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Hydrocarbon Class Analysis of Conventional and Synthetic Aviation Turbine Fuels by ASTM D8396

Flow-modulated GCxGC-FID using the Agilent Reverse Flow Modulator and 8890 GC

Author

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Abstract

This application note demonstrates the performance of the Agilent Reversed Flow Modulator (RFM) and Agilent 8890 GC through molecular group-type analysis of aviation turbine fuel and synthetic aviation turbine fuel (SATF) by comprehensive multidimensional gas chromatography with flame ionization detection (GCxGC-FID) per ASTM D8396. Method precision was explored using both hydrogen and helium carrier gases and yielded quantitative precision below 1.0 %RSD for 39 out of 42 compounds and 42 out of 42 compounds, respectively, across 10 consecutive replicate injections of a gravimetric standard. GCxGC data analysis was conducted using GC Image – GCxGC Edition, and the demonstration of reconciling GCxGC peak movement using GC Image's affine transformation capabilities is also highlighted. Finally, the method is used to show the group-type quantification of a reference jet fuel, an HEFA and an FT-SPK SATF, two kerosene reference materials, and a diesel-FAMEs blend.

Introduction

Nearly 33 years after the advent of GCxGC[1], ASTM D8396 represents the first standardized GCxGC method from the consensus-based standards organization. For many years, thermally modulated GCxGC systems attached to large cryogenic dewars and high-resolution mass spectrometers were the dominant form factor and workflow. Despite their enormous increase in compositional information over traditional GC, these GCxGC/MSD systems found use primarily in research-oriented laboratories of academic and industrial institutions. The development of flow modulation has enabled GCxGC without the need for cryogenic utilities, and the refinement of flow modulation technology has greatly increased the accessibility of GCxGC analysis.

The RFM uses a cryogen-free design that leverages additional carrier gas flow to facilitate modulation. The RFM is a capillary flow technology (CFT) device featuring a chemically inert and low thermal mass microfluidic flow path fabricated on a plate slightly smaller than a credit card. This allows mounting of the RFM on the inside wall of the GC oven and discrete routing of the additional gas supply lines. When combined with an 8890 GC, the resulting RFM GCxGC system has the same benchtop footprint as a conventional 8890 GC, and from the outside, both are visually indistinguishable. This is an attractive feature for production/QC laboratories that often weigh long-term capability as a major factor when budgeting available bench space. Columns are connected to the RFM using a simple CFT nut and a gold-plated flexible metal ferrule to ensure leak-free connections and enable column changes in minutes. Combining this design with the exceptional retention time precision of the RFM results in a GCxGC method that is just as easy to revalidate as a conventional GC method following any periodic maintenance.

ASTM D8396 is a "group-type" GCxGC analysis that quantifies total normal paraffins, isoparaffins, naphthenes, one-ring aromatics, and two-ring (and larger) aromatics in jet fuel. While similar in reported output to other chromatographic fuels test methods such as ASTM D1319 and D6379, D8396 produces substantially more compositional information than practically all other standard GC test methods. Some jet fuel samples shown in this application note yielded over 1,000 individual compounds when separated by GCxGC, and every individual chromatographic peak is classified based on its elution pattern to produce the final group-type results.

Figure 1 shows a 3D rendering of the GCxGC chromatogram of a reference jet fuel and reveals many minor species that would otherwise be inseparable using a conventional GC method. From this perspective, D8396 is more like detailed hydrocarbon analysis (DHA) than D1319, but unlike DHA, this method configuration is compatible with jet and diesel fuels. Indeed, D8396 represents a paradigm shift in the amount of compositional information available to the user and serves as an excellent introduction for users new to GCxGC.
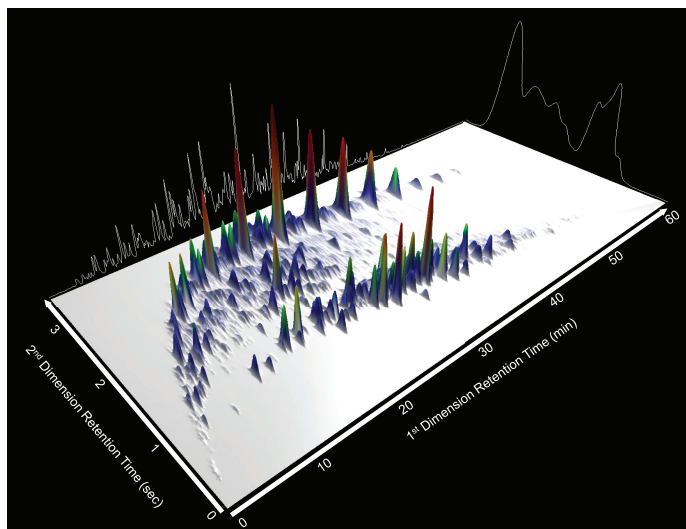

Figure 1. 3D rendering of the reference jet fuel GCxGC separation with composite projections of both dimensions.

GC Image GCxGC Edition Software (GC Image, LLC, Lincoln, Nebraska) is a GCxGC data analysis solution that is packed with features combining intuitive usability with advanced functionality. An LCxLC version is also available. Separate from instrument acquisition software, GC Image can import an expansive list of GC data formats, including Agilent OpenLab CDS and legacy ChemStation data files, as well as opensource NetCDF. In addition to the core functionality necessary for D8396 workflows, GC Image also includes a robust compound classification schema using identification templates and an expansive suite of automated template transformation algorithms to simplify the reconciliation of peak movement following instrument maintenance. This feature provides key functionality for the successful long-term implementation of GCxGC methods and is described in detail later.

Experimental

An 8890 GC was configured with an Agilent 7693A autosampler, split/splitless (SSL) inlet, RFM, and two flame ionization detectors (FID). The second FID is an optional but highly recommended addition and was connected to the outlet of the restrictor column to actively monitor and ensure that the modulation channel was not overfilled during the run. To facilitate modulation, the RFM was paired with a pneumatic switching device (PSD) connected to the carrier gas supply. Both the hydrogen and helium carrier methods used a "reverse column configuration". The first-dimension column was a mid-polar DB-17, and the second-dimension column was a non-polar DB-1HT. The DB-17 was chosen over a more-polar phase (such as a polyethylene glycol "wax" phase) for its robustness and ability to elute heavier polyaromatic species at lower temperatures. The DB-1HT was manually cut to a length of 5.00 m from an original length of 30 m. Both the hydrogen and helium carrier methods used uncoated deactivated fused silica with an internal diameter of 0.10 mm cut to lengths of 1.99 and 2.64 m, respectively, as the restrictor column. Detailed instrument configurations and method parameters can be found in Table 1, and a picture and flow schematic of the RFM is shown in Figure 2.

