Application Note

EMPOWERING RESULTS
Elemental Analysis | GC Mass Spectrometry | Metallography

Instrument: QuadJet™ SD

Quantitation of Olefin Content in Plastic-Derived Pyrolysis Oils

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Key Words: Plastics, Pyrolysis Oil, Petroleum Alternative, Olefins, Alkenes

Introduction

The global plastic waste crisis has become a major environmental challenge, with over 9 billion tons of plastic waste produced by 2021. Around 400 million tons of plastic are added to this growing problem yearly, mainly driven by increasing production and consumption patterns[1]. Conventional recycling methods have proven insufficient in managing this volume of waste, prompting researchers to explore innovative solutions, such as chemical conversion processes. One of the most promising methods is pyrolysis, which uses high temperatures to break down plastics and produce pyrolysis oils with chemical characteristics similar to those of fossil fuels. However, these potential alternative fuels contain high concentrations of olefins (up to 72 wt%)[2]. Due to their similar molecular properties, olefins often coelute with other compounds or elute in regions assigned to different hydrocarbon classes, leading to their classification alongside these compounds when characterizing complex mixtures. This overlap has historically made distinguishing olefins from other hydrocarbons challenging during detailed analysis. Comprehensive two-dimensional gas chromatography with flame ionization detection (GCxGC-FID) has proven to be one of the most effective analytical methods for analyzing these complex mixtures, allowing for the detailed separation and identification of the hydrocarbons present while providing efficient, high-resolution chromatographic separations[3].

A dimethyl disulfide (DMDS) and iodine derivatization reaction can shift olefins from their original position on the chromatogram. Since FID is a quantitative technique, this approach accurately calculates the wt% of olefins that have been chromatographically relocated. Through this method, we are pushing the instrument to its full potential, maximizing its capability to distinguish and quantify olefins without the need for mass spectrometry. This solution is a cost-effective and efficient alternative for the detailed characterization of olefins in complex mixtures that provides reliable and accurate results.

