

Instrument: Pegasus® BTX 4D**Characterization of Fischer-Tropsch Synthetic Paraffinic Kerosene and Traditional Aviation Turbine Fuel**

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Introduction

The synthetic aviation fuels (SAF) market provides an alternative to traditional fossil-based aviation fuels derived from crude oil by using renewable and sustainable feedstock. This market is expected to grow significantly in the next decade due to regulations like the EU's ReFuelEU proposal and the United States' Sustainable Aviation Fuel Grand Challenge that promote the use of sustainable aviation fuels to reduce air quality impacts and greenhouse gas emissions. Many of the existing certified SAF processing pathways reduce or eliminate the total aromatics and sulfur content, reducing particulate and sulfur-oxide emissions. However, a certain amount of aromatic content is still necessary to maintain the proper freeze points, viscosity, and polymeric sealing properties in a jet fueling system, making it important to balance understanding of not only the physical properties, energy content, and emissions profiles of a new fuel, but also the individual components in its chemical makeup that affect these bulk properties. For new fuels to gain approval for use, detailed characterization is required to meet regulatory requirements such as ASTM D7566 and ASTM D1655, which provide specifications for fuels allowed in co-processing and blending for commercial use in the United States. With a combination of comprehensive two-dimensional gas chromatography (GCxGC) and time-of-flight mass spectrometry (TOFMS), the high-quality information necessary for deeper understanding of the composition of synthetic aviation fuels can be produced and utilized to expedite the certification process.

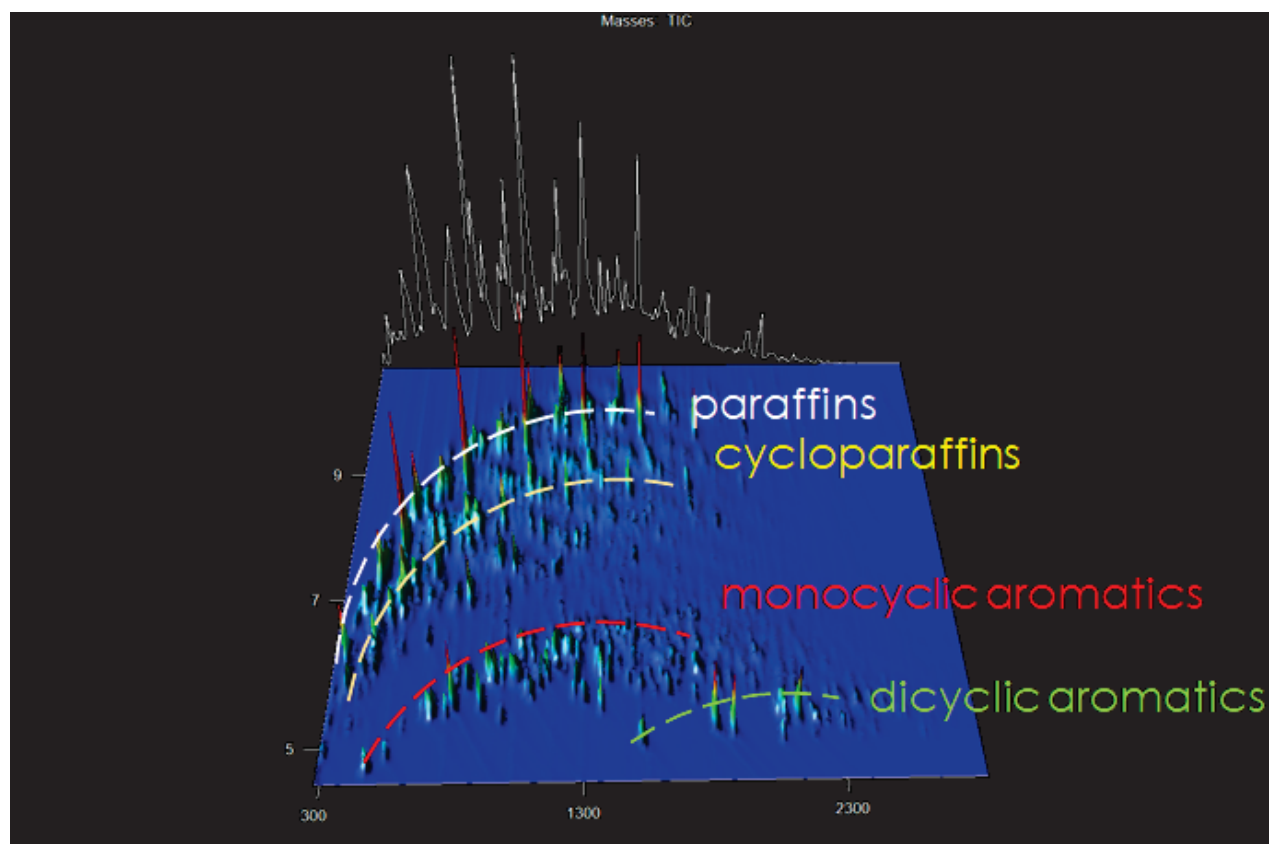


Figure 1. GCxGC 3D surface plot of commercial aviation turbine fuel with Total Ion Chromatogram (TIC) shown. Reconstructed trace of what a single dimension of GC separation would have looked like is shown in white. Elution bands of paraffins (white), cycloparaffins (yellow), monocyclic aromatics (red), and dicyclic aromatics (green) are indicated by dotted lines.

