Quantifying Olefins in Alternative Fuels using ChromaTOF Tile Analytical Software and Two-Dimensional Gas Chromatography

A Thesis

Presented to

Tha Faculty of the Department of Chemistry and Biochemistry

California State University, Los Angeles

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

In

Chemistry

By

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December 2024

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ABSTRACT

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Over the last few decades, there has been a tremendous buildup of plastic garbage in landfills and the environment, amounting to over 6 billion tons. This study presents a novel method for characterizing and quantifying aliphatic olefins in gasoline-like fuels derived from plastic waste conversion. The approach utilizes comprehensive two-dimensional gas chromatography with a flame ionization detector (GC×GC-FID) in combination with a derivatization technique using DMDS and a series of olefin standards ranging from C_5 to C_{24}. A new method for the characterization and quantification of olefins in alternative and petroleum-based fuels by comprehensive two-dimensional gas chromatography (GC×GC) with the help of ChromaTOF Tile software will be developed. GC×GC coupled with a flame ionization detector (FID) is an instrumental platform that produces complex results. The pixel-based and peak tile-based Fisher ratio algorithms have effectively reduced multi-dimensional data by identifying chemical compounds that vary between sample classes while remaining constant in others. The tile-based Fisher-ratio algorithm significantly improves the sensitivity contrast of true positives against a background of potential false positives and noise. Samples obtained from the University of Chemistry and Technology, Prague, from the Czech Republic, and Purdue University were be analyzed before and after derivatization, and ChromaTOF Tile software will be used to process them.

ACKNOWLEDGE

I would like to express my sincere gratitude to my group member, Genesis, for their invaluable support throughout this project. I also extend my appreciation to CREST-CATSUS for their resources and funding. A special thanks goes to my PI, Dr. Vozka, for their mentorship and continued encouragement. Finally, I would like to acknowledge LECO for providing essential tools and support for the analytical work.

We extend our sincere gratitude to the members of the committee Dr. Petr Vozka; Dr. Yong Ba; Dr. Olaseni Sode; Dr. Liz Humston-Fulmer for their invaluable guidance, constructive feedback, and unwavering support throughout this endeavor. Your expertise, dedication, and insightful contributions have been instrumental in shaping this work and ensuring its success. Thank you for your time, effort, and commitment to excellence, which have left a lasting impact on this project and our professional growth.

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CHAPTER 1

Introduction

1.1 Plastic Waste and Plactic Waste Conversion Processes

The ubiquity and affordability of plastic products have led to a substantial increase in their daily usage. Globally, more than 380 million tons of plastic are produced annually, with polyolefins accounting for 57% of this production. However, the accumulation of plastic waste has reached critical levels, with around 6 billion tons disposed of in landfills and oceans.[1] Of this waste, only 9% is recycled, and 12% is incinerated. Polyolefins, including polyethylene (PE) and polypropylene (PP), are the most common types of plastic waste, representing 63% of landfill plastic waste. Their widespread production—over 178 million tons in 2015 alone—is driven by their low cost and reduced toxicity.[2]

To address this growing issue, methods like pyrolysis and hydrothermal processing are increasingly employed to convert polyolefin waste into oils with fuel-like properties. Pyrolysis involves breaking down plastic waste into oil by heating it to high temperatures in the absence of oxygen. This process produces oil with properties similar to conventional fuels by breaking long-chain hydrocarbons into smaller ones. Hydrothermal processing, on the other hand, heats aqueous slurries of organic waste under high pressure, simulating the natural fossil fuel formation process. This technique accelerates the conversion of plastic waste into renewable fossil fuel alternatives.

Recent advances have demonstrated the effectiveness of these methods. For instance, Jin et al. successfully converted polyolefin waste into clean fuels with high yields (87%) and minimal char content (0.5%) using a low-pressure hydrothermal processing (LP-HTP) technique. Similarly, researchers from the University of Chemistry and Technology in Prague and Purdue University

employed pyrolysis and LP-HTP to transform plastic waste into alternative fuels. These conversion products were analyzed using comprehensive two-dimensional gas chromatography (GC×GC) to quantify olefin content.

Thermochemical processes, such as pyrolysis and thermal cracking, depolymerize polyolefins by breaking strong C–C bonds, resulting in smaller molecules suitable for fuels or chemical feedstocks. This bond cleavage generates reactive free radicals, and during beta scission, two carbon atoms are removed from the polymer chain, producing olefins. Notably, a critical distinction between petroleum-based fuels and these alternatives is their higher olefin content, which enhances their potential for use in various industrial applications.

1.2 Physical Properties of Olefins

Olefins, commonly known as alkenes, are unsaturated hydrocarbons characterized by at least one carbon-to-carbon double bond. Depending on their molecular structure, alkenes can exist as gases, liquids, or solids at room temperature, and their boiling points are similar to those of alkanes. The double bonds in alkenes create 120° bond angles at the involved carbon atoms, while other carbons maintain a bond angle of 109.5°[3]. This geometric arrangement prevents alkenes from packing tightly together, which weakens their London dispersion forces compared to alkanes, resulting in slightly lower melting and boiling points.

Ethene, propene, and butene are colorless gases at room temperature. Alkenes with carbon chains between C5 and C15 are typically liquids, while those with more than 15 carbon atoms per molecule are solids. Due to their non-polar nature, alkenes are less dense than water and are insoluble in polar solvents but soluble in non-polar ones. The boiling points of alkenes increase with molecular mass, as longer carbon chains enhance intermolecular forces and raise boiling points.

1.3 Geochemical Applications and Industrial Significance

The presence of unsaturated aliphatic hydrocarbons, or olefins, is a common occurrence in numerous crude oils and condensates. Despite this, few researchers have investigated the potential utility of olefins as tools for resolving geochemical problems.[4] Olefins, the most reactive hydrocarbon component of gasoline, play a significant role in gum creation, even though the exact mechanism(s) for gum formation are not fully understood. Free radical chain reactions, initiated by peroxide radical addition to the double bond(s), ultimately lead to a variety of methods of gum production. Therefore, analytical techniques are required to ascertain the olefin concentration of gasoline, harm with production and quality control. Although a high olefin content may be harmful to engine cleanliness, as olefins can build up and create deposits in fuel systems, the distribution and concentration of olefins in oils are rarely studied.[5] Despite olefin concentrations ranging from a few parts per million in gasoline and diesel to tenths of a percent by weight in the pyrolysis of plastic waste, they are anticipated to be produced at a rate of 400 million tons per year using methods such as fluid catalytic cracking, steam creaking, and dehydrogenation.[5] Olefins are not found in natural petroleum; thus, their importance iprocessing petroleum is increased given that the quantity and type of olefins depend on those conditions.[6] As a result, analyzing ranging from gases to heavy fractions has become critical for industries that rely on hydrocarbons.[6]

1.4 Importance of olefin quantification in fuels

Olefins are measured in cracked petroleum fractions and related streams using chemical and physical methods. Chemical methods rely on the relatively high chemical reactivity (C=C) of the ethylenic bond brought on by the presence of labile pi-electrons. For hydrotreated pyrolysis bio-oils, Auersvald et al. used GC-MS analysis and bromine number titration (e.g., ASTM D1159).[6] The resolution of one-dimensional GC may be inadequate for comprehensive and accurate

measurement of even the volatile fraction.[7] The main analytical challenge is quantifying different olefin types. This complicates quantification when dealing with complicated samples.[8] Dimethyl disulfide (DMDS) and iodine (I_2) solution was employed in a derivatization method that Carlson et al. described to derivatize olefins in a sample.[9]

The investigation of complex alternative fuel samples led to the development of a olefin characterization and quantification technique. Comprehensive two-dimensional gas chromatography (GCxGC) was used because of its higher separation capability, which makes it simpler to analyze complex samples.

1.5 Gas Chromatography and Comprehensive Two-Dimensional Gas Chromatography

Gas chromatography (GC) works by exploiting the different affinities of vaporized compounds for various surfaces.[10] In this technique, an inert carrier gas transports a sample mixture through a column. As the sample moves through the column, individual compounds interact with the column's stationary phase to varying degrees, causing some to move slower than others. A detector generates a signal for each compound as it exits the column, with the signal strength corresponding to the amount of that compound present. Typically, compounds with lower boiling points travel through the column faster, resulting in shorter retention times. However, since retention time alone is not unique to a specific compound, it can be challenging to differentiate between components in complex mixtures, such as fuels.[11]

Comprehensive Two-Dimensional Gas Chromatography (GC×GC) enhances separation by using two columns with different phase selectivities, connected by a modulator. This approach offers several advantages: improved separation, increased sensitivity, structured chromatograms, more reliable compound identification, less sample preparation, and better resolution and peak capacity.[10,2] The thermal modulator divides the flow from the primary column into smaller sections

for further analysis. The dual-state quad jet trapping system uses cryogenic cooling and heating jets in two zones to focus the analytes, cooling them with liquid nitrogen (LN2) before re-vaporizing them for further separation in the secondary column. The process involves alternating between cold jets to trap and focus analytes. The hot jets release previously trapped compounds into the secondary column for further separation based on a different stationary phase.