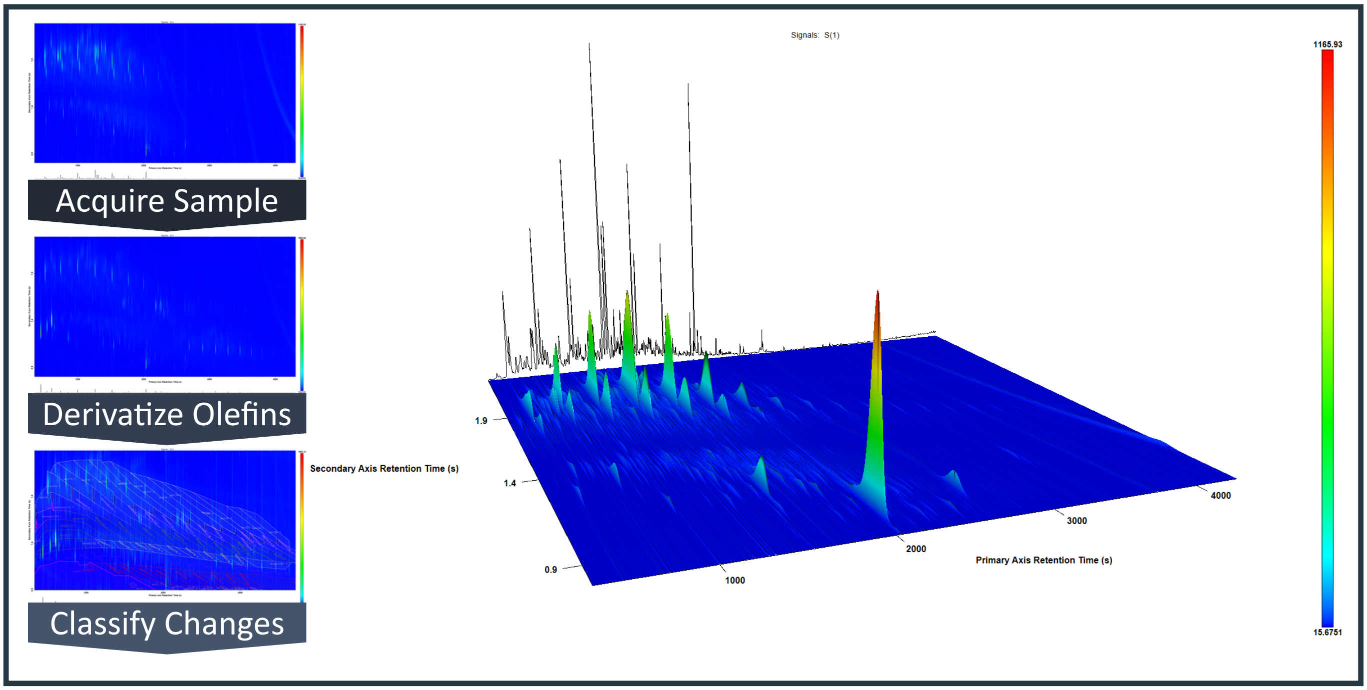

Figure 1. Left Top: Contour plot of underivatized fuel. Left Middle: Contour plot of derivatized fuel showing the change in elution pattern of derivatized olefins. Left Bottom: Contour plot showing derivatized fuel with classification regions used for quantitation of olefins by carbon number overlaid. Right: 3D surface plot of waste plastic fuel showing the resolution benefits and the structured chromatogram created by GCxGC, with the band of peaks in the back of the plot corresponding to the paraffins, olefins, and naphthenes, and the larger peaks in the front of the plot corresponding to aromatic compounds. A reconstructed trace of what a single dimension of GC separation would have looked like is shown in black.

Experimental

Pyrolysis oil sample made from waste polyethylene (PE) foil in the gasoline distillation range was analyzed using the LECO *QuadJet* thermally modulated comprehensive two-dimensional gas chromatograph coupled with flame ionization detection (GCxGC-FID). Two sample preparation methods were employed: (1) dilution with pentane at a 1:50 ratio and (2) derivatization with iodine solution[4]. The GCxGC-FID parameters optimized for these analyses are shown in Table 1. Data processing and interpretation were carried out using ChromaTOF® software. Classification templates were developed around elution bands for monocycloalkanes (MCA) by carbon number and for derivatized olefins regions as revealed by *ChromaTOF* Tile.

Table 1. Acquisition parameters.

Gas Chromatograph	**LECO QuadJet™ Thermal GCxGC**
Injection	0.5 μL liquid injection, split 1:20 @ 285 °C
Carrier Gas	He @ 1.5 mL/min, constant flow
Column One	Rxi-17SilMS, 29.5 m x 0.25 mm ID x 0.25 μm coating (Restek, Bellefonte, PA, USA)
Column Two	DB-1HT, 1.30* m x 0.25 mm ID x 0.25 μm coating *0.9 m coiled in 2nd oven
Temperature Program	3 min at 40 °C, ramped 3.0 °C/min to 285 °C, hold for 1 min
Secondary Oven	+35 °C relative to the primary oven
Modulator Temperature	+20 °C relative to the secondary oven
2nd Dimension Separation Time	1.7 s, hot pulse time 0.28 s
Flame Ionization Detector	
Temperature	300 °C
Data Collection Rate	200 Hz
Hydrogen Flow	40 mL/min
Air Flow	450 mL/min
Makeup (He) + Column Flow	50 mL/min

Each of the two samples, underivatized and derivatized, was analyzed five times to ensure reproducibility. The resulting data were imported into *ChromaTOF* Tile software (version 1.3.35.0). The data type was set to "Pegasus® BT, FID" to match the instrument configuration. The method parameters used for data processing and analysis were configured according to the specifications outlined in Table 2.

Table 2. *ChromaTOF* Tile processing parameters.

Method	***ChromaTOF* Tile**
Tile size D1 (modulation)	7
Tile size D2 (point)	2340
S/N threshold	50
D1 signal to base threshold	2
D1 signal to base threshold	1
Samples that must exceed S/N threshold	10
Statistical threshold type to apply	F-ratio
F-ratio threshold	20

Results and Discussion

GCxGC provides a significant amount of detailed information about a sample and has the advantage of producing structurally-ordered chromatograms. Figure 2 shows the contour plot of the fuel sample made from PE-foil pyrolysis overlaid with a classification template, which provides a wealth of information about its chemical composition. The multitude of peaks at different concentrations, corresponding to changing color intensity on the plot, represent various compounds present in the fuel, including hydrocarbons, oxygenates, and potential trace contaminants. Each peak corresponds to a specific compound eluting from the chromatographic column at a different retention time based on its physical and chemical properties. The complexity of this chromatogram is immediately apparent, displaying a myriad of peaks varying in height, width, and retention time.

