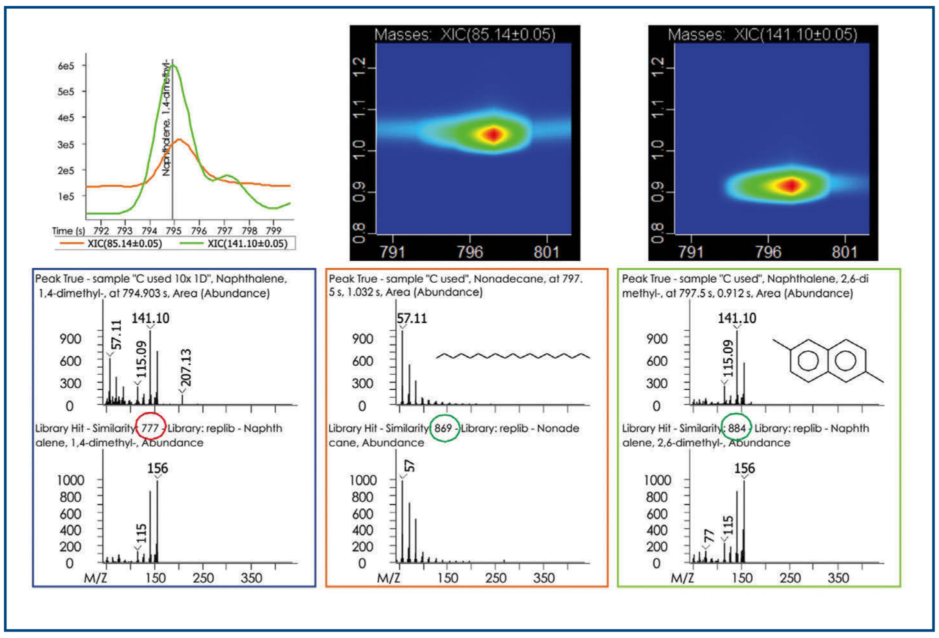

Figure 6: The deconvolution example shown here compares the results of 1D vs. GCxGC analysis.

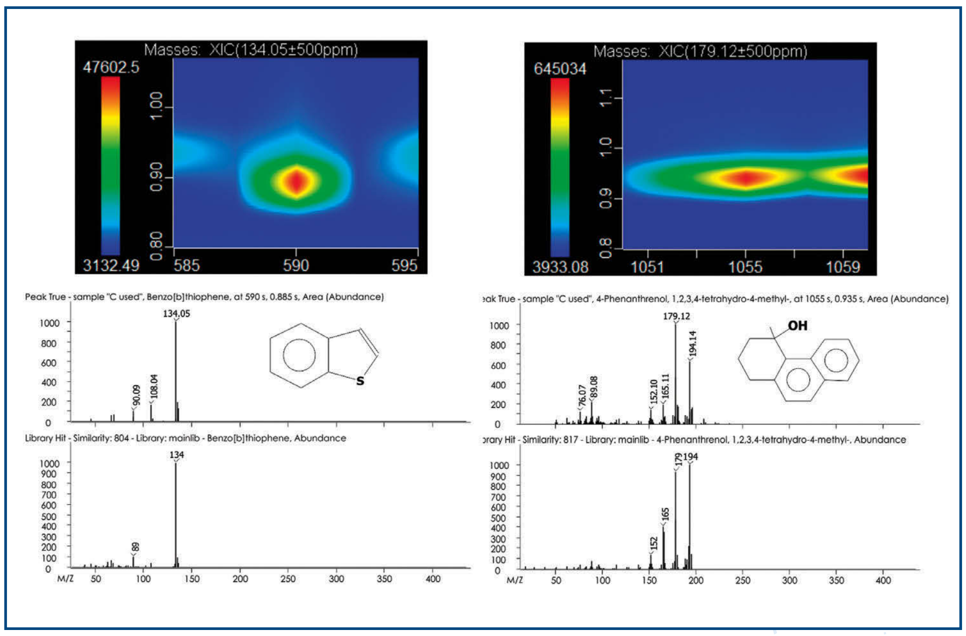

Figure 7: Nontargeted compounds containing oxygen and sulfur were identified in used engine oil.