The structured nature of GCxGC chromatograms allows for quick identification of compound classes that prove crucial for determining the constituents of a synthetic aviation fuel. With thousands of compounds present, the complexity of the data requires simple visualization and orientation to interpret, which GCxGC provides in elution bands of similarly structured analytes, as can be seen in Figure 1. However, even separation with multidimensional chromatography alone is not enough to isolate individual species and provide confident identification. For further compound class-level differentiation, the ability to plot individual mass channels that correspond to characteristic fragment masses can provide clarity and better define the elution space, as can be seen in Figure 2, where the common classes of interest are laid out for a sample of traditional commercial jet fuel. While all these classes are present to some degree in traditional fossil-fuel sourced aviation fuels, the new processes used in the production of synthetic aviation fuels yield a very different distribution than traditional classes.

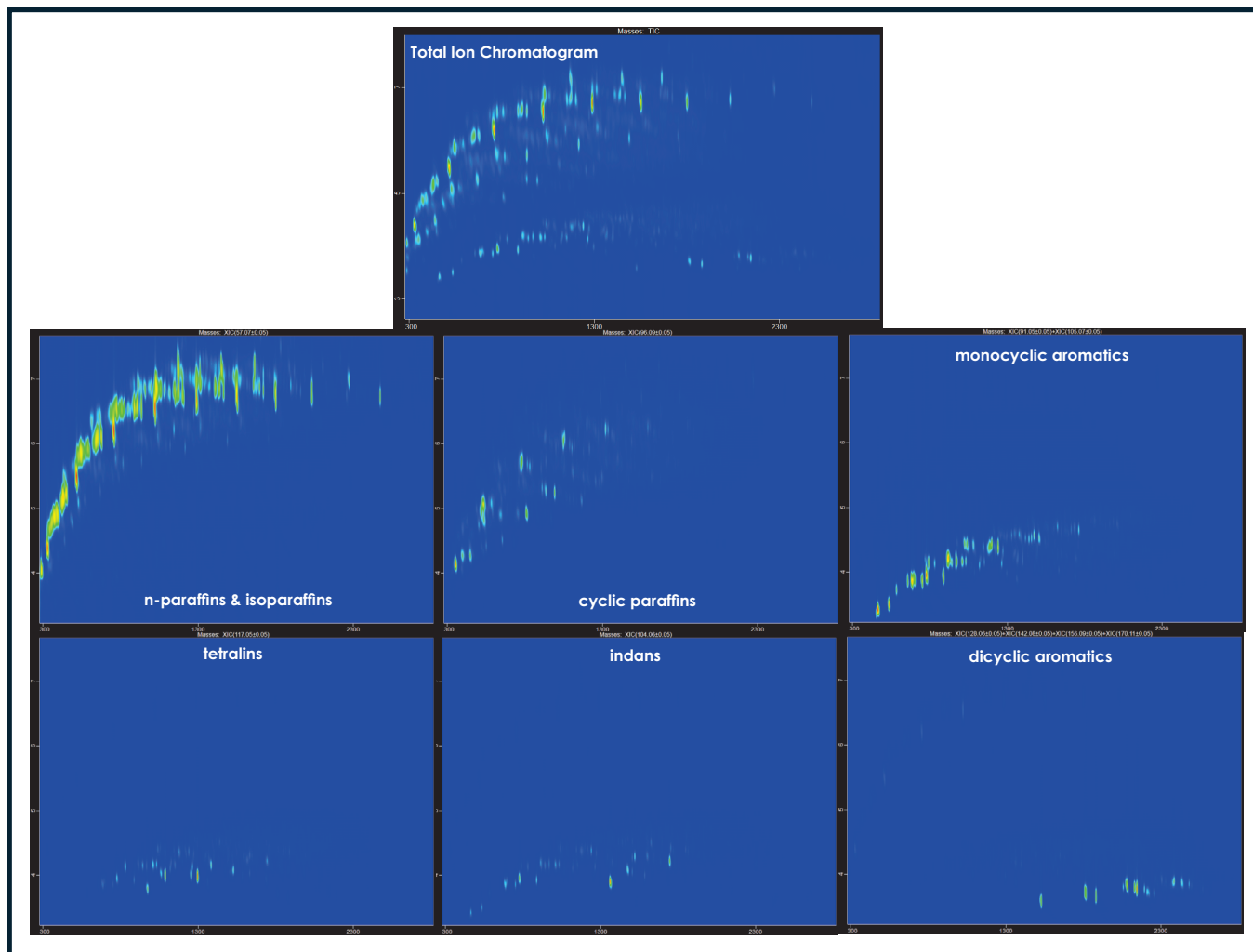


Figure 2. GCxGC contour plots of traditionally sourced commercial aviation turbine fuel with each plot displaying a different set of masses. Characteristic fragmentation masses are plotted for each class of compound: m/z 57.07 for *n*-paraffins and isoparaffins; m/z 96.09 for cyclic paraffins with a 6-carbon-ring based structure; m/z 104.06 for indans; m/z 117.05 for tetralins; m/z 91.05 and m/z 105.07 for alkylbenzene-type monocyclic aromatics; m/z 128.06, m/z 142.08, m/z 156.09, and m/z 170.11 for alkylnaphthalene-type dicyclic aromatics.