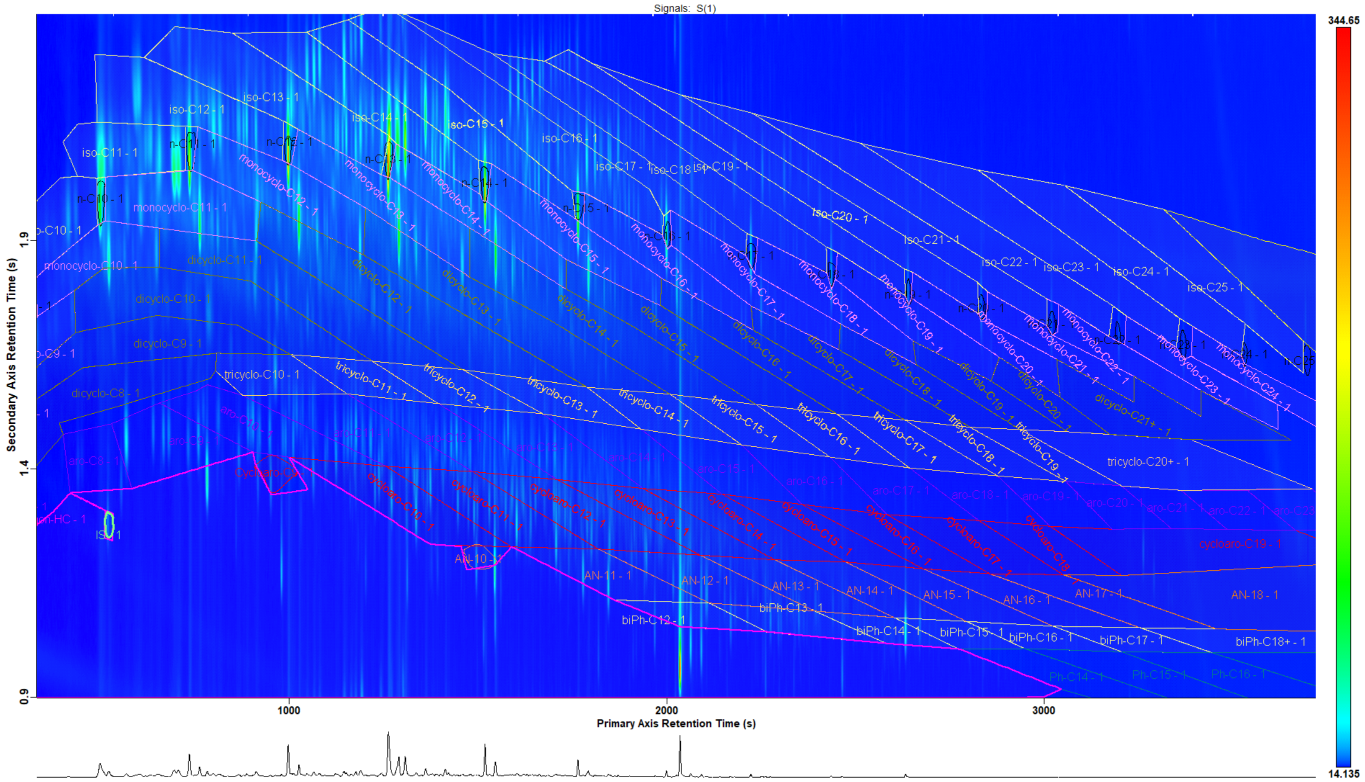

Figure 2. Contour plot of PE-derived pyrolysis fuel, with classification template overlaid showing the group-type structured nature of GCxGC chromatogram.

Figure 3 shows the contour plots of the fuel sample before and after derivatization, clearly indicating the change in sample composition. Because derivatization is a chemical technique that modifies certain functional groups within molecules, the volatility, thermal stability, and detectability of a targeted group of compounds can be changed. In this case, the iodine derivatization reveals previously masked olefin compounds. By altering their chemical structure, their chromatographic elution patterns are changed. The complexity of these plots presents a significant analytical challenge, as a direct comparison between the two chromatograms to identify changes induced by the derivatization process is an intricate and time-consuming task.