The selectivity of the stationary phase in GC is critical since the retention of compounds depends on their interactions with the column. Non-polar columns primarily separate compounds by boiling point, while polar columns separate them based on polarity. For optimal separation, It's important to use orthogonal columns for optimal separation, meaning the columns have opposite polarity. In GC×GC, orthogonality is achieved by pairing columns with different stationary phases—for example, a non-polar first column followed by a polar second column (normal-phase configuration). Alternatively, in a reversed-phase setup, a polar first column is followed by a non-polar second column, allowing for greater separation of compounds based on their polarity and boiling points.

1.6 Introduction to ChromaTOF Tile software

ChromaTOF Tile software provides an industry-first data comparison tool that identifies statistically significant differences between classes of samples, reducing days-to-weeks of work down to hours or even minutes [12]. ChromaTOF Tile applies a retention window tile grid across every data set and then compares the Fischer ratios of every mass of each tile for every sample. ChromaTOF Tile applies a retention window tile grid across every data set and then compares the Fischer ratios of every mass of each tile for every sample (also called tile-based F-ratio analysis). This software also understands how GCxGC chromatograms work to accommodate normal retention time variation by using an appropriate tile size and checks for redundant hits between

tiles. The comparative analysis uses tile-based F-ratio analysis to identify the differences between the gasoline before and after derivation [12].

The tile-based F-ratio software processes GC×GC pixel-level data by summing it into a 2D grid of tiles, effectively reducing data complexity in the 2D time domain. Four 2D grids of tiles are applied to optimally capture each peak, allowing for a comparison between pre- and post-derivatization samples to track the movement of olefins. A major challenge in non-targeted chemometric methods for 2D separations is the misalignment of chromatographic peaks between sample runs. To address this, a novel algorithmic approach was developed that combines the efficiency of a tile-based, peak-focused method with the precision of pixel-based approaches. This tile-based F-ratio software not only ensures effective data reduction and robust chemical pattern detection but also mitigates the impact of peak misalignment.

CHAPTER 2

Method

2.1 Sample Preparation

Pyrolysis oil sample made from waste tires in the gasoline distillation range were analyzed using thermally modulated comprehensive two-dimensional gas chromatography coupled with a flame ionization detection (GCxGC-FID), LECO's QuadJet. Two sample preparation methods were employed: (1) dilution with pentane at a 1:50 ratio and (2) derivatization with DMDS and iodine solution.

Fuel samples (13.2-17.9 mg) in n-pentane (200 µL) were treated with 1.2 mL of neat dimethyl disulfide (DMDS) (Sigma Aldrich, St. Louis, MO) and 0.3 mL of iodine solution (60 mg of iodine in 1 mL of diethyl ether) in a 2 mL GC vial. Reaction mixtures were held for at least 1 hour at 70 ℃ and then cooled to room temperature. 200 µL of 10% sodium thiosulfate solution was added to the vial and vortexed until color disappeared. After derivatization, the organic phase containing DMDS and the sample was transferred to a GC vial.

2.2 Instrument Preparation

The He and H_2 gas tanks and the low- and high-pressure liquid nitrogen dewars were turned on. GC×GC ChromaTOF SD software was opened on the desktop and the methods for the experiment were selected. The GC vial filled with the sample was then loaded into the autosampler. The sequence was selected, and our sample was named along with the vial location, repetitions, AS method, Chromatographic method, and DP method. The sequence was run, prompting the instrument for data collection for the chromatogram. Once finished, the chromatogram and peak data were displayed and automatically saved.

2.3 Gas Chromatography setting

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 (figure 1) were developed by combining different analytes identified in individual samples, enabling a comprehensive characterization of the aviation fuel compositions.

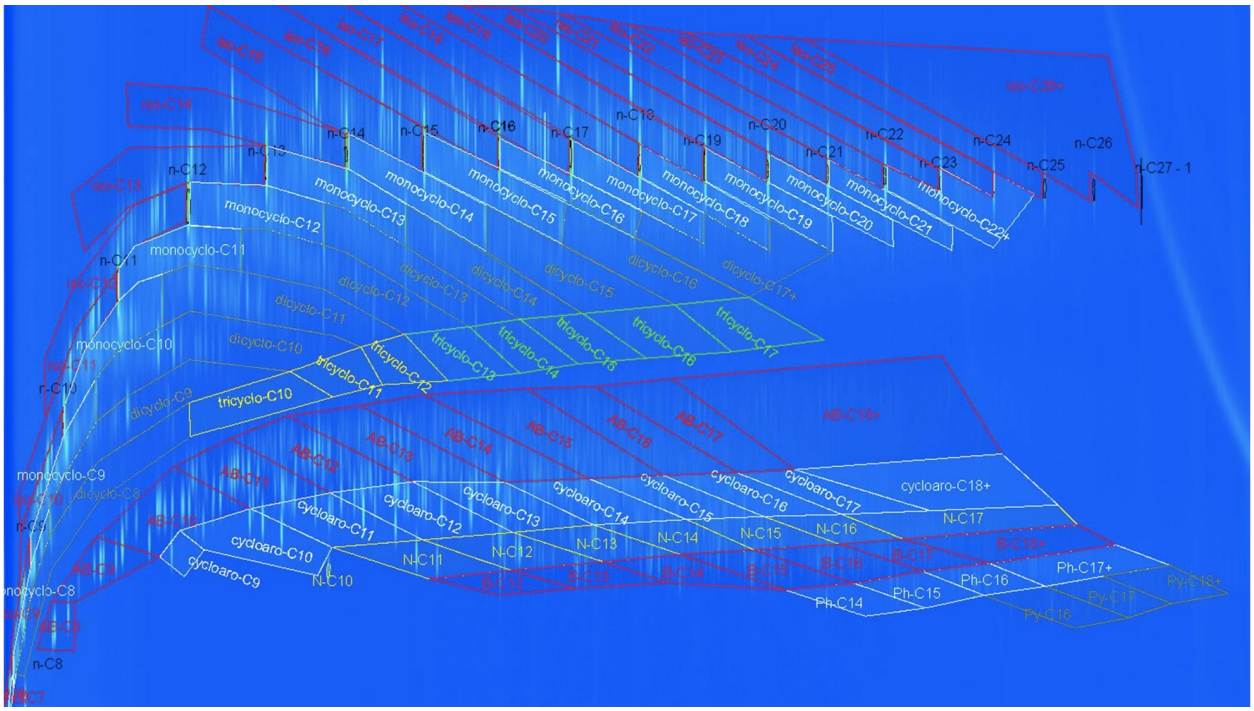


Figure 1. Model classification of hydrocarbons.

Reprinted from How to obtain a detailed chemical composition for middle distillates via GC×GC-FID without the need of GC×GC-TOF.MS , *Fuel Vol 247, Petr Vozka, Gozdem Kilaz, Pages 368-377, (2019), with permission from Elsevier.*

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
Modulation Period	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

2.4 ChromaTOF Tile setting

Each of the two samples 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 the example in Table 2.

Table 2. ChromaTOF Tile setting.

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

The values in Table 1 remain unchanged, but we adjust the S/N threshold to 10 and modify the signal-to-base thresholds for D1 and D2 to 4 and 2 for analyis 2,4-dimethyl-1-decene, 1-Hexadecene, and 1-octadecene in fuel containing no alkenes.

The previously discussed derivatization technique using DMDS and an I_2 solution was used. Olefin standards ranging from C_6-C_{24} were analyzed to determine their elution locations. A standard mixture containing a homologous series of n-alkanes, 1-alkenes (-mono-olefins), monoaromatic compounds, and naphthalene derivatized using the DMDS method (insert citation). The procedure for detecting the olefins in the gasoline sample involves utilizing iodine as a catalyst to attach a thiomethyl group to the sample. Next, using tile-based F-ratio analysis, the method was applied to profiling olefins in a gasoline sample. The 1-alkenes and a group of C_5 olefins were the products of this procedure, producing retention data and a library of mass spectra. Several olefins in the original gasoline sample were identified by comparing the retention data and mass spectra obtained from the sample with the library's retention data and mass spectra. Because it enables specific retention times and mass spectra to be associated with individual olefins, making it simpler to separate them from other chemicals in the mixture, this approach is effective for identifying olefins in complex mixes like gasoline.

This method involves attaching a thiomethyl group to a sample using iodine as a catalyst to facilitate the identification of olefins in gasoline. The resulting sample, with the thiomethyl group attached, is then compared to the original sample, making it easier to detect the presence of olefins. In theory, one should be able to find both the places where the products "emerge" and the places where olefins "disappear." However, the sample attaching a thiomethyl group will elute in a less crowded region of the 2D chromatographic space due to the elution properties of the GC–GC

column set used, and their discovery by tile-based F-ratio analysis will be simpler than that of the original olefins that coelute with other constituents in the gasoline.

Areversed-phase column configuration was employed, where compounds first underwent separation by polarity in the primary column. As the temperature increased, the compounds were further separated by boiling point in the secondary column, enhancing the distinction between different types of hydrocarbons, such as alkanes, cycloalkanes, and aromatics. This configuration improved the peak capacity, allowing for a more detailed analysis of the sample.

The tile-based F-ratio software processes GC×GC pixel-level data by summing it into a 2D grid of tiles, effectively reducing data complexity in the 2D time domain. Four 2D grids of tiles are applied to optimally capture each peak, allowing for a comparison between pre- and post-derivatization samples to track the movement of olefins. A major challenge in non-targeted chemometric methods for 2D separations is the misalignment of chromatographic peaks between sample runs. To address this, a novel algorithmic approach was developed that combines the efficiency of a tile-based, peak-focused method with the precision of pixel-based approaches. This tile-based F-ratio software not only ensures effective data reduction and robust chemical pattern detection but also mitigates the impact of peak misalignment.