Experimental

Table 1 shows the thermally modulated GCxGC and TOFMS parameters used to analyze a variety of aviation fuel samples diluted with hexane in a 100:1 ratio. Data processing was performed using ChromaTOF[®] software, with automatic Peak Find and Library Search. Peaks were automatically deconvoluted and compared to the NIST23 spectral library. Classification templates were developed using a combination of the different analytes in individual samples as well as a gravimetric reference mix containing alkane, cycloalkane, monoaromatic, and diaromatic compounds.

Table 1. Acquisition Parameters

Gas Chromatograph	LECO QuadJet™ Thermal GCxGC
Injection	1 μ L liquid injection, split 100:1 @ 300 °C
Carrier Gas	He @ 1.0 mL/min, constant flow
Column One	Rxi-17SilMS, 30 m x 0.25 mm ID x 0.25 μ m coating (Restek, Bellefonte, PA, USA)
Column Two	Rxi-5MS, 1.45* m x 0.25 mm ID x 0.25 μ m coating *1.05 m coiled in 2 nd oven
Temperature Program	0.5 min at 40 °C, ramped 3.0 °C/min to 300 °C, hold for 5 min
Secondary Oven	+15 °C relative to primary oven
Modulator Temperature	+15 °C relative to primary oven
2nd Dimension Separation Time	8 s, hot pulse time 2.40 s
Transfer Line	350 °C
Mass Spectrometer	LECO Pegasus BTX
Ion Source Temperature	250 °C
Mass Range	35-900 m/z
Acquisition Rate	200 spectra/s

Results and Discussion

While differences in composition between traditional jet fuels are relatively subtle, with slightly varying ratios of specific compounds as can be seen in comparative contour plots in Figure 3, the variety of processes currently approved for synthetic aviation fuels used as blending components leads to contour plots with differences that often appear much more obvious.