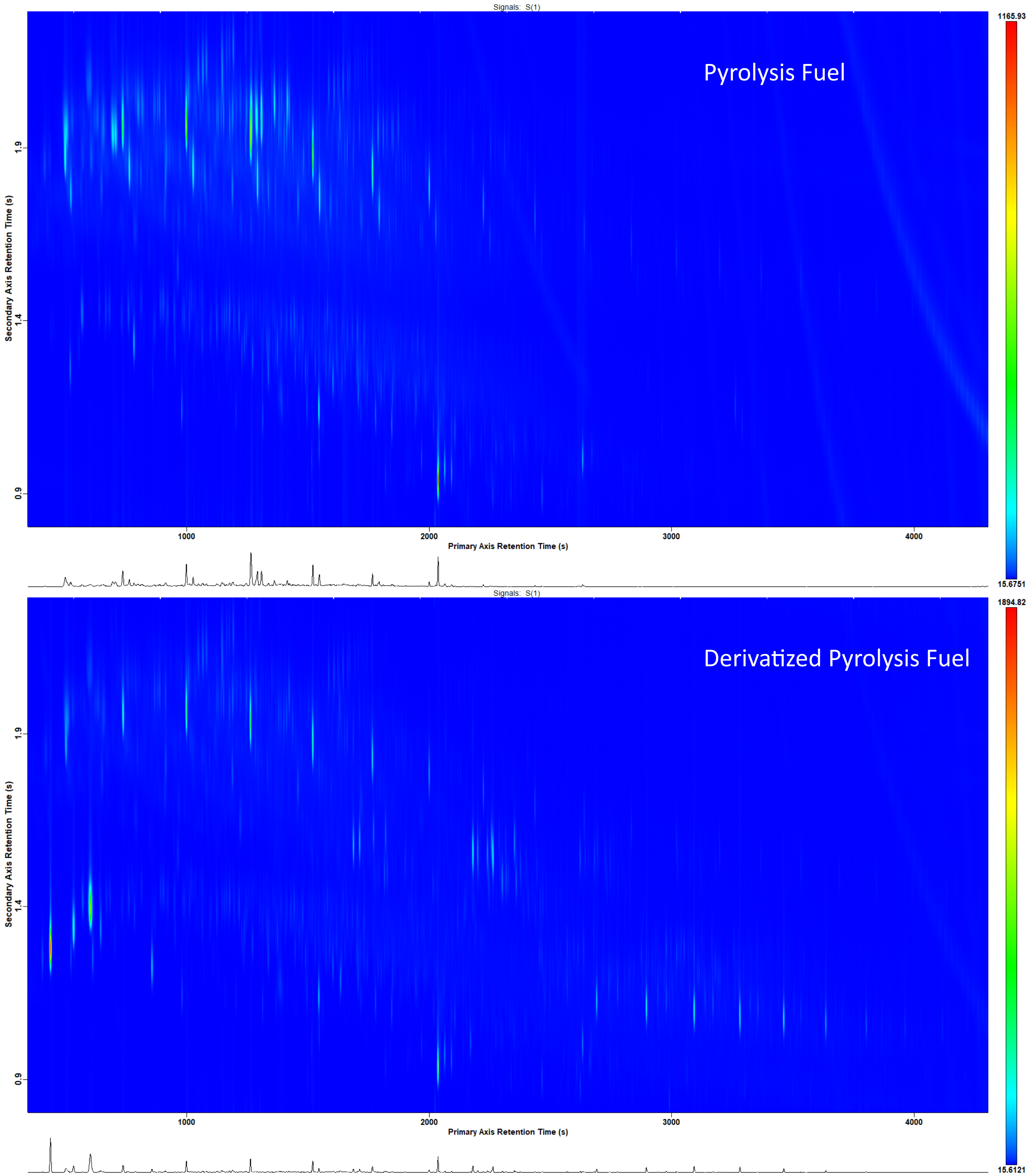

Figure 3. Top: Colored contour plot of waste polyethylene-foil-derived pyrolysis fuel, with reconstructed single-dimension GC trace in black. Bottom: Colored contour plot of waste polyethylene-foil-derived pyrolysis fuel after iodine derivatization process, with reconstructed single-dimension GC trace in black, showing the change in elution pattern indicative of olefin presence.