Table 1. Agilent 8890 GC configuration for the hydrogen and helium carrier methods (continued on next page).

	Hydrogen Carrier Method	Helium Carrier Method
Sampler	Agilent 7693A Automated Liquid Sampler (ALS)	Agilent 7693A Automated Liquid Sampler (ALS)
Inlet	Split/Splitless	Split/Splitless
Column 1	Agilent DB-17, 20 m × 0.18 mm, 0.18 µm (p/n 121-1722)	Agilent DB-17, 20 m × 0.18 mm, 0.18 µm (p/n 121-1722)
Column 2	Agilent DB-1HT, 5 m × 0.32 mm, 0.10 µm (p/n 123-1111) manually cut to length	Agilent DB-1HT, 5 m × 0.32 mm, 0.10 µm (p/n 123-1111) manually cut to length
Restrictor Column	Deactivated Fused Silica, 1.99 m × 0.10 mm (p/n 160-2635-10) manually cut to length	Deactivated Fused Silica, 2.64 m × 0.10 mm (p/n 160-2635-10) manually cut to length
Detector	FID	FID
Carrier Gas	Hydrogen	Helium
Runtime	63.33 min	63.33 min
Consumables		
Inlet Septa	Advanced Green, nonstick (p/n 5183-4759)	
Inlet Liner	Agilent inlet liner, Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)	
ALS Syringe	Blue Line, 5 µL, fixed needle, 23-26s/42/cone (p/n G4513-80206)	
Carrier Gas Filter	Agilent Gas Clean purifier kit for carrier gas, 1/8 in (p/n CP17976)	
FID Gas Filter	Agilent Gas Clean purifier kit for FID, 1/8 in (p/n CP736530)	
Flow Rate, Inlet, and ALS		
Column 1 Flow	0.3 mL/min	0.3 mL/min
Column 2 Flow	15 mL/min	20 mL/min
Restrictor Column Flow	0.36 mL/min	0.36 mL/min
Septum Purge	6 mL/min	6 mL/min
Injection Volume	0.1 µL	0.1 µL
Mode	Split, 400:1	Split, 400:1
Temperature	300 °C	300 °C
Oven Program		
Initial Temperature	40 °C	40 °C
Initial Hold	0 min	0 min
Ramp 1 Rate	3 °C/min	3 °C/min
Ramp 1 Setpoint	230 °C	230 °C
Ramp 1 Hold	–	–
Reversed Flow Modulator		
Modulation Delay	0.01 min	0.01 min
Modulation Period	3.5 s	6 s
Inject Time	0.12 s	0.12 s

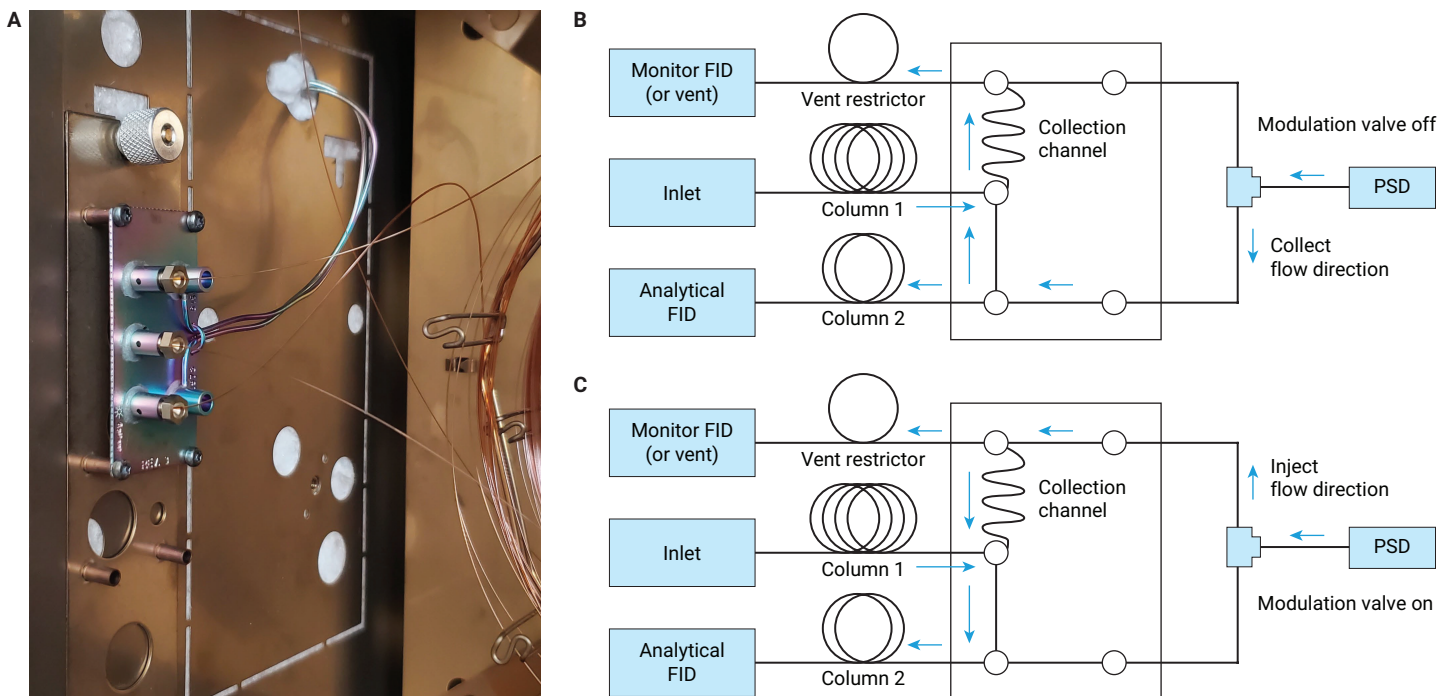|	Hydrogen Carrier Method	Helium Carrier Method
Detector		
Data Rate	200 Hz	200 Hz
Temperature	300 °C	300 °C
Air	400 mL/min	400 mL/min
Hydrogen	30 mL/min	30 mL/min
Make-up (N_2)	30 mL/min	30 mL/min
Carrier Gas Flow Correction	Column + Fuel = Constant	Constant Makeup and Fuel Flow

Figure 2. The Agilent Reversed Flow Modulator mounted inside the Agilent 8890 GC oven (A) and the carrier gas flow path through the RFM during collection (B) and rapid injection (C) of column 1 eluent onto column 2.