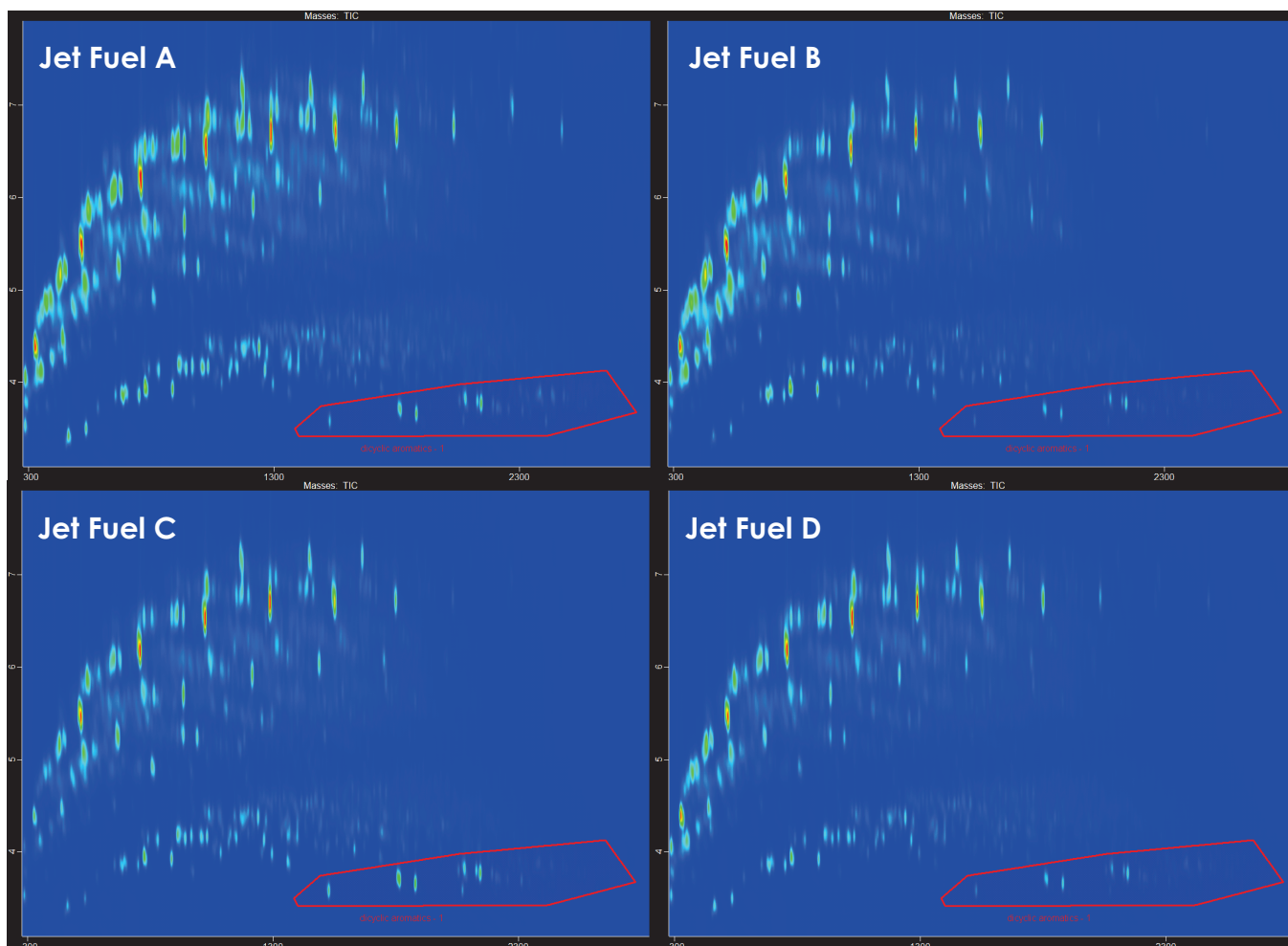


Figure 3. GCxGC contour plots comparing the TIC of four different traditional jet fuels A-D. Distribution of hydrocarbons generally follows the expected trend for traditional fossil-derived fuels, with a wide range of paraffins and aromatic compounds present. Examples of slight variations in the speciation of each fuel, for example, in the dicyclic aromatic region, can be noted in the bottom right of each plot, with jet fuel A and jet fuel C containing a higher amount of naphthalene relative to the methyl- and dimethyl- naphthalene isomers.

The Fischer-Tropsch (FT) catalytic chemical process converts carbon monoxide and hydrogen from synthesis gas blends produced by woody biomass or coal into larger hydrocarbons, whose typical formations depend largely on the types of catalyst and reaction temperatures. As illustrated in the comparison of low-temperature Fischer-Tropsch Synthetic Paraffinic Kerosene (LTFT-SPK) and high-temperature Fischer Tropsch Synthetic Paraffinic Kerosene (HTFT-SPK) in Figure 4 below, higher temperatures tend to shift the reaction toward products with more branching, lower carbon number, and higher hydrogenation. In general, paraffins are the dominant species in FT-SPK, which are currently allowed in blends of synthetic aviation fuel up to 50%, according to ASTM D7566 Annex A1.

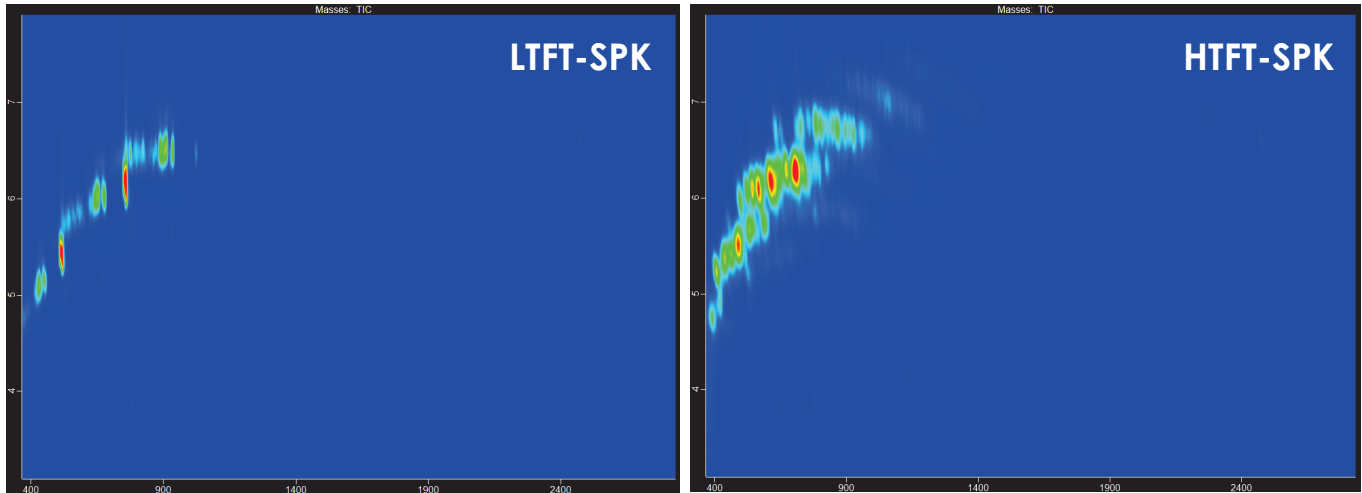


Figure 4. GCxGC contour plot comparing the TIC of low-temperature to high-temperature Fischer-Tropsch derived synthetic paraffinic kerosene, demonstrating the greater prevalence of isoalkanes and other branched paraffins in the HTFT-SPK compared to the n-alkane-dominated LTFT-SPK.

An example of the addition of aromatics that changes the FT-SPK product to FT-SPK/A, which is also allowed in blends up to 50% according to ASTM D7566 Annex 4, is shown in Figure 5, where it can easily be seen that a larger portion of the FT-SPK/A sample is composed of monocyclic aromatic hydrocarbons.