The introduction of *ChromaTOF* Tile software has revolutionized the process of comparing complex chromatograms, particularly in analyzing fuel samples such as the ones obtained from PE plastic waste shown in Figure 3. This advanced analytical tool has significantly enhanced the ability to detect and interpret subtle changes in chemical compositions, as demonstrated in Figure 4 through Figure 7.

Figure 4 presents a comprehensive comparison of two chromatograms representing this sample before and after derivatization. The upper chromatogram displays the underivatized fuel sample, while the lower chromatogram shows the same fuel after undergoing the derivatization process. This overlaid visualization allows for an immediate appreciation of the global changes induced by derivatization, demonstrating the ability to align chromatograms, use color-coding to highlight differences, offer overlay options, and automatically label peaks.

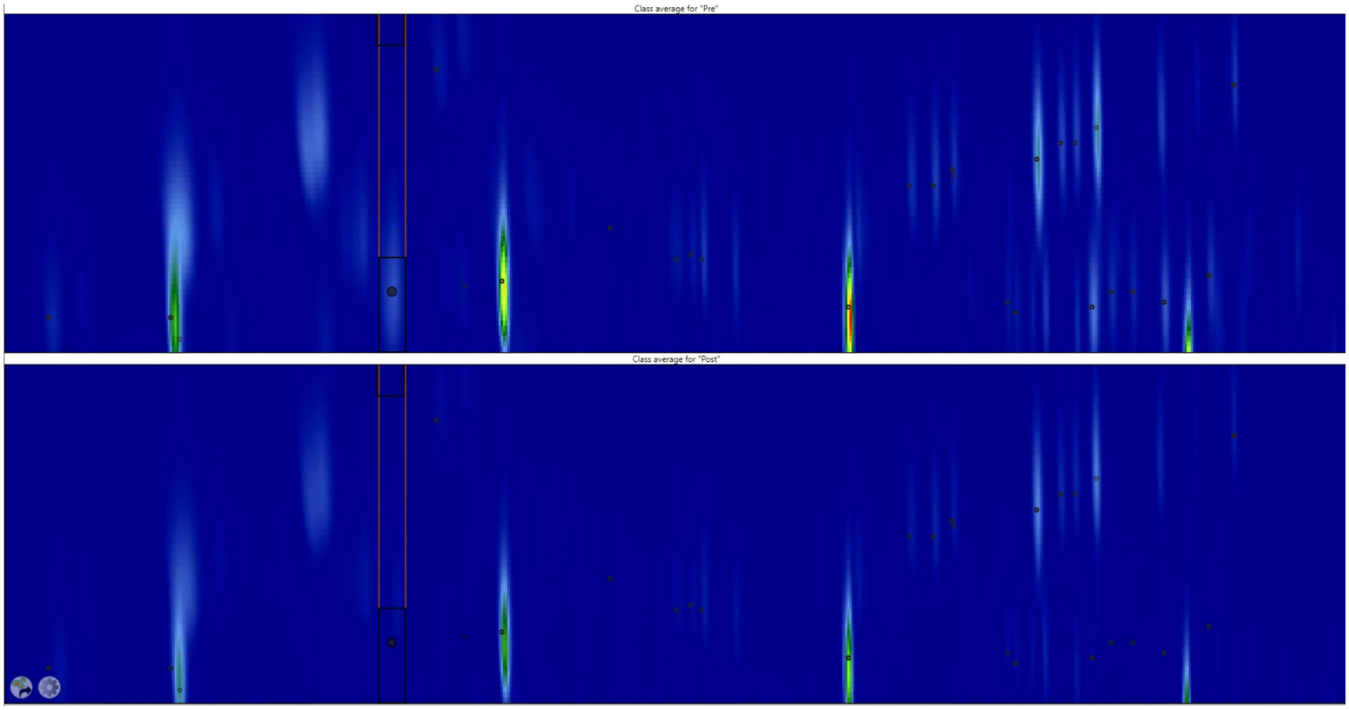

Figure 4. Comparative analysis view from ChromaTOF Tile of PE-derived pyrolysis fuel chromatograms highlighting original olefin elution region with distinct comparison of peak presence on top showing fuel pre-derivatization vs peak absence on bottom plot showing fuel post-derivatization.