CHAPTER 3

Result

3.1 Derivatization method developed

To assess and quantify olefin content in fuel samples, a specialized standard mixture, referred to as the "supermixture," was prepared. This supermixture was added to a base fuel, designated as "Fuel Zero," which was specifically chosen for its negligible olefin content. The near absence of olefins in Fuel Zero is a result of its hydrogenation-based production process, which effectively saturates olefins. While trace amounts of olefins might theoretically persist, complementary validation techniques confirmed the absence of detectable olefins.

Using the prepared samples, the newly developed analytical method was employed to quantify olefin content via Flame Ionization Detection (FID). Figure 2 illustrates representative chromatograms of the 50% Fuel Zero + supermixture sample, both before and after derivatization.

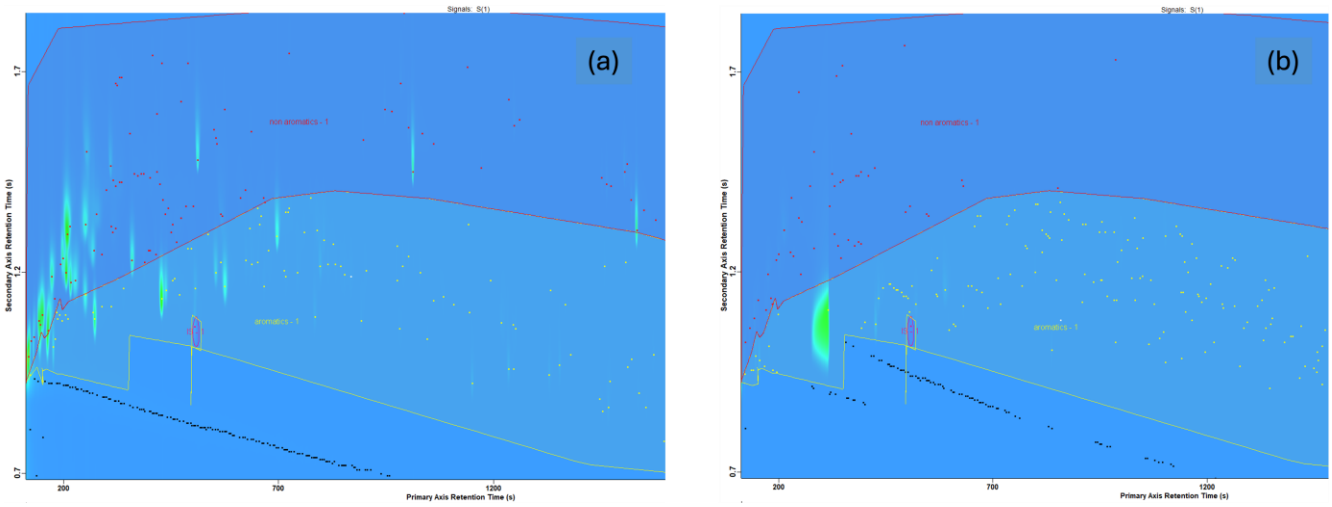


Figure 2. Non-aromatic and aromatic regions of 50% Fuel Zero + Supermixture pre- (A) and post-derivatization (B).

3.2 ChromaTOF Tile software

3.2.1 2,4-Dimethyl-1-decene

We conducted a straightforward experiment using 2,4-Dimethyl-1-decene as the test compound. The results Figure 3, demonstrate a clear shift in the peak corresponding to 2,4-Dimethyl-1-decene, marked by the blue arrow, after undergoing the derivatization reaction. This shift suggests a significant alteration in the chemical properties and structure of the compound post-reaction. Furthermore, the red arrow points to the emergence of a new peak, which likely represents a derivative formed during the process.

Figures 3 and 4 provide a more granular view of these results. The zoomed-in sections of the peaks offer greater clarity, allowing for a more refined comparison of the pre- and post-derivatization states. This closer inspection helps to more accurately identify the changes in the chromatographic profile, including the appearance of the new peak. By enhancing the resolution and focusing on specific regions of the chromatogram, these figures make the derivatization process easier to understand and visually interpret.

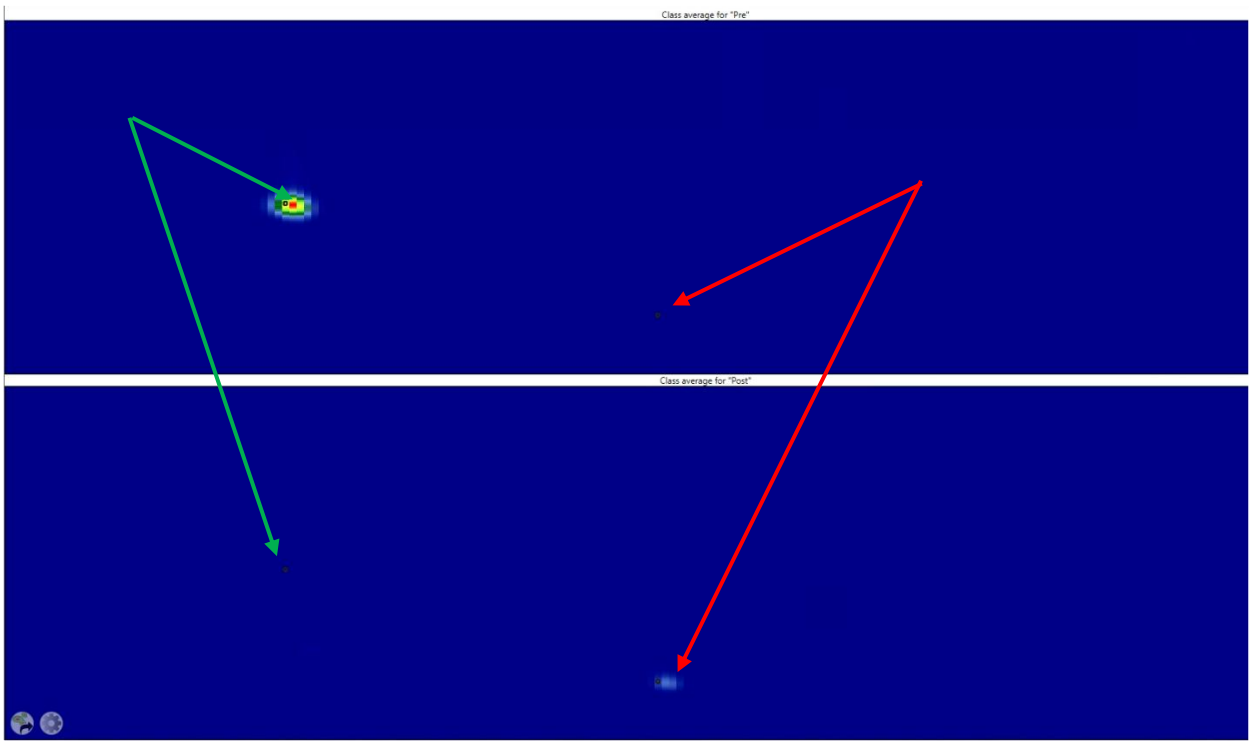


Figure 3. Comparative analysis of 2,4-dimethyl-1-decene Chromatograms on ChromaTOF Tile: pre-derivatization (Top) vs. post-derivatization (Bottom).

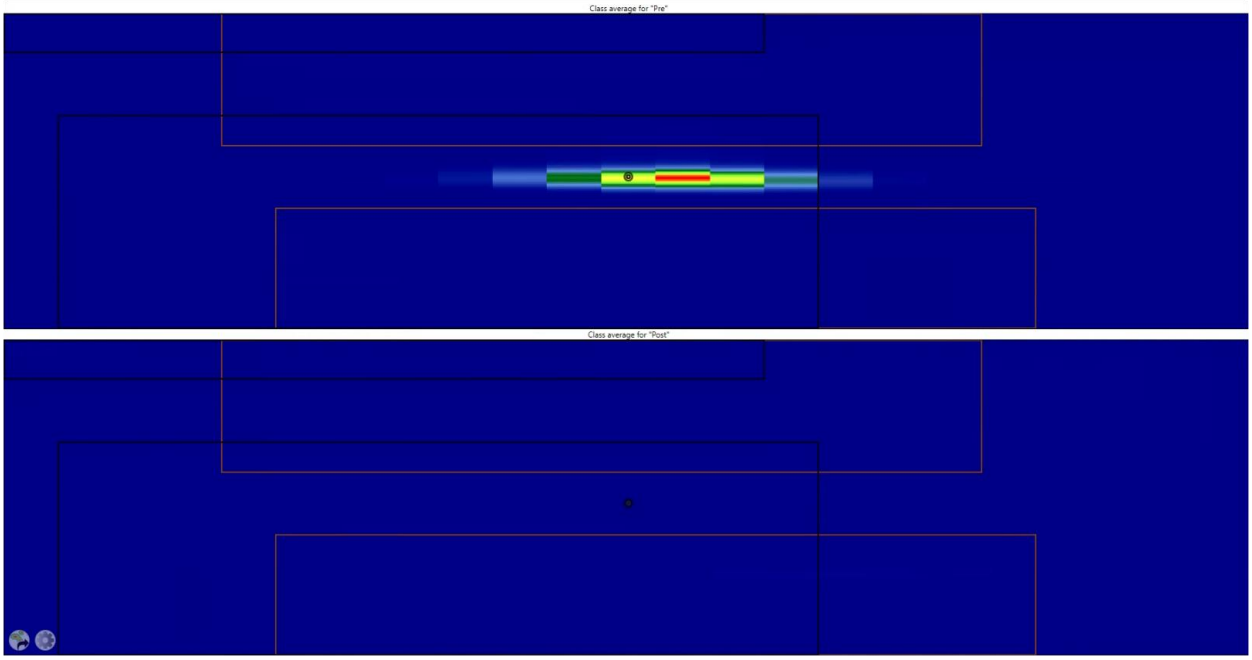


Figure 4. Zoomed-in comparative analysis of 2,4-dimethyl-1-decene Chromatograms green narrow: pre-derivatization (top) showing distinct peak vs. post-derivatization (bottom) exhibiting peak absence.