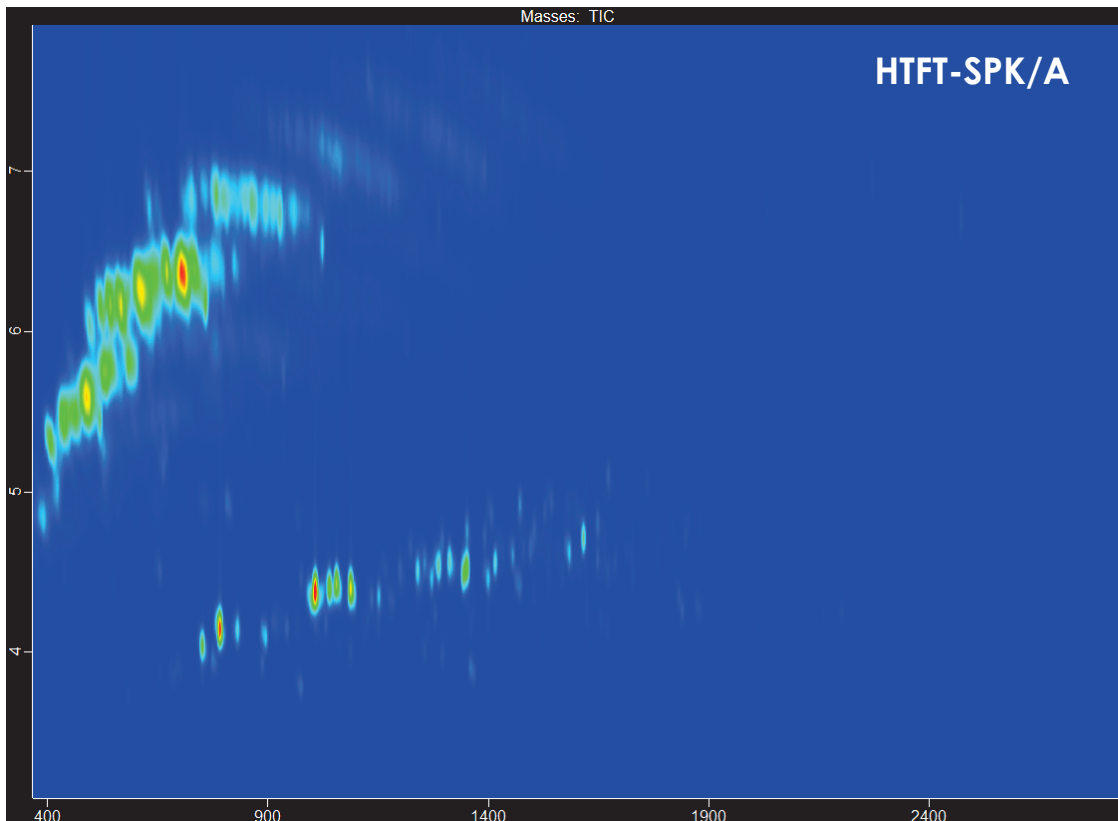


Figure 5. GCxGC contour plot showing high-temperature Fischer-Tropsch blend with aromatics (HTFT-SPK/A).

While these contour plots are useful visualizations for bulk composition of samples, the benefits of GCxGC can extend beyond just easy-to-interpret images. The increase in chromatographic resolution between different chemical species also improves the ability to effectively deconvolve peaks and produce cleaner spectra for better library matches than can be seen in a similar area of the chromatogram in a single dimension of GC separation alone.

In the HTFT-SPK/A sample, one example of a zoomed-in area of the chromatogram shows three peaks that have the same first-dimension separation time: a branched paraffin, linear alkane, and isoalkylbenzene. The second dimension of separation provides clear chromatographic resolution between the peaks, resulting in library similarity scores of greater than 850/1000 for each identification, as seen in Figures 6-8.

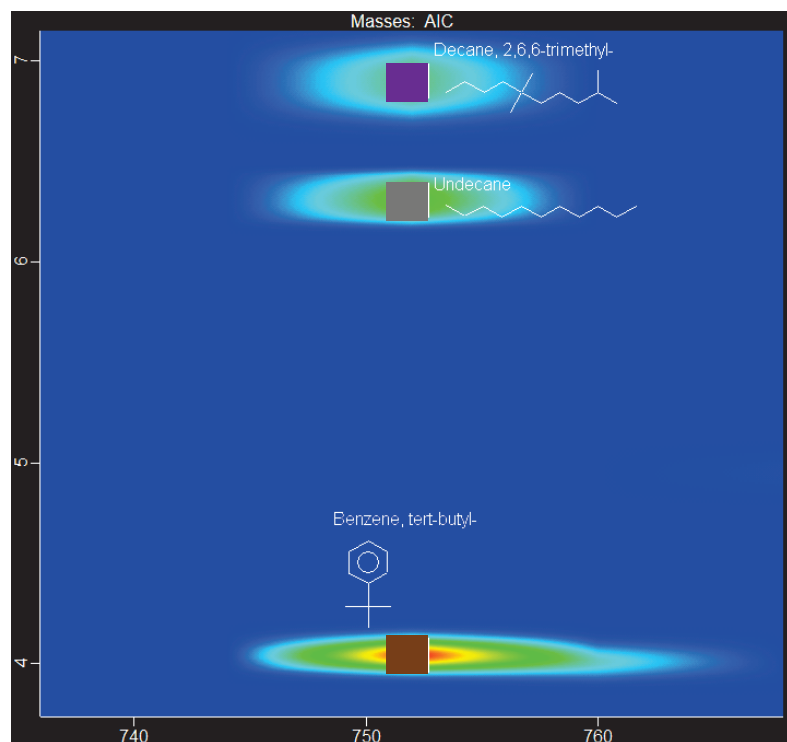


Figure 6. Zoomed-in section of GCxGC contour plot of HTFT-SPK/A showing the resolution of three distinct peaks that share the same first-dimension retention time, automatically labeled with putative identification and structure