Figure 5 showcases *ChromaTOF* Tile's zooming capability, allowing for enhanced resolution, detailed peak comparison, identification of new or disappeared peaks, and fine structure analysis. The software's power lies in its automated and sophisticated comparison abilities, including automated peak detection and integration, deconvolution of overlapping peaks, statistical analysis, machine learning algorithms for pattern recognition, diverse data visualization tools, and compound identification when coupled with mass spectrometry data. These features collectively enable efficient, accurate, and insightful analysis of complex fuel compositions and the effects of chemical modifications.

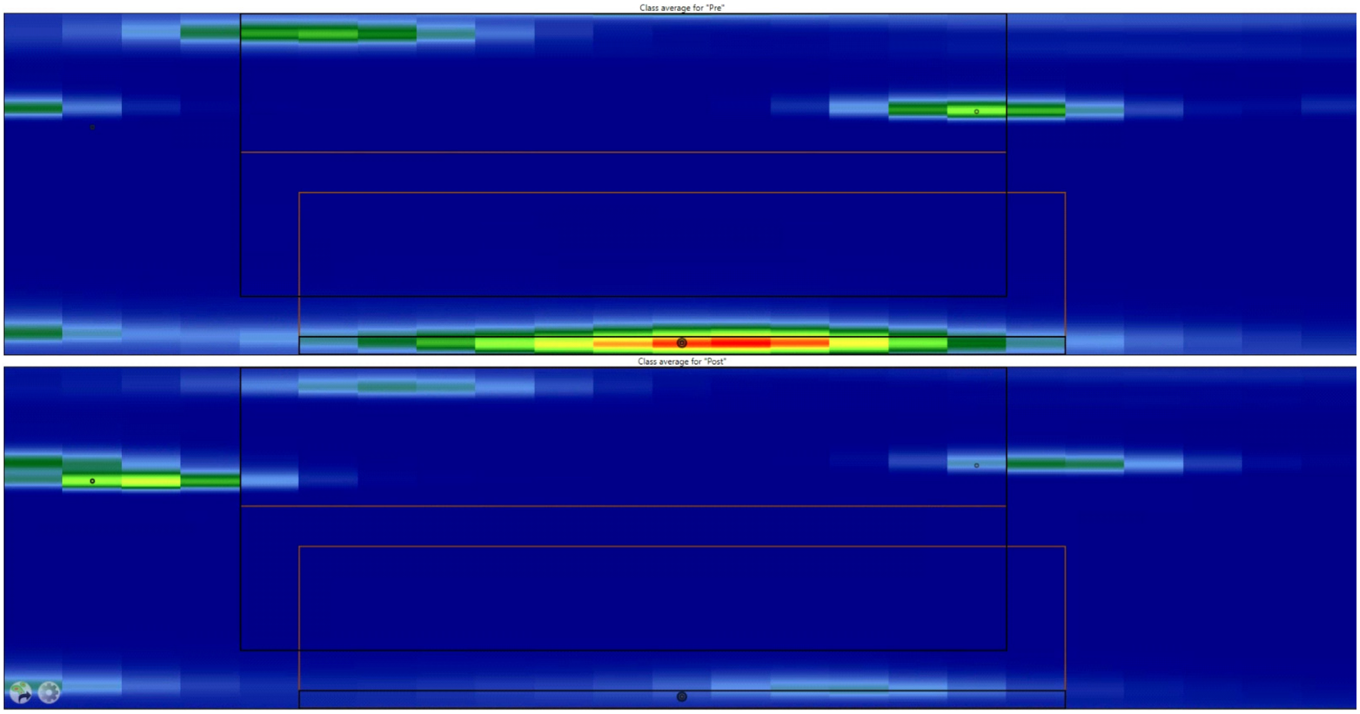

Figure 5. Zoomed-in comparative analysis view from ChromaTOF Tile of PE-derived pyrolysis fuel chromatograms highlighting original olefin elution region with distinct comparison of peak presence on top showing fuel pre-derivatization vs peak absence on bottom plot showing fuel post-derivatization.

While Figure 4 and Figure 5 showed the change from presence to absence, corresponding to the original olefin elution areas, Figure 6 and Figure 7 show how *ChromaTOF* Tile highlights the regions that changed from absence to presence, corresponding to the derivatized olefin elution areas.