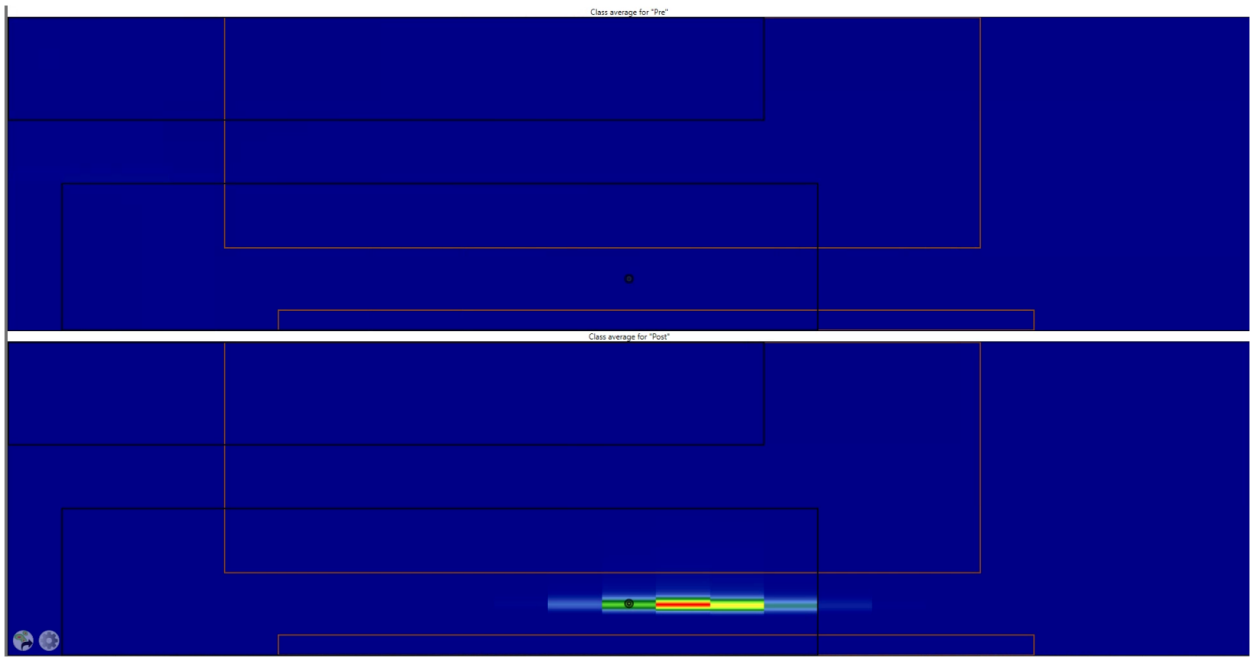


Figure 5. Zoomed-in comparative analysis of 2,4-dimethyl-1-decene Chromatograms red narrow: pre-derivatization (top) with no peak and bottom with peak appeal.

3.2.2 Detectiton of 1-Hexadecene and 1-Octadecene in Zero-Fuel Samples without Alkenes.

Figure 6 illustrates the presence of 1-Hexadecene and 1-Octadecene in Fuel Zero prior to the derivatization process. In contrast, Figure 7 shows the chromatographic profile of the same sample after derivatization. At first glance, it can be challenging to determine which peaks have disappeared and which new peaks have emerged following the reaction. Without advanced analytical tools, the subtle changes might go unnoticed.

However, by leveraging the capabilities of ChromaTOF Tile, we gain a much clearer understanding of the changes in the chromatogram. As demonstrated in Figure 8, ChromaTOF Tile has accurately identified that the peaks corresponding to 1-Hexadecene and 1-Octadecene have completely disappeared after the reaction, confirming that these compounds are no longer present in the derivatized sample.

To investigate these changes further, we zoomed in on the region where the 1-Hexadecene peak was originally located. As shown in Figures 9 and 10, a new peak has emerged in close proximity to where 1-Hexadecene was previously detected. Despite this complexity, ChromaTOF Tile's advanced peak comparison tools could able to accurately differentiate between the original peak that disappeared and the new peak that appeared post-reaction.

This ability to zoom in and resolve fine details in the chromatogram is essential for tracking subtle chemical transformations. Without such tools, distinguishing between overlapping or closely spaced peaks, especially in complex mixtures, would be extremely difficult. The clear visualization provided by Figures 9 and 10 demonstrates ChromaTOF Tile's robustness in distinguishing and comparing peaks, even in cases where the chromatographic changes are minimal or obscured by the presence of other compounds.

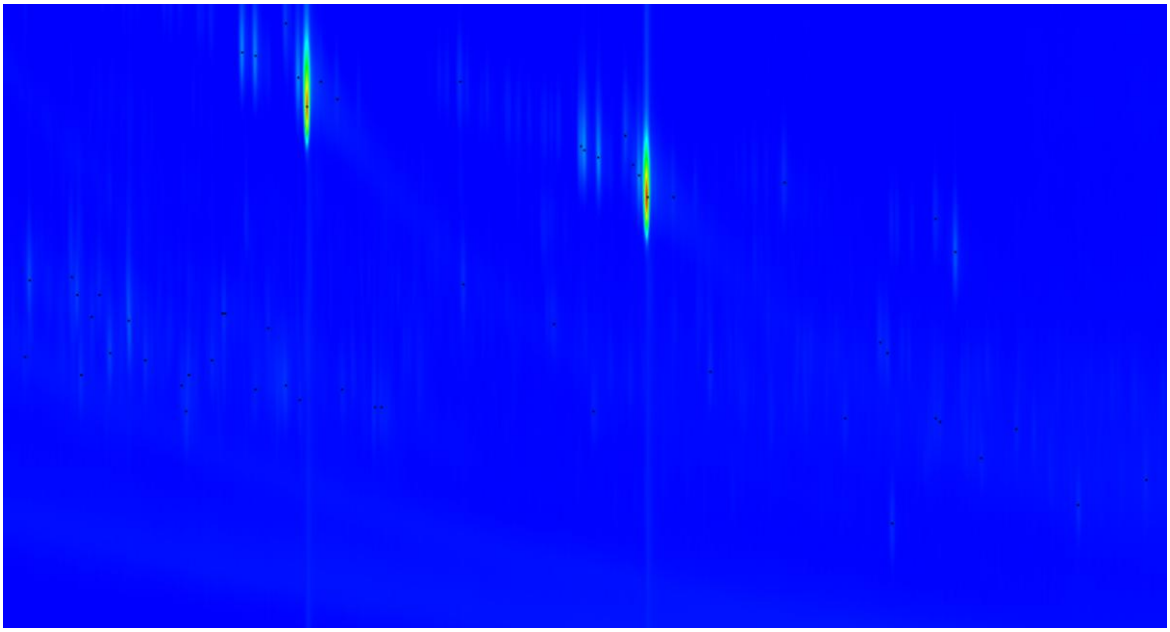


Figure 6. Chromatogram of zero fuel with 1-hexadecene and 1-octadecene before derivation.

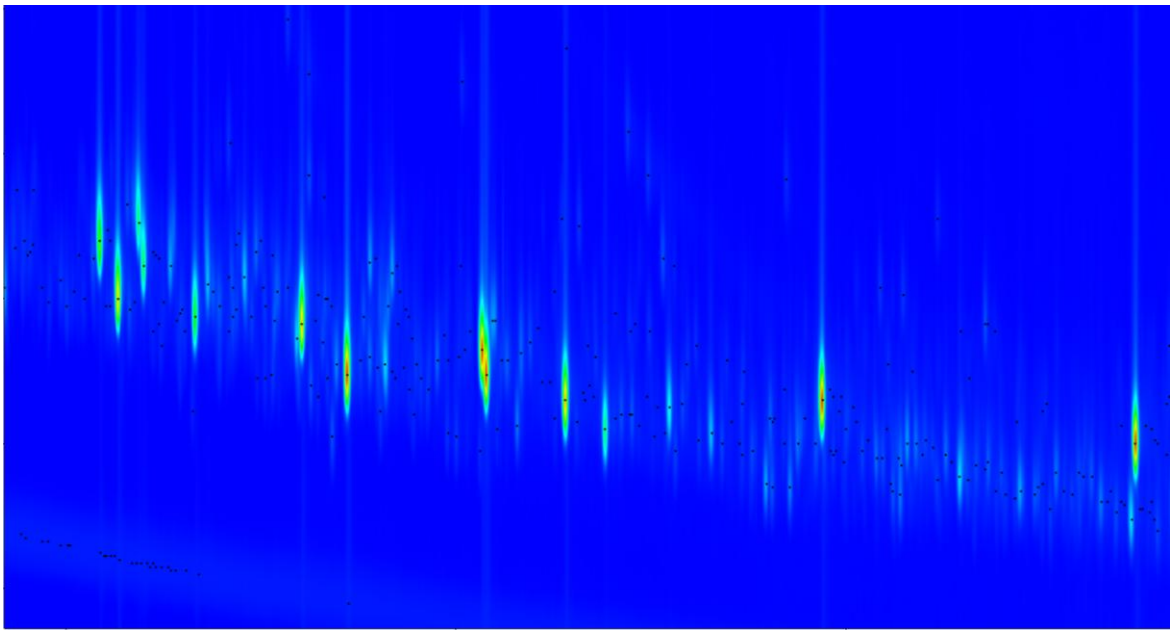


Figure 7. Chromatogram of zero fuel with 1-hexadecene and 1-octadecene after derivation.