Gravimetric (part number 00.02.716) and reference (part number 00.02.717) jet fuel standards were purchased from PAC (Petroleum Analyzer Company, Houston, Texas), and the 1616b Sulfur in Kerosene standard reference material was purchased from NIST (National Institute of Standards and Technology, Gaithersburg, Maryland). Sweetened kerosene (part number CRMU-DEKR) was purchased from LGC (LGC Group, Teddington, England). SATF samples and FAMEs mixtures were customer-provided. Finished diesel was purchased from a local fuel station in Wilmington, Delaware.

Data acquisition was performed using Agilent OpenLab CDS 2.7. GCxGC data analysis was conducted using GC Image GCxGC Edition v2024r1. Quantitation of individual compounds and molecular classes was done using normalization with the relative response factors published in ASTM D8396.

Results and discussion

Gravimetric standard analysis

The gravimetric jet fuel standard includes many compounds commonly found in conventional jet fuels and serves as a quantitative check and to establish the initial boundaries between the molecule classes reported by ASTM D8396. Figure 3 shows the chromatogram of the gravimetric standard using the hydrogen carrier method with the delineation between each molecular class, and Figure 4 shows the same for the helium carrier method. The general class elution pattern in a reverse column setup is that the normal and isoparaffins elute at the top, the naphthenes elute below the paraffins, and the aromatics elute below the naphthenes. Within the aromatics region, single-ring species elute at the top and polyaromatic species elute further toward the bottom as the number of fused rings increases. This pattern holds true for the naphthenes as well, though tricyclic naphthenes are uncommon in conventional fuels and may coelute with the monoaromatics.
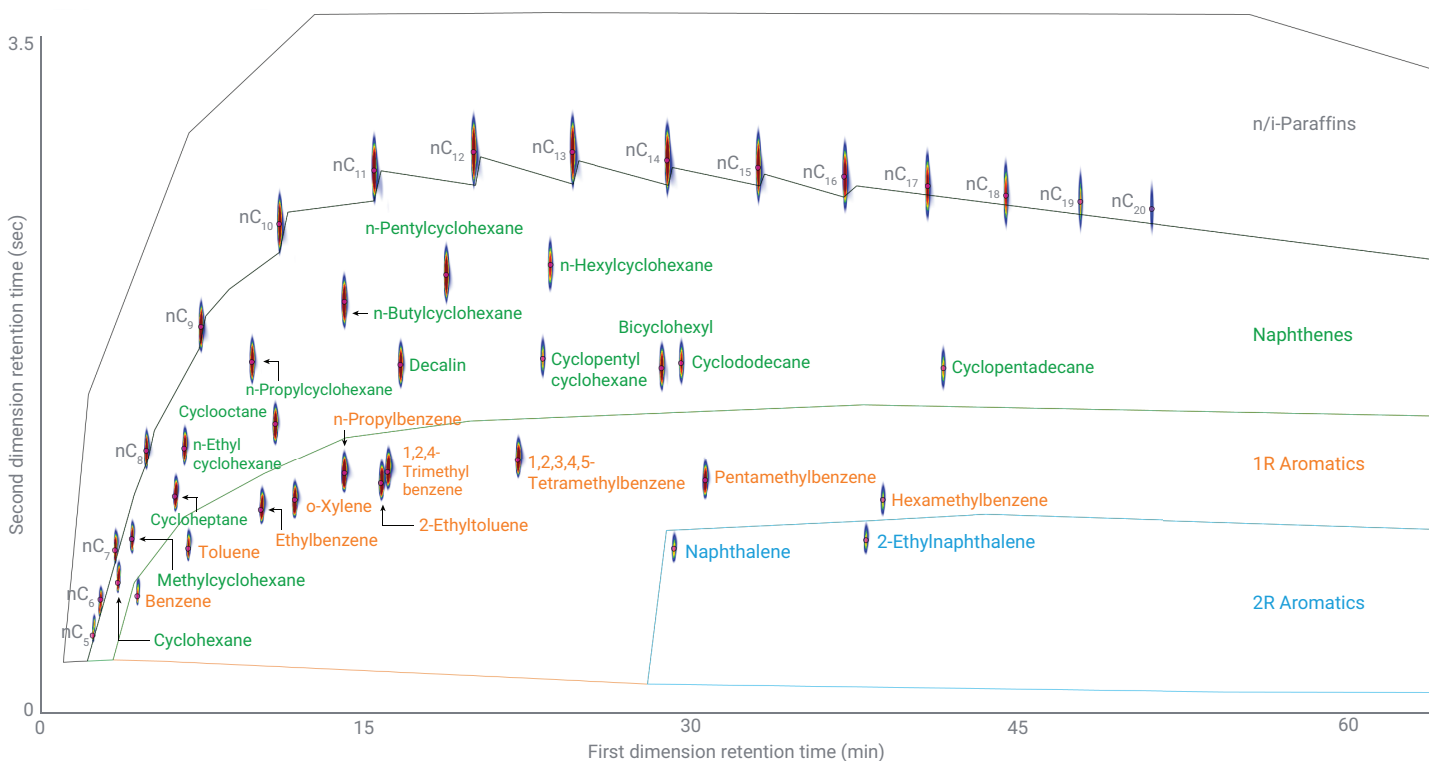