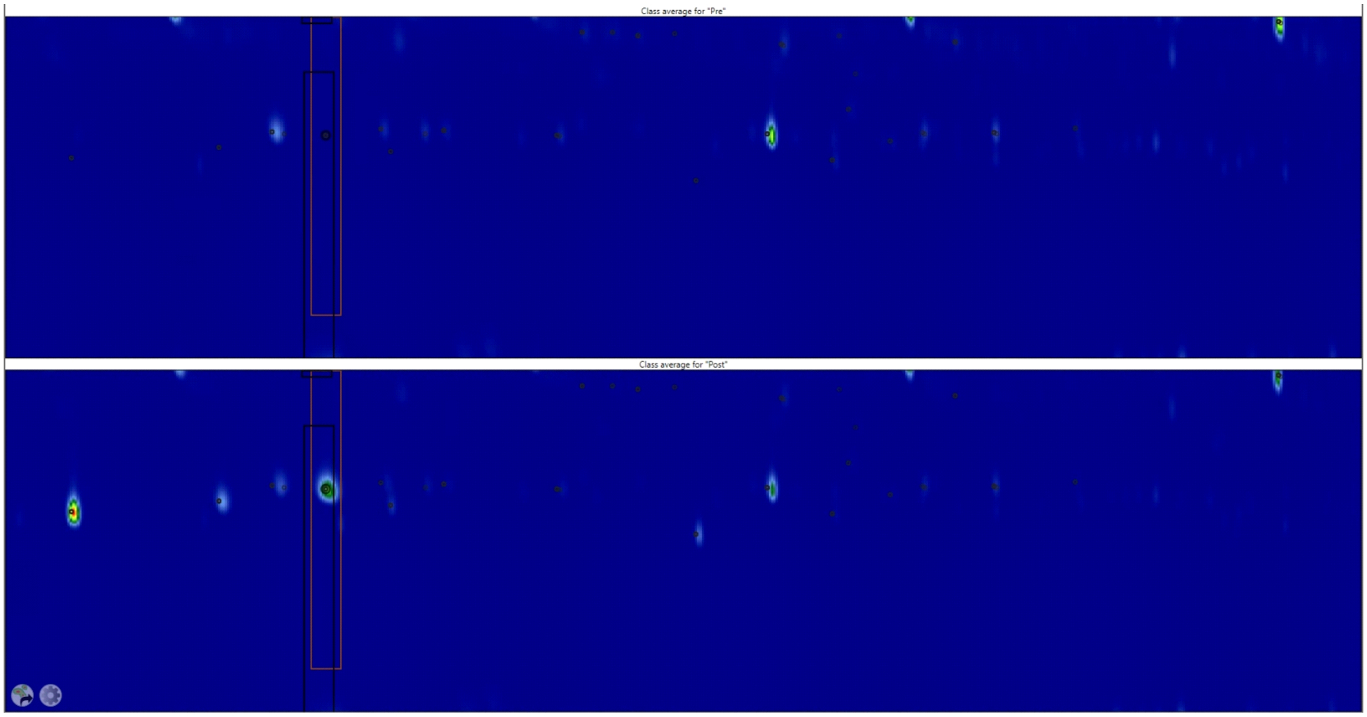

Figure 6. Comparative analysis view from ChromaTOF Tile of PE-derived pyrolysis fuel chromatograms highlighting derivatized olefin elution region with distinct comparison of peak absence on top showing fuel pre-derivatization vs peak presence on bottom plot showing fuel post-derivatization.