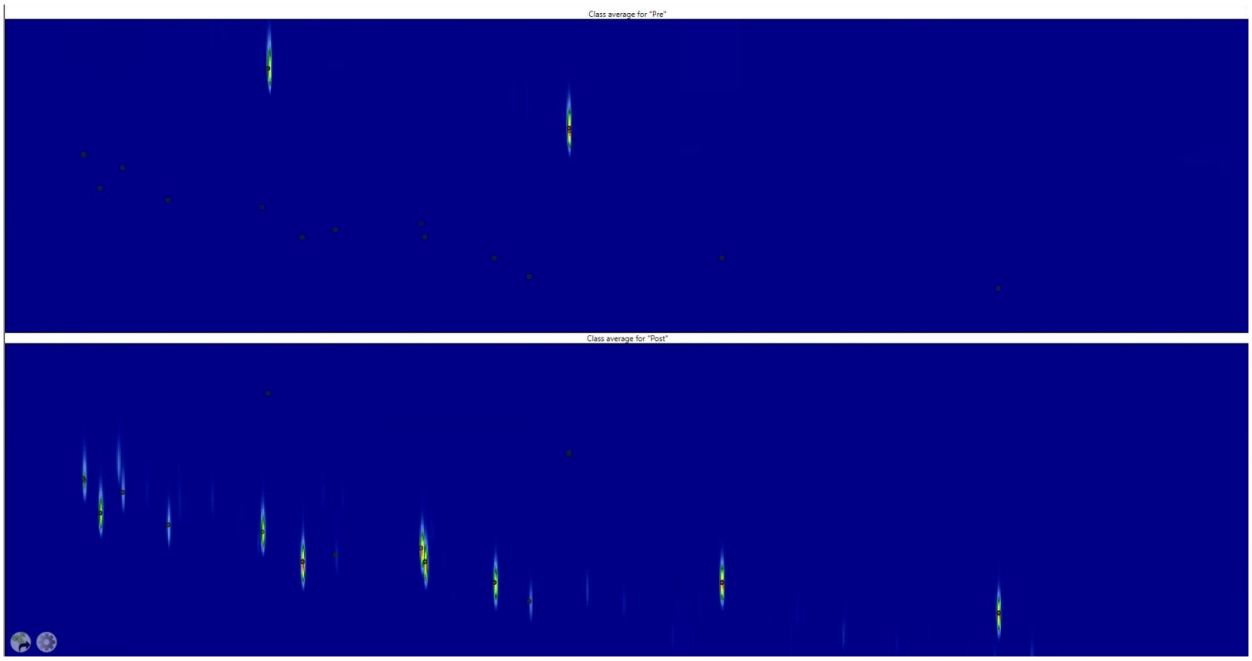


Figure 8. Comparative analysis of zero fuel with 1-hexadecene and 1-octadecene chromatograms in chromatof tile: pre-derivatization (top) showing distinct peak vs. post-derivatization (bottom) exhibiting peak absence.

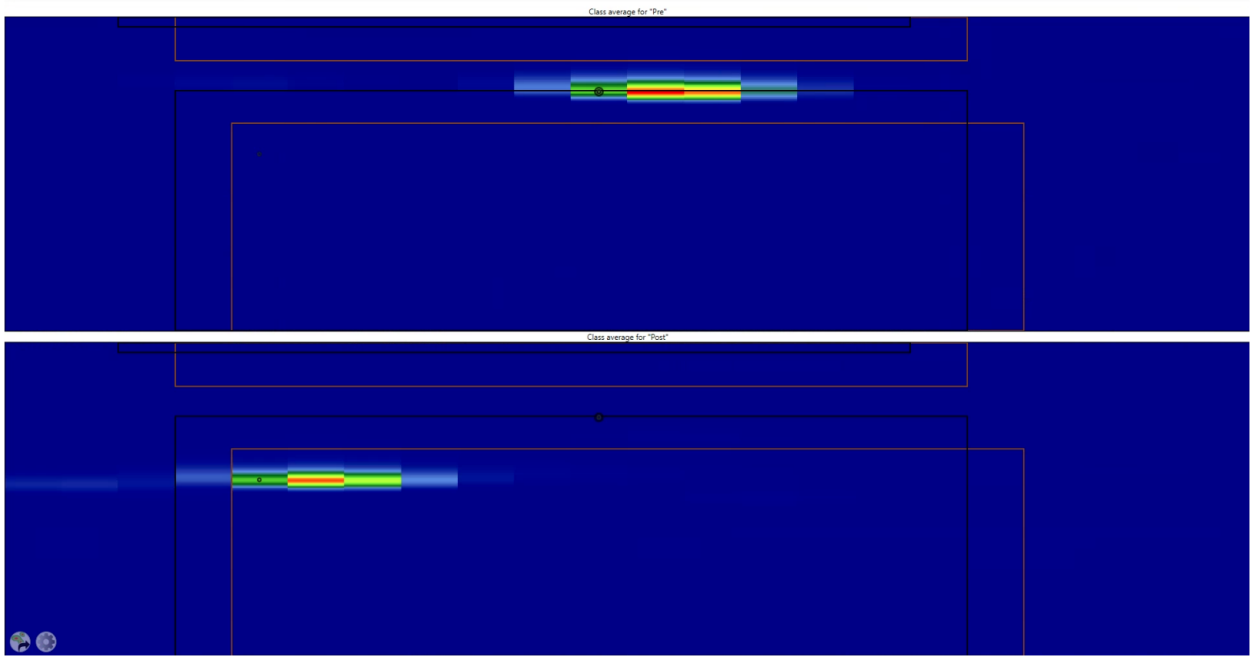


Figure 9. Zoomed-in comparative analysis of 1-hexadecene chromatograms: pre-derivatization (top) showing distinct peak vs. post-derivatization (bottom) exhibiting peak absence.

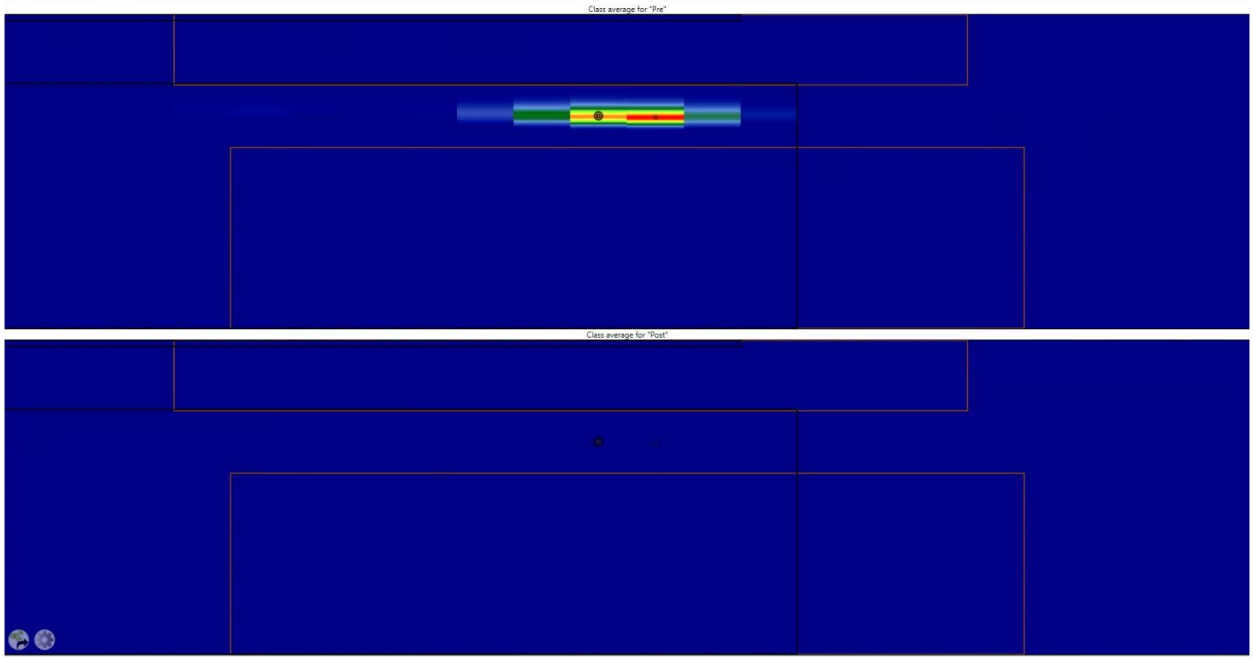


Figure 10. Zoomed-in comparative analysis of 1-octadecene chromatograms: pre-derivatization (top) showing distinct peak vs. post-derivatization (bottom) exhibiting peak absence.