Figure 3. GCxGC-FID chromatogram of the gravimetric jet fuel standard using the hydrogen carrier method.
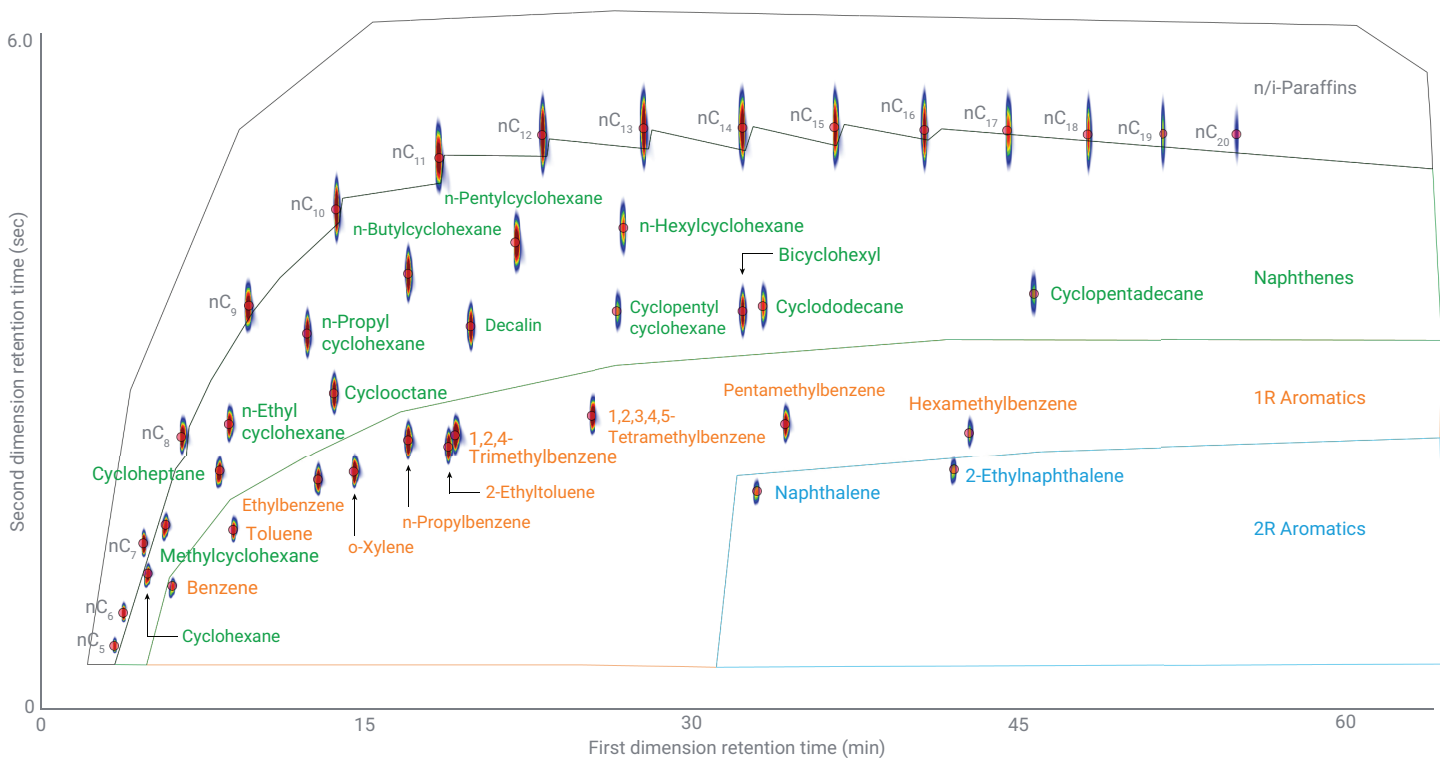
Figure 4. GCxGC-FID chromatogram of the gravimetric jet fuel standard using the helium carrier method.

To evaluate the precision of the RFM, 10 consecutive replicate injections of the gravimetric standard were analyzed, and the precision results for both methods are shown in Table 2. As shown, the retention time repeatability is exceptional, with perfect agreement for x-dimension retention and near-zero variance for y-dimension retention. The RFM also exhibits tight quantitative precision with nearly all compounds having less than 1.0% RSD across 10 consecutive replicates for both methods. In the gravimetric standard, 2-ethyltoluene and 1,2,4-trimethylbenzene elute very closely at high concentrations are good candidates for manual integration. Their results were included without manual correction for the hydrogen method to serve as an indicator for users concerned with quantifying critical pairs outside the scope of D8396. It should be noted that these data were collected under reproducibility conditions with the helium and hydrogen methods running on two different instruments on different days.

Table 2. Precision study (n = 10) of the hydrogen and helium carrier methods using the gravimetric standard.