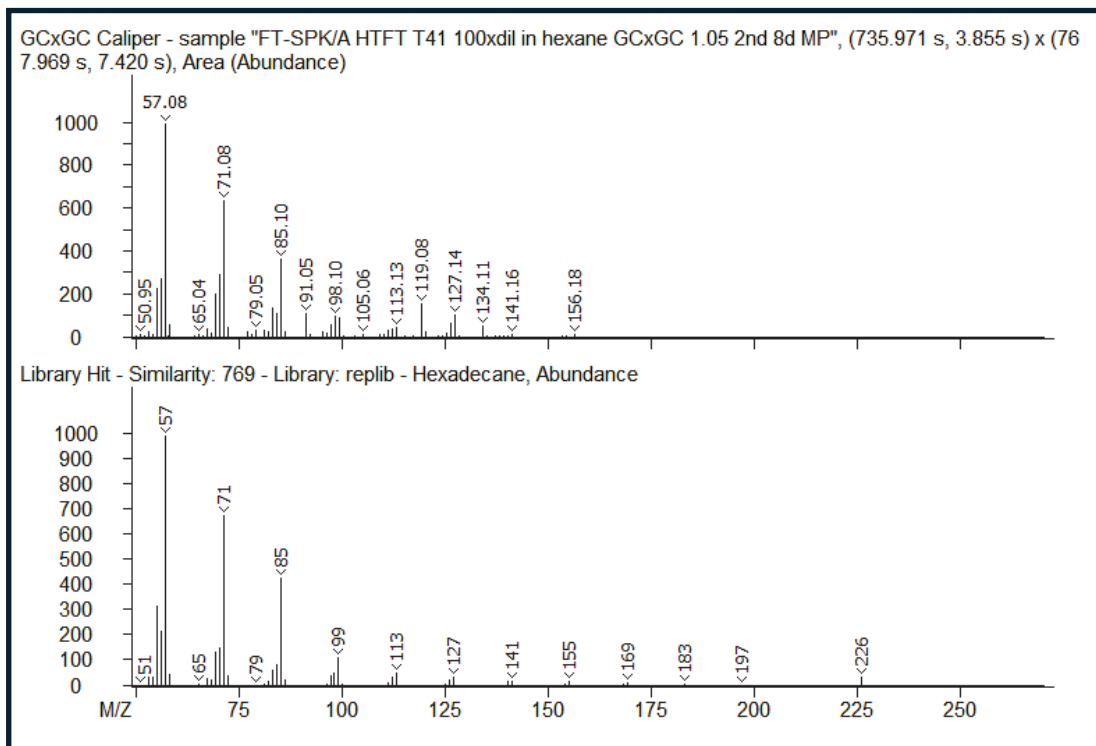


Figure 7. GCxGC caliper spectra of the zoomed-in region illustrates what the mass spectrum would have looked like with only a single dimension of GC separation (top), along with the corresponding library hit (bottom). The identity of the signal at that first-dimension retention time is incorrectly assigned as hexadecane.