3.2.3 Compared Folie PE fuel before and after derivatization

Figures 11 and 12 present the chromatograms of Folie PE fuel before and after derivatization, respectively. These chromatograms provide a wealth of information about the fuel's chemical composition, as evidenced by the numerous peaks visible in both figures.

Figure 11 displays the chromatogram of the underivatized Folie PE fuel, showcasing its inherent chemical profile. The multitude of peaks represents various compounds present in the fuel, including hydrocarbons, oxygenates, and potential trace contaminants. Each peak corresponds to a specific molecule or group of structurally similar molecules, eluting from the chromatographic column at different retention times based on their physical and chemical properties.

In contrast, Figure 12 illustrates the chromatogram of the same Folie PE fuel sample after undergoing a derivatization process. The complexity of these chromatograms is immediately apparent, with each figure containing a myriad of peaks varying in height, width, and retention time. This complexity presents a significant analytical challenge. A direct comparison between the two chromatograms to identify changes induced by the derivatization process is an intricate and time-consuming task.

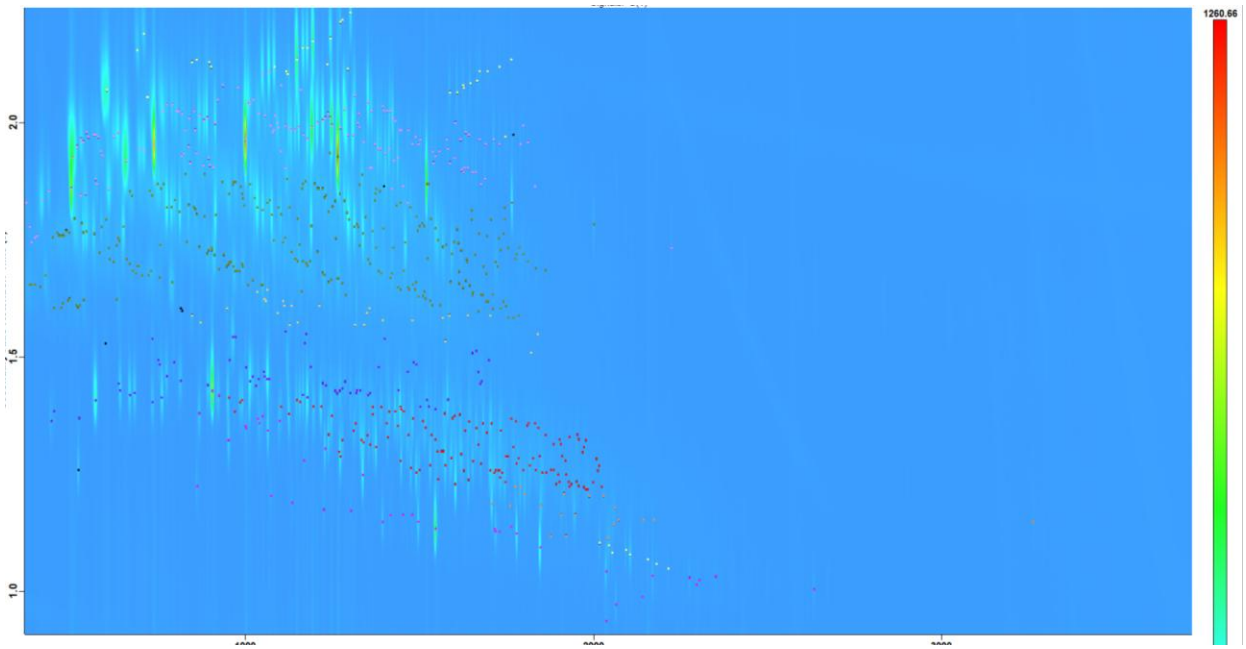


Figure 11. Chromatogram of Folie PE fuel before derivation.

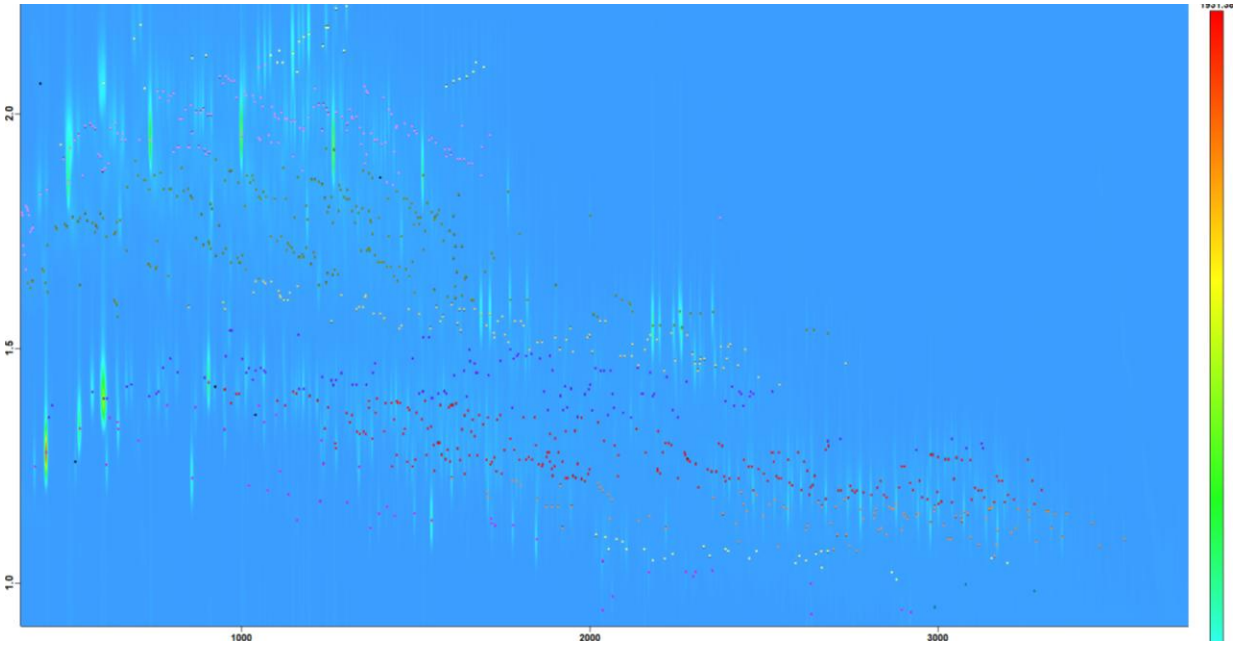


Figure 12. Chromatogram of Folie PE fuel after derivation.

The introduction of ChromaTOF Tile software has revolutionized the process of comparing complex chromatograms, particularly in the analysis of fuel samples such as Folie PE fuel. This

advanced analytical tool has significantly enhanced our ability to detect and interpret subtle changes in chemical compositions, as demonstrated in Figures 13 and 14.

Figure 13 presents a comprehensive comparison of two chromatograms representing fuel 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 side-by-side visualization allows for an immediate appreciation of the global changes induced by derivatization. Figure 13 demonstrates its ability to align chromatograms, use color-coding to highlight differences, offer overlay options, and automatically label peaks. Figure 14 showcases the software'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. The introduction of ChromaTOF Tile software has revolutionized the process of comparing complex chromatograms, particularly in the analysis of fuel samples such as Folie PE fuel. This advanced analytical tool has significantly enhanced our ability to detect and interpret subtle changes in chemical compositions, as demonstrated in Figures 13 and 14.

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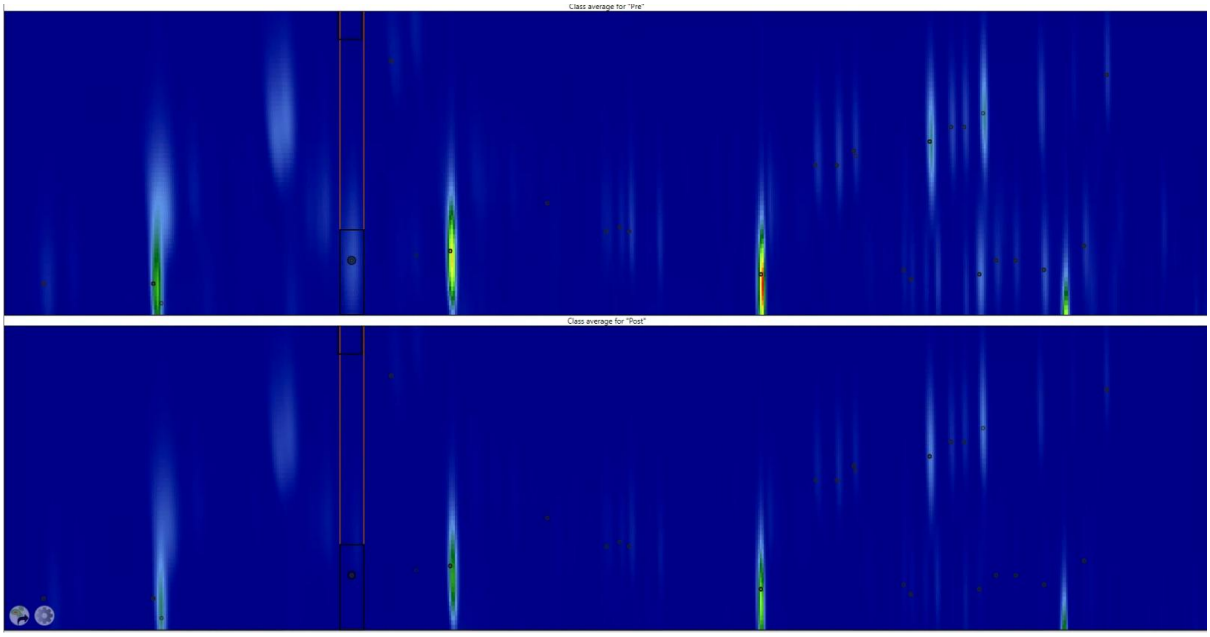


Figure 13. Comparative analysis of folie pe fuel chromatograms: pre-derivatization (top) showing distinct peak vs. post-derivatization (bottom) exhibiting peak absence.