Compound	First Dimension Retention (n = 10)				Second Dimension Retention (n = 10)				%Mass (n = 10)				
	Hydrogen Method		Helium Method		Hydrogen Method		Helium Method		Hydrogen Method		Helium Method		
	Average (min)	Sigma (min)	Average (min)	Sigma (min)	Average (sec)	Sigma (sec)	Average (sec)	Sigma (sec)	Average (%Mass)	%RSD	Average (%Mass)	%RSD	Expected (%Mass)
nC_5	2.92	0.0000	3.80	0.0000	0.46	0.0000	0.68	0.0016	0.46	1.14	0.52	0.84	0.5
nC_6	3.27	0.0000	4.20	0.0000	0.64	0.0026	0.95	0.0026	0.96	0.74	1.01	0.89	1.0
nC_7	3.91	0.0000	5.10	0.0000	0.87	0.0000	1.53	0.0021	1.93	0.52	2.07	0.36	2.0
nC_8	5.31	0.0000	6.80	0.0000	1.36	0.0021	2.42	0.0000	2.42	0.28	2.53	0.44	2.5
nC_9	7.76	0.0000	9.80	0.0000	1.96	0.0024	3.50	0.0016	3.45	0.17	3.52	0.27	3.5
nC_{10}	11.26	0.0000	13.70	0.0000	2.45	0.0016	4.31	0.0024	3.99	0.18	4.04	0.64	4.0
nC_{11}	15.52	0.0000	18.30	0.0000	2.71	0.0024	4.73	0.0026	4.74	0.62	4.73	0.28	4.75
nC_{12}	19.95	0.0000	22.90	0.0000	2.81	0.0021	4.92	0.0024	5.24	0.53	5.26	0.43	5.25
nC_{13}	24.38	0.0000	27.50	0.0000	2.80	0.0021	4.97	0.0024	5.47	0.16	5.48	0.23	5.5
nC_{14}	28.64	0.0000	31.90	0.0000	2.77	0.0033	4.98	0.0026	4.95	0.54	4.91	0.68	5.0
nC_{15}	32.72	0.0000	36.00	0.0000	2.72	0.0037	4.98	0.0024	4.22	0.25	4.03	0.44	4.25
nC_{16}	36.57	0.0000	40.00	0.0000	2.68	0.0024	4.96	0.0021	3.42	0.54	3.37	0.87	3.5
nC_{17}	40.31	0.0000	43.70	0.0000	2.64	0.0026	4.96	0.0034	2.70	0.49	2.48	0.52	2.75
nC_{18}	43.81	0.0000	47.30	0.0000	2.60	0.0039	4.93	0.0035	1.95	0.48	1.87	0.98	2.0
nC_{19}	47.13	0.0000	50.70	0.0000	2.56	0.0034	4.92	0.0044	0.96	0.40	0.92	0.48	1.0
nC_{20}	50.34	0.0000	54.00	0.0000	2.53	0.0035	4.92	0.0057	0.47	0.62	0.41	0.81	0.5
Methylcyclohexane	4.67	0.0000	6.10	0.0000	0.93	0.0026	1.68	0.0016	1.28	0.36	1.29	0.41	1.25
n-Ethylcyclohexane	7.00	0.0000	8.90	0.0000	1.37	0.0021	2.52	0.0024	1.99	0.20	2.05	0.29	2.0
n-Propylcyclohexane	10.03	0.0000	12.40	0.0000	1.79	0.0000	3.28	0.0016	2.74	0.15	2.81	0.41	2.75
n-Butylcyclohexane	14.17	0.0000	16.90	0.0000	2.08	0.0021	3.77	0.0024	3.54	0.18	3.60	0.56	3.5
n-Pentylcyclohexane	18.72	0.0000	21.70	0.0000	2.21	0.0000	4.03	0.0000	3.93	0.17	4.00	0.21	4.0
n-Hexylcyclohexane	23.39	0.0000	26.60	0.0000	2.26	0.0026	4.15	0.0016	1.47	0.15	1.46	0.40	1.5
Cyclohexane	4.02	0.0000	5.30	0.0000	0.72	0.0000	1.27	0.0000	1.22	0.50	1.30	0.42	1.25
Cycloheptane	6.59	0.0000	8.50	0.0000	1.13	0.0024	2.12	0.0016	2.01	0.28	2.07	0.40	2.0
Cyclooctane	11.08	0.0000	13.60	0.0000	1.49	0.0021	2.78	0.0000	2.78	0.23	2.84	0.43	2.75
Cyclododecane	29.28	0.0000	32.80	0.0000	1.79	0.0021	3.50	0.0026	1.28	0.35	1.27	0.49	1.25
Cyclopentadecane	41.01	0.0000	44.90	0.0000	1.76	0.0026	3.61	0.0024	0.75	0.52	0.72	0.45	0.75
Decalin	16.68	0.0000	19.70	0.0000	1.77	0.0016	3.34	0.0026	2.82	0.23	2.79	0.31	2.75
Cyclopentylcyclohexane	23.04	0.0000	26.30	0.0000	1.81	0.0016	3.46	0.0021	0.80	0.57	0.75	0.99	0.75
Bicyclohexyl	28.41	0.0000	31.90	0.0000	1.76	0.0024	3.46	0.0026	2.47	0.57	2.42	0.32	2.35
Benzene	4.90	0.0000	6.40	0.0000	0.65	0.0000	1.17	0.0000	0.51	0.93	0.51	0.63	0.5
Toluene	7.17	0.0000	9.10	0.0000	0.88	0.0000	1.63	0.0016	1.07	0.49	1.06	0.36	1.05
o-Xylene	11.96	0.0000	14.50	0.0000	1.12	0.0000	2.12	0.0000	2.79	0.19	2.79	0.38	2.75
Ethylbenzene	10.44	0.0000	12.90	0.0000	1.07	0.0000	2.06	0.0021	2.05	0.26	2.05	0.52	2.0
2-Ethyltoluene	15.81	0.0000	18.70	0.0000	1.20	0.0000	2.34	0.0016	2.91	2.23	2.94	0.40	3.0
n-Propylbenzene	14.17	0.0000	16.90	0.0000	1.25	0.0016	2.39	0.0016	4.04	0.15	4.09	0.29	4.0
1,2,4-Trimethylbenzene	16.10	0.0000	19.00	0.0000	1.26	0.0016	2.44	0.0016	3.77	1.72	3.69	0.31	3.5
1,2,4,5-Tetramethylbenzene	21.93	0.0000	25.10	0.0000	1.32	0.0016	2.60	0.0016	2.82	0.30	2.76	0.31	2.75
Pentamethylbenzene	30.33	0.0000	33.80	0.0000	1.22	0.0024	2.52	0.0021	2.03	0.27	1.99	0.35	2.0
Hexamethylbenzene	38.27	0.0000	42.00	0.0000	1.12	0.0026	2.45	0.0024	0.52	0.28	0.50	0.44	0.5
Naphthalene	28.93	0.0000	32.50	0.0000	0.89	0.0024	1.96	0.0021	0.55	0.12	0.53	0.48	0.55
2-Ethylnaphthalene	37.51	0.0000	41.24	0.0000	0.92	0.0000	2.12	0.0097	0.55	0.23	0.51	0.50	0.55

These results illustrate a major advantage of the RFM with the collection and reinjection of eluent controlled by Agilent's 6th-generation EPC technology. The PSD controlling the carrier gas flow to the RFM works in tandem with the inlet EPC to make real-time pressure adjustments at the modulator which yields exceptional retention time repeatability in GCxGC applications. When combined with GC Image's template transformation capabilities (discussed later), the RFM greatly accelerates both the act of changing the columns in the instrument and the process of reconciling the resulting minor peak movements observed during data analysis.

In addition to the high degree of retention precision afforded by the RFM, this system configuration is designed with extra retention space by using a short modulation period and a low final oven temperature. From the second-dimension retention data for the gravimetric standard in Table 2 and the chromatograms in Figures 3 and 4, approximately one-third of the vertical retention space is unused. This provides flexibility to users who wish to fine-tune the separation through mild changes to the oven ramp rate and modulation period to meet their specific requirements. Additionally, the DB-17 phase has a maximum programmable temperature of 300 °C compared to the jet fuel method final oven temperature of 230 °C, and heavier samples can be analyzed by simply increasing the final oven temperature.