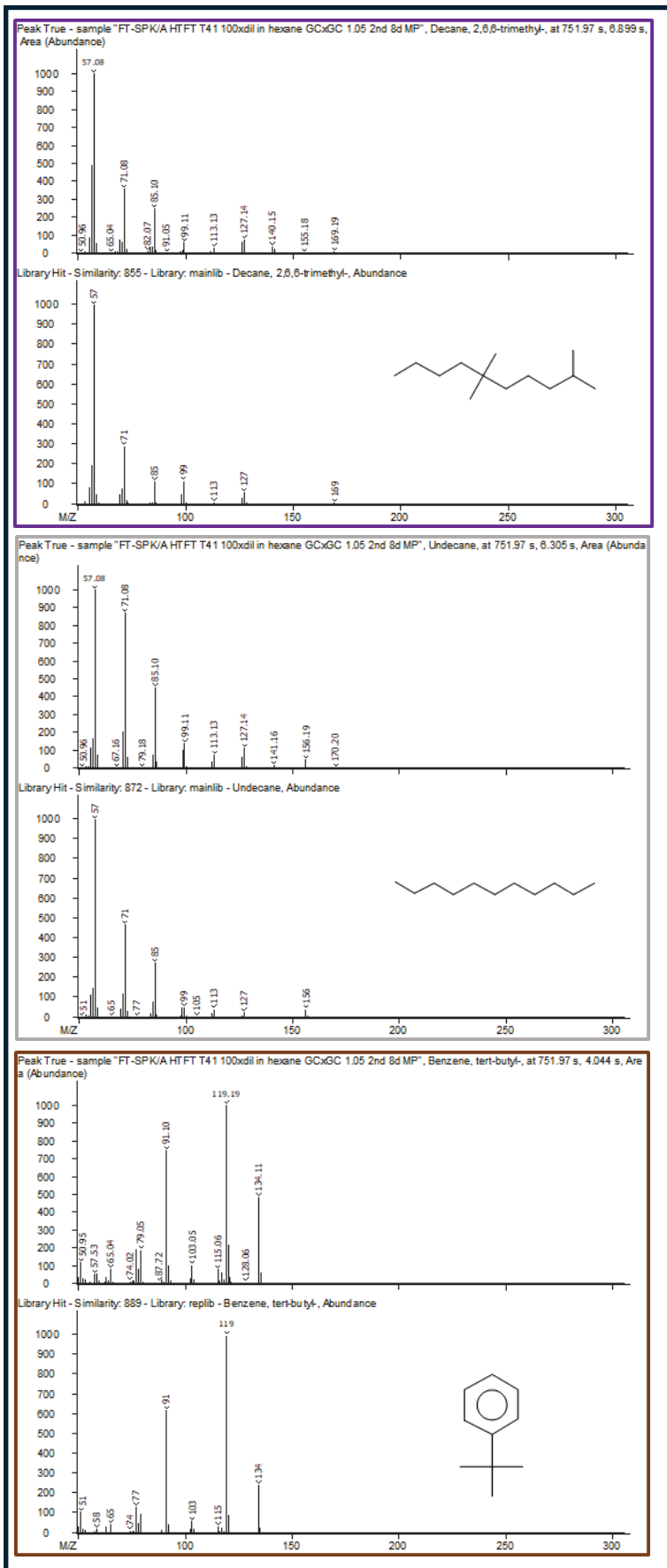


Figure 8. Peak True spectra of each peak identified in the region previously shown in Figure 6 are shown with corresponding library spectra. Because of the second dimension of chromatographic separation, cleaner deconvoluted spectra lead to better, more-accurate identification of each individual peak.

Another example of this is shown in Figure 9, where four analytes from different compound classes coelute in the same first dimension time, but are clearly resolved in the second dimension with excellent library matches and similarity scores above 850/1000.