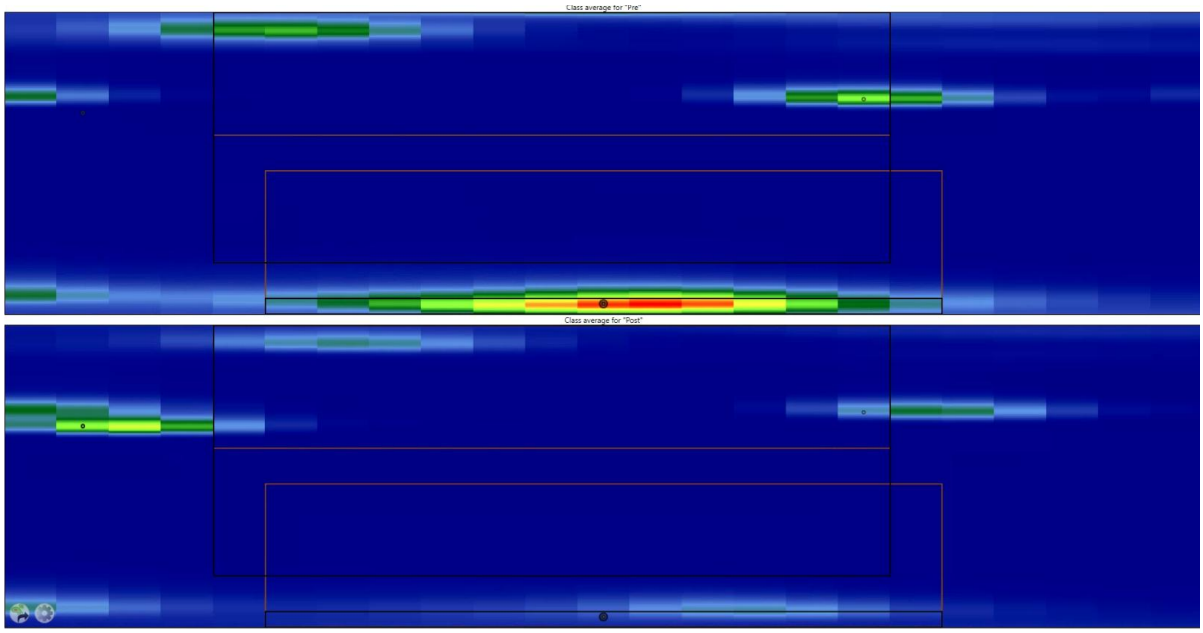


Figure 14. Zoomed-in comparative analysis of folie pe fuel chromatograms: pre-derivatization (top) showing distinct peak vs. post-derivatization (bottom) exhibiting peak absence.

Figure 15 provides a comparative analysis of Folie PE fuel chromatograms, with the pre-derivatization chromatogram displayed at the top, showing a notable absence of peaks, while the post-derivatization chromatogram, at the bottom, reveals a distinct peak. This indicates a clear difference between the two states. Figure 16 offers a zoomed-in view of this comparison, further emphasizing the disparity between the chromatograms. The top portion, representing the pre-derivatization state, continues to show no significant peak, whereas the bottom, post-derivatization, distinctly exhibits the presence of a peak, highlighting the chemical transformation.

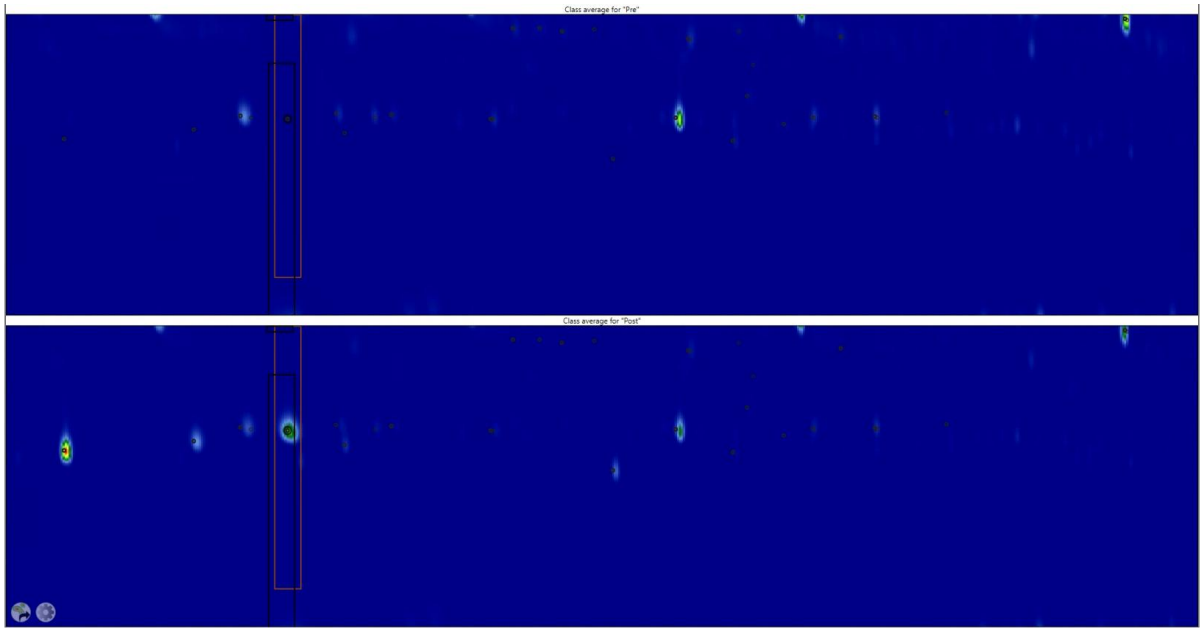


Figure 15. Comparative analysis of folie pe fuel chromatograms: pre-derivatization (top) exhibiting peak absence vs. post-derivatization (bottom) showing distinct peak.

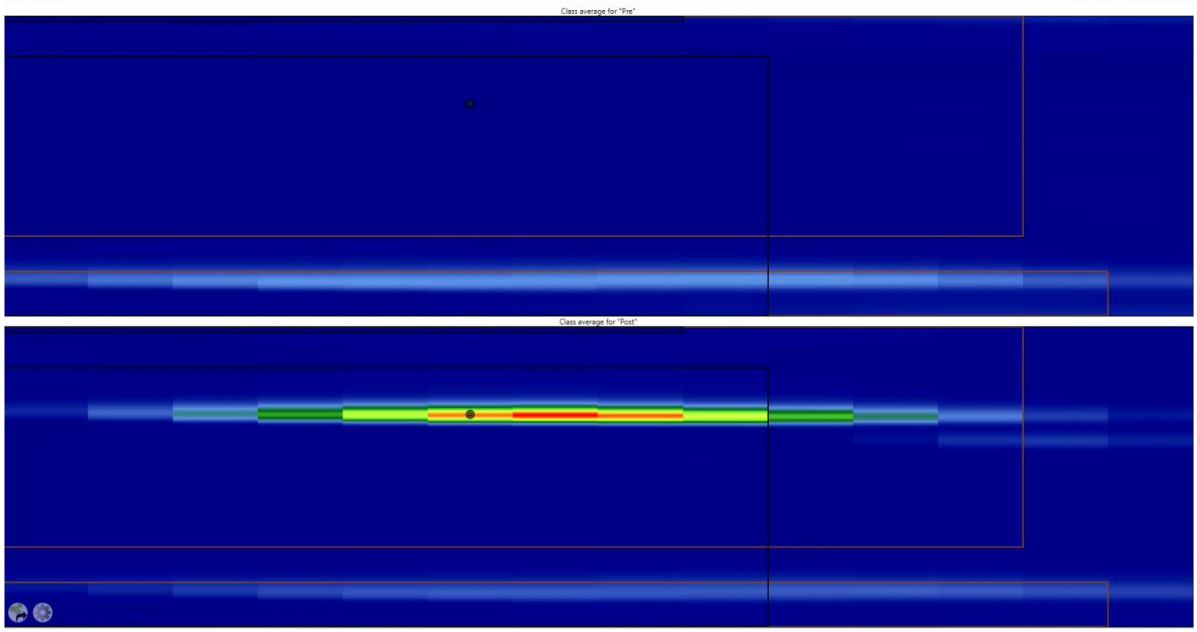


Figure 16. Zoomed-in comparative analysis of folie pe fuel chromatograms: pre-derivatization (top) exhibiting peak absence vs post-derivatization (bottom) showing distinct peak

3.3 ChromaTOF Software – Quantitative Analysis

GC×GC offers a highly detailed analysis of a sample, with the added benefit of generating structured, visually organized chromatograms. Figure 15 presents a contour plot of a fuel sample derived from PE-foil pyrolysis, overlaid with a classification template that reveals extensive insights into the fuel's chemical composition. The plot showcases numerous peaks at varying concentrations, represented by changes in color intensity, corresponding to different compounds in the sample, such as hydrocarbons, oxygenates, and possible trace contaminants. Each peak indicates a distinct compound eluting from the chromatographic column at a unique retention time, determined by its specific physical and chemical properties. The complexity of the chromatogram is evident, with peaks of various shapes, sizes, and retention times, providing a rich and detailed picture of the fuel's composition.