Comparison of hydrogen and helium separations

Figure 5 shows the separation of the jet fuel reference standard using the hydrogen method. Each shaded circle marks the apex of an integrated peak, and the color of the marker indicates the assigned molecular class (the red markers are compounds that are also present in the gravimetric mixture). The narrow blue vertical "blobs" are chromatographic peaks and the intensity of their corresponding detector response on the Z-axis (toward the reader) is shown using a rainbow color gradient that progresses from blue (low signal) to red (high signal). As shown, the RFM produces sharp peaks that result in distinct molecular regions and unambiguous classification of practically all compounds in jet fuel.
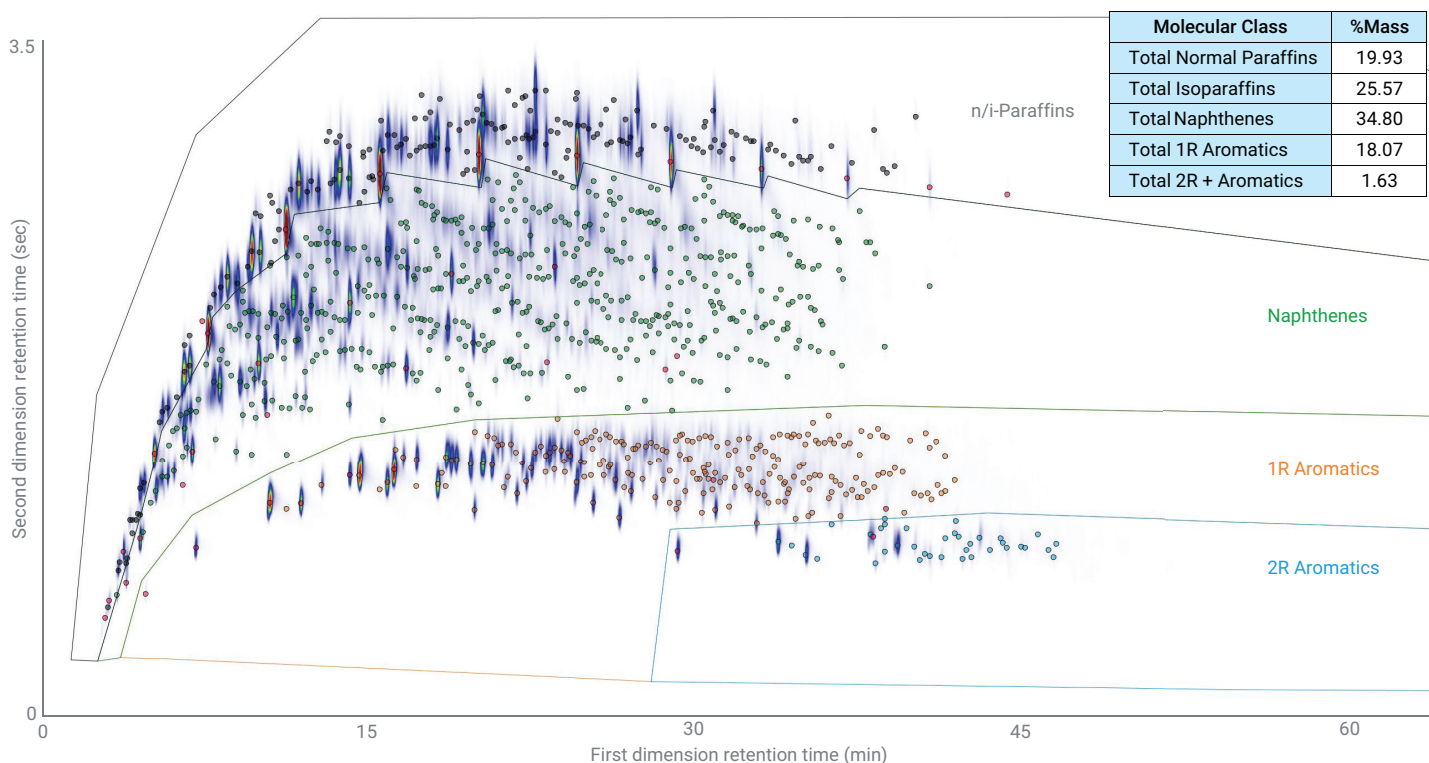

Molecular Class	%Mass
Total Normal Paraffins	19.93
Total Isoparaffins	25.57
Total Naphthenes	34.80
Total 1R Aromatics	18.07
Total 2R + Aromatics	1.63

Figure 5. GCxGC-FID chromatogram of the 717 Jet Fuel Reference sample using the hydrogen carrier method.
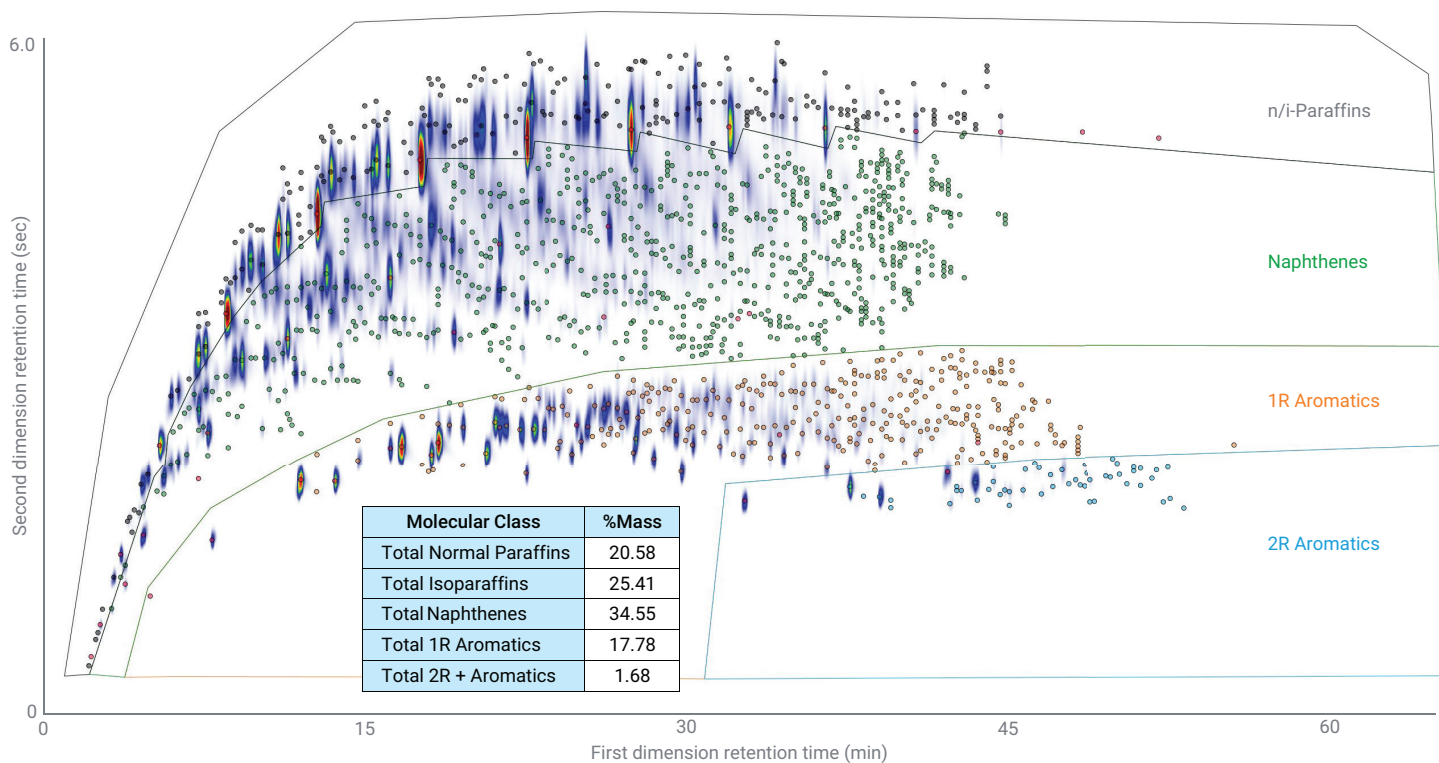
Figure 6. GCxGC-FID chromatogram of the 717 Jet Fuel Reference sample using the helium carrier method.