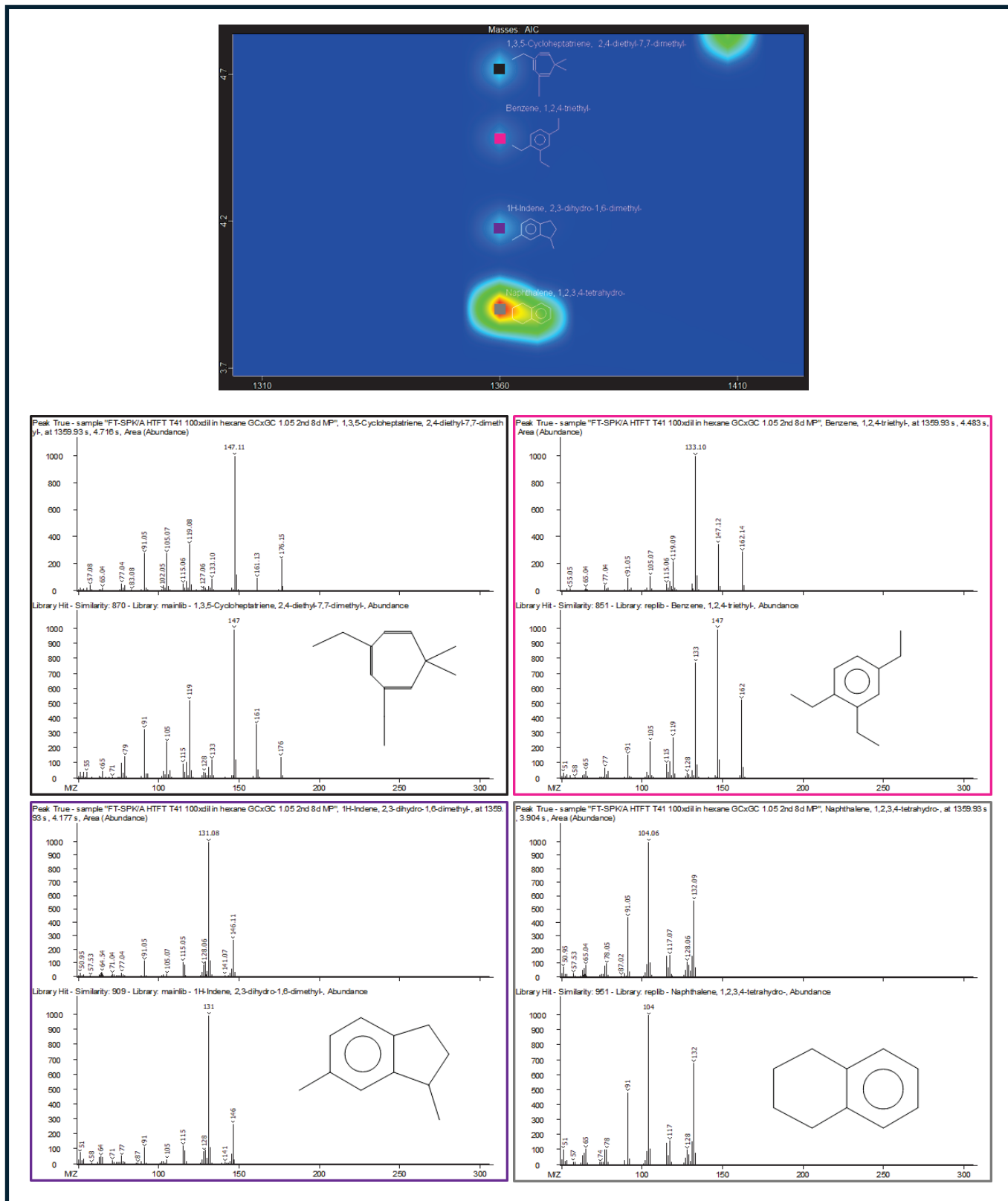


Figure 9. (Top) Zoomed-in section of contour plot of HTFT-SPK/A sample showing a region with four peaks chromatographically resolved by GCxGC in the same first-dimension retention time. Peak True spectra for each peak identified are shown with corresponding library spectra, with each peak belonging to a different structural class.

While the combination of multiple dimensions of chromatography with mass spectral information can seem overwhelming at first glance, the *ChromaTOF* suite of software tools makes it easy to filter through the rich data and target specific analytes of interest. In one sample of traditional aviation fuel, over 11,000 features were found using the automated Peak Find with deconvolution algorithm. With the addition of a Peak Filter based on library search results, Figure 10 shows how simple it is to sift through the wealth of data and focus on peaks with both high library match similarity scores and interesting characteristics (such as heteroatomically substituted sulfur-containing compounds), which may be important for preventing catalyst poisoning or understanding emissions profiles.

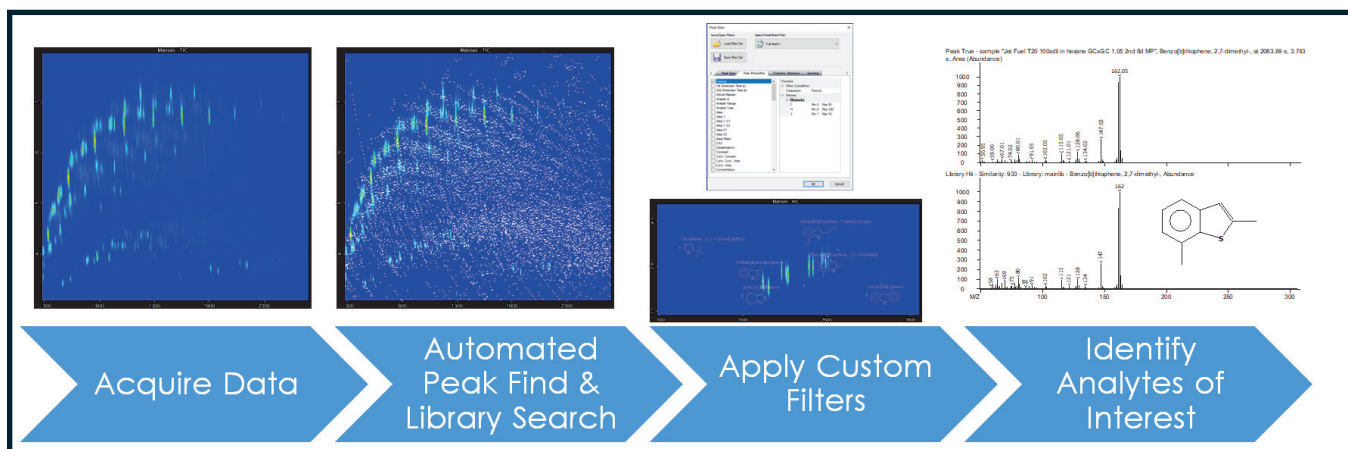


Figure 10. Data processing workflow for semi-targeted analysis of traditional aviation fuel, showing the power of custom peak filtering for narrowing focus to potential analytes of interest.

Conclusion

The combined power of enhanced chromatographic separation from GCxGC and rich spectral information from TOFMS makes the *Pegasus BTX 4D* an instrument capable of both general and detailed characterization of aviation fuels. From tracing traditional hydrocarbon elution patterns to spectral identification of heteroatom-containing species with the aid of built-in software tools in *ChromaTOF*, the process to gaining understanding of the makeup of future fuels for certification can be simplified within a single workflow.

References

- <https://aviationweek.com/business-aviation/aircraft-propulsion/viewpoint-bio-based-aromatics-point-way-burning-100-saf>
- <https://www.marketsandmarkets.com/Market-Reports/sustainable-aviation-fuel-market-70301163.html>
- https://afdc.energy.gov/fuels/sustainable_aviation_fuel.html
- <https://aviationweek.com/special-topics/sustainable-aviation-fuel/saf-market-worth-13112-billion-2033>
- <https://guidehouseinsights.com/reports/market-outlook-for-sustainable-aviation-fuels>
- <https://www.netl.doe.gov/research/carbon-management/energy-systems/gasification/gasifipedia/ftsynthesis>
- <https://skynrg.com/sustainable-aviation-fuel/technology-basics/>



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