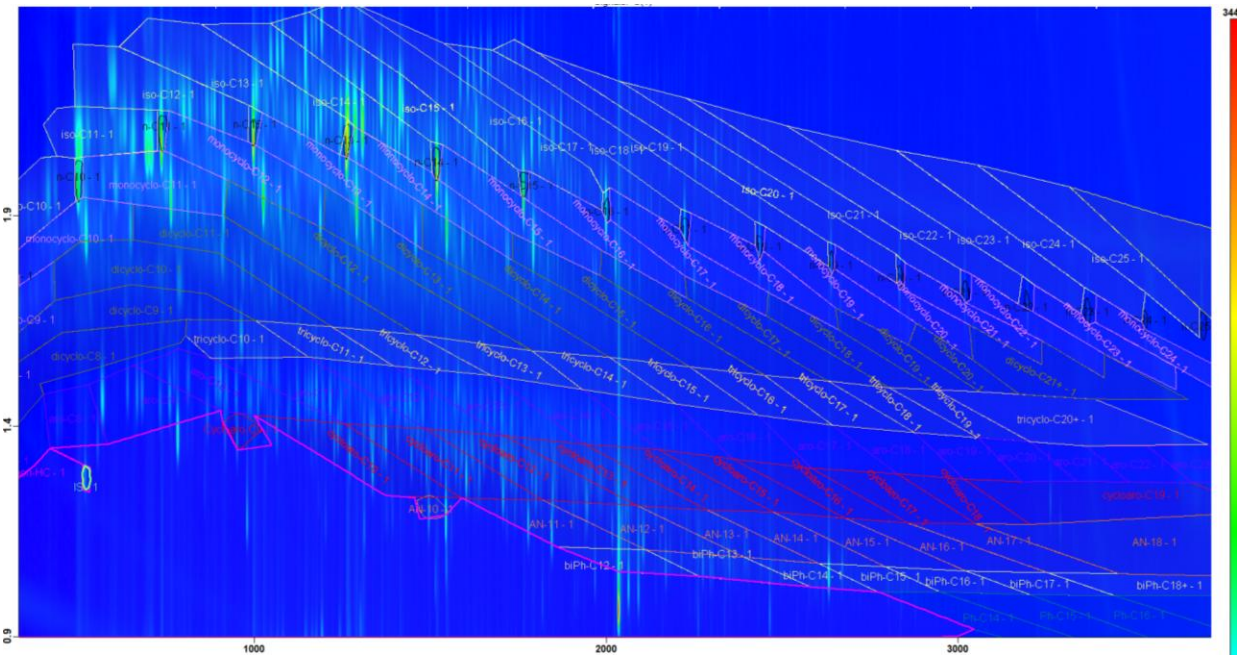


Figure 17. Contour plot fuel with classification template overlaid showing the group-type structured nature of GCxGC chromatogram.

Applied to a gasoline-like pyrolysis oil sample, the olefin content at the level of individual carbon numbers can be calculated. For example, in the C_9 region, the monocycloalkane peak area before

derivatization was 56524.36 (6.41 wt.%). Following derivatization and normalization, the peak area was reduced to 13891.51. By calculating the difference in these peak areas, the oelfin content for the C_9 region was determined to be 4.84 wt.%, with the remaining 1.58 wt.% attributed to monocycloalkanes. This demonstates 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.

Table 3. Percent of each monocycloalkanes in pyrolysis gasoline.

	Pre-derivatization		**Post-derivatization**			**True result**	
C #	**p.a.**	**wt. %**	**p.a**	**After Norm (p.a.)**	**Olefins (p.a.)**	**Monocyclo (wt.%)**	**Olefins (wt.%)**
C5	52883.75	6	38374.69	31454.66	21429.09	3.57	2.43
C6	81707.23	9.27	65393.26	53601.03	28106.2	6.08	3.19
C7	86175.05	9.78	64515.59	52881.63	33293.42	6	3.78
C8	50744.41	5.76	50393.38	41306.05	9438.36	4.69	1.07
C9	56524.36	6.41	16947.64	13891.51	42632.85	1.58	4.84
C10	1839.73	0.21	553.02	453.3	1386.43	0.05	0.16
Total	**329874.5**	**37.44**	**236177.6**	**193588.2**	**136286.4**	**21.97**	**15.47**

3.4 Limitation

While ChromaTOF Tile offers cutting-edge capabilities for detecting and comparing chromatographic peaks, some inherent limitations to its functionality should be considered when interpreting results. One of the key limitations lies in its reliance on peak recognition algorithms. Although highly advanced, these algorithms may encounter challenges when faced with extremely low signal-to-noise ratios or in situations where peaks are closely overlapping. In such cases, the software may struggle to fully resolve the individual peaks, potentially leading to inaccuracies in identifying or quantifying specific components. For complex or noisy chromatograms, even with

powerful tools like ChromaTOF Tile, there may be limitations in precisely distinguishing between multiple overlapping peaks.

Another limitation stems from the software's dependence on proper calibration and sample preparation. For ChromaTOF Tile to deliver accurate results, it is crucial that the instrumentation is properly calibrated and that sample preparation is carried out meticulously. In highly complex mixtures or matrices containing unknown components, the software might have difficulty distinguishing between structurally similar compounds, particularly if derivatization reactions result in similar retention times or mass spectral patterns. This can complicate peak identification, especially when dealing with isomers or closely related compounds. Furthermore, when analyzing novel compounds or reactions that generate products not already cataloged in its database, ChromaTOF Tile may not have sufficient reference information, leading to challenges in identifying unknown compounds. In such instances, manual interpretation becomes necessary, often requiring cross-validation with complementary analytical techniques like NMR, FTIR, or LC-MS to confirm the identity of compounds or reaction products.

In addition, while ChromaTOF Tile's zoom-in functionality and comparative analysis tools significantly enhance the clarity of peak detection, they cannot entirely substitute for expert judgment. The software can provide highly detailed and sophisticated visualizations of chromatograms, but the ultimate interpretation of the data still requires an understanding of the underlying chemistry, as well as experience in handling complex mixtures and chromatographic techniques. Human expertise remains critical in cases where the software's output might not be straightforward, such as when new, unexpected peaks arise or when the sample contains unknown substances that require further investigation.

Moreover, the quality of the input data can limit the software's effectiveness. If the chromatographic separation itself is not optimal —due to poor resolution, insufficient retention times, or inadequate sample preparation—the software’s ability to accurately analyze the data will be constrained. In these cases, even ChromaTOF Tile’s advanced algorithms may not be able to compensate for fundamental issues in the chromatographic process.

CHAPTER 4

Conclusion

ChromaTOF Tile played a pivotal role in detecting and accurately comparing the chromatographic changes observed throughout our analysis. Its high level of precision enabled us to thoroughly examine even the most subtle peak movements, highlighting the software's effectiveness in processing and interpreting complex chromatographic data. In chemical reactions such as derivatization, where small structural or chemical changes can be difficult to detect, ChromaTOF Tile's ability to identify minor shifts in peak positions proved essential. These capabilities far surpass those of less advanced tools, which may not offer the resolution or detail required for such intricate analysis.

The software’s advanced zoom-in feature, coupled with its robust peak comparison algorithms, enabled us to confidently confirm the disappearance of 1-Hexadecene and 1-Octadecene following the derivatization reaction. This level of accuracy is crucial, particularly in areas such as fuel analysis, where even minor compositional changes can have a significant impact on the performance, stability, and efficiency of fuels. By tracking the chemical transformations with such precision, ChromaTOF Tile provides a clear view of how specific compounds behave in response to derivatization or other chemical processes.

Moreover, the ability to zoom in on specific regions of the chromatogram, as demonstrated in the analysis of the 1-Hexadecene peak, allowed us to detect the emergence of new peaks that might otherwise have gone unnoticed. This highlights the value of ChromaTOF Tile in distinguishing between original peaks and new ones, even when they are closely spaced or partially overlapping. In this way, the software offers a powerful combination of high-resolution visualization and accurate peak comparison, making it an invaluable tool for researchers who need to carefully monitor changes in complex mixtures.

In conclusion, ChromaTOF Tile significantly enhances our ability to visualize, interpret, and compare chromatographic data with an unprecedented level of detail. Its strengths lie in its precision, capacity for zoomed-in analysis, and the accuracy with which it can differentiate between peaks, even in cases of complex chemical reactions. This makes it an ideal tool not only for fuel analysis but also for a wide range of applications involving complex mixtures and subtle chemical transformations. By providing clear and detailed insights into these changes, ChromaTOF Tile helps ensure that we can confidently track the impact of reactions like derivatization, offering a deeper understanding of the chemical processes at play.

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