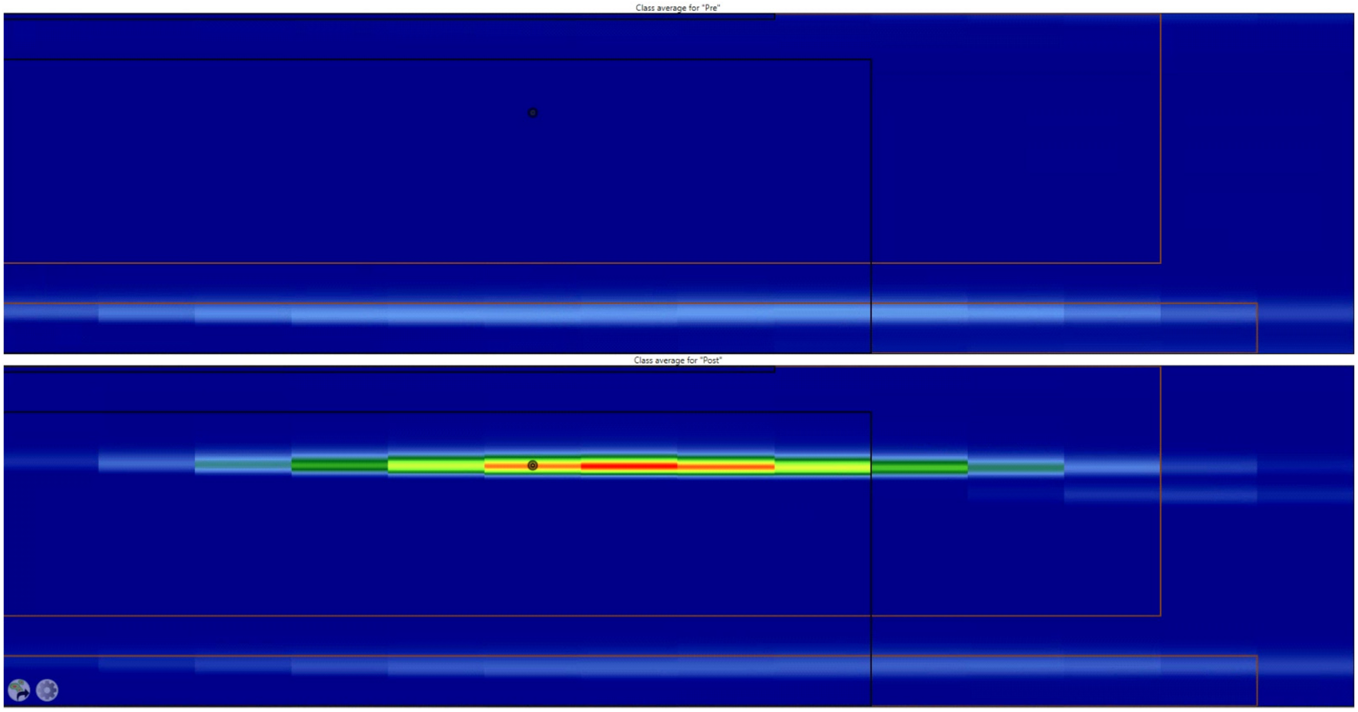

Figure 7. Zoomed-in comparative analysis view from ChromaTOF Tile of PE-derived pyrolysis fuel chromatograms highlighting derivatized olefin elution region with distinct comparison of peak absence on top showing fuel pre-derivatization vs peak presence on bottom plot showing fuel post-derivatization.

Applying the knowledge of where peaks shifted in this PE-foil-derived pyrolysis oil sample, the olefin content at the level of individual carbon numbers was calculated. For example, in the C9 region, the monocycloalkane peak area before derivatization was 6.41 wt%. Following derivatization and normalization, the peak area was reduced, and the real concentration of C9 monocycloalkanes was only 1.58 wt%. By calculating the difference in these peak areas, the olefin content for the C9 region was determined to be 4.84 wt%. This demonstrates the effectiveness of this method in not only quantifying the total olefin content, but also providing detailed, carbon-specific quantification, which is critical for a comprehensive understanding of the sample's hydrocarbon composition, as can be seen in Table 3.

Table 3. Peak area changes in monocycloalkane (MCA) region pre-and post-derivatization for fuel derived from polyethylene foil. The change in areas corresponds to olefin content. Peak areas were normalized and converted to weight percent (wt%) by carbon number and combined for total values.

Calculated Olefin Content in PE-Pyrolysis Fuel Oil					
Pre-Derivatization			**Post-Derivatization**		
MCA	MCA *peak area*	MCA *wt%*	MCA *(true) peak area*	MCA *calculated (wt%)*	*Olefins calculated (wt%)*
C5	52883.75	6.00	38374.69	3.57	2.43
C6	81707.23	9.27	65393.26	6.08	3.19
C7	86175.05	9.78	64515.59	6.00	3.78
C8	50744.41	5.76	50393.38	4.69	1.07
C9	56524.36	6.41	16947.64	1.58	4.84
C10	1839.73	0.21	553.02	0.05	0.16
Total	329874.53	37.44	236177.58	21.97	15.47

Conclusion

After simple, single-step derivatization, the increased chromatographic resolution provided by the LECO QuadJet GCxGC, in conjunction with powerful software tools provided by *ChromaTOF* and *ChromaTOF* Tile, creates automated workflows for more accurate, detailed quantitation of olefins in plastic-derived pyrolysis oils.

References

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