Molecular Class	%Mass
Total Normal Paraffins	20.58
Total Isoparaffins	25.41
Total Naphthenes	34.55
Total 1R Aromatics	17.78
Total 2R + Aromatics	1.68

The RFM (and flow modulation in general) requires a fast re-injection of the collected column 1 eluent onto column 2 to produce sharp peaks, and this is done using a high column 2 flow. However, this high flow results in very high linear velocities through column 2, and hydrogen exhibits significantly less band broadening than helium at high linear velocities. This makes hydrogen the preferred carrier gas for flow-modulated GCxGC.

The helium carrier separation of the 717 reference jet fuel is shown in Figure 6 and is visually similar to the hydrogen carrier separation in Figure 5. However, the helium method requires increasing the modulation period from 3.5 to 6.0 seconds and reduces the first-dimension resolution by the same proportion. This can be seen by visually comparing the number of resolved isoparaffin peaks (circular markers)

between any given normal paraffin in both separations. For group-type analyses such as ASTM D8396, this resolution loss may lead to minor biases when quantifying normal paraffins but otherwise agrees closely with results obtained using hydrogen.

The Agilent 8890 GC is designed to use hydrogen as a carrier gas and includes several built-in safety features to support the safe use of hydrogen carrier. In addition to these standard features, the 8890 can be outfitted with the optional Hydrogen Sensor Module Series 2 (part number G6598A), which actively monitors for free hydrogen in the oven and shuts down all hydrogen flow modules if the level reaches 1%, well below the reported[2] lower flammability limit of 4% and lower explosion limit of 18.3%.

GC Image templates

The analysis of GCxGC data, sometimes containing thousands of individual peaks, is made simple in GC Image using identification templates. Much like a map with cities and borders between countries, templates use a combination of points, lines, and shapes to identify compounds and demarcate between molecular groups and classes. Applying a template to a chromatogram in GC Image copies the recorded template information (compound identity, molecular class, internal standard association, etc.) to the chromatographic data. Just like in conventional GC, these boundaries are commonly determined using chemical standards and may require revalidation following instrument maintenance. GC Image greatly simplifies this process using an intuitive workflow to adjust and fit the template to the new separation using a series of affine transformations. For D8396 workflows, manually assigning four to eight peaks in the gravimetric mixture near the corners of the chromatogram can produce an aligned and transformed template in under one minute.

Opening the **Interactive Match and Transform** option in GC Image and selecting **Affine Transform** allows the user to assign peaks in the template to known peaks (such as those in the gravimetric standard) in the new separation. As individual peaks are assigned, GC Image shows real-time graphical feedback on the calculated new locations for all template peaks using lead lines that connect circles marking the new locations with the originals. Not all peaks must be assigned, and the process can be stopped at any time if the desired transformation is achieved. Figure 7 illustrates the Interactive Match and Transform process being used to create the helium method template by reconciling the hydrogen method template (colored magenta) with the helium method gravimetric separation (Figure 7A). The small hollow magenta markers indicate the original location of the hydrogen method template peaks, and the connective lines illustrate their calculated new locations as more peaks are manually assigned. As shown in Figure 7B, manually assigning just the naphthalene and nC_{20} peaks visibly reconciles most of the peak identities to the point where manual reconciliation of the remainder is trivial. Further assignment of nC_7, nC_{10}, and ethylbenzene results in better reconciliation of the remaining peaks at the front of the separation and is shown in Figure 7C, with the fully reconciled template shown in Figure 7D.
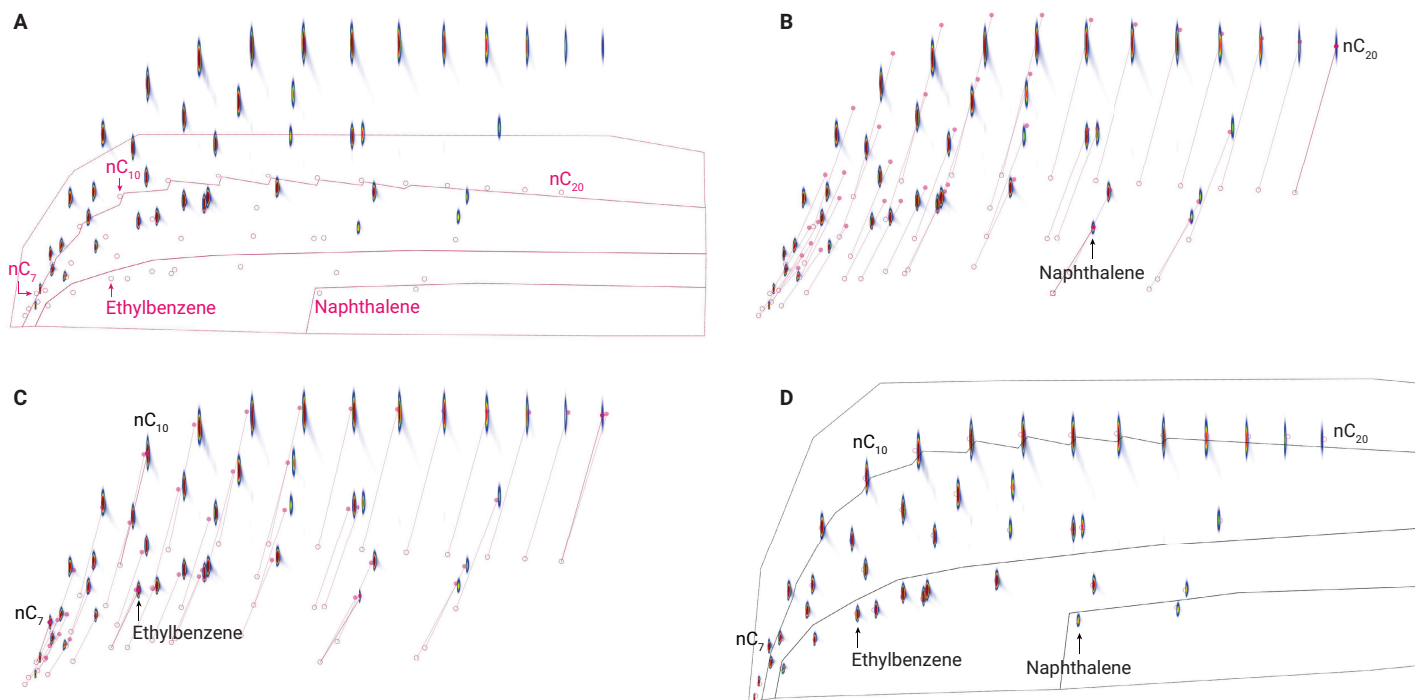

Figure 7. (A) Overlay of hydrogen carrier template (magenta) with the helium carrier method gravimetric standard chromatogram. (B) Calculated affine transformation of hydrogen carrier template peaks after assigning nC_{20} and naphthalene. (C) Calculated affine transformation of hydrogen carrier template peaks after assigning ethylbenzene, nC_7, and nC_{10}. (D) Resulting helium carrier template (black) after reconciling the hydrogen carrier template using the Interactive Match and Transform capability in GC Image.

Example SATF and conventional jet fuel chromatograms

The molecular class identification templates developed using the gravimetric and reference jet fuels are also used when analyzing unconventional mixtures such as SATF. Figure 8 shows the hydrogen carrier separation of a Fischer-Tropsch synthetic paraffinic kerosene (FT-SPK), which was acquired as part of a collaborative study. While drastic changes in composition can result in minor peak movements, the high degree of retention precision of the RFM helps users delineate between molecular classes for confident quantification. Even though the FT-SPK sample is mostly paraffinic, the separation between the paraffin and naphthene regions is clear, and several compounds that were identified in the gravimetric mixture are also present (magenta peak markers).
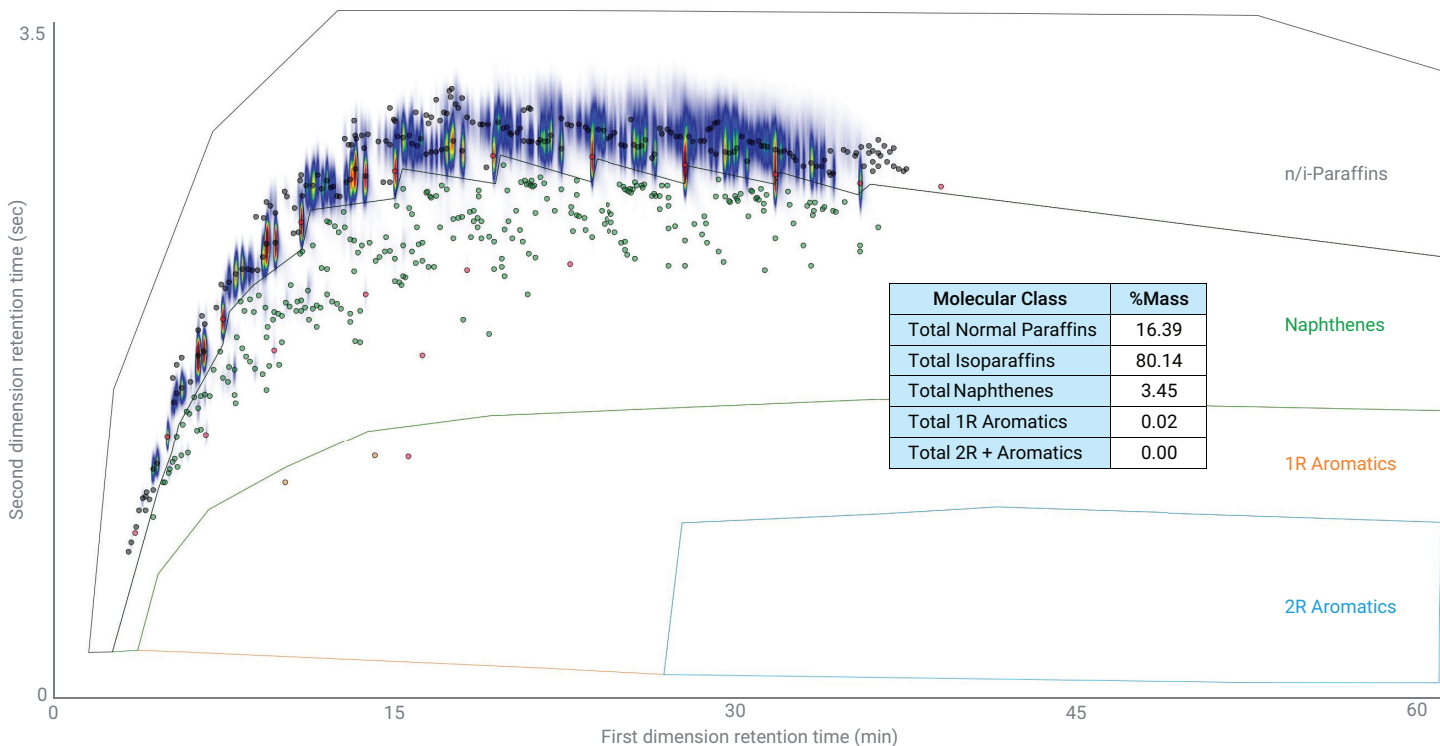

Molecular Class	%Mass
Total Normal Paraffins	16.39
Total Isoparaffins	80.14
Total Naphthenes	3.45
Total 1R Aromatics	0.02
Total 2R + Aromatics	0.00

Figure 8. GCxGC-FID chromatogram of an FT-SPK sample.

Figure 9 shows the GCxGC-FID chromatogram for a hydroprocessed ester and fatty acid (HEFA) SATF. This material is similar in composition to FT-SPK in that it is almost entirely paraffinic; however, the chromatogram reveals that the class distribution of this HEFA sample is more isoparaffinic and centered around C_{16} and C_{17}. This granular level of detail can provide valuable process insights for users formulating new SATF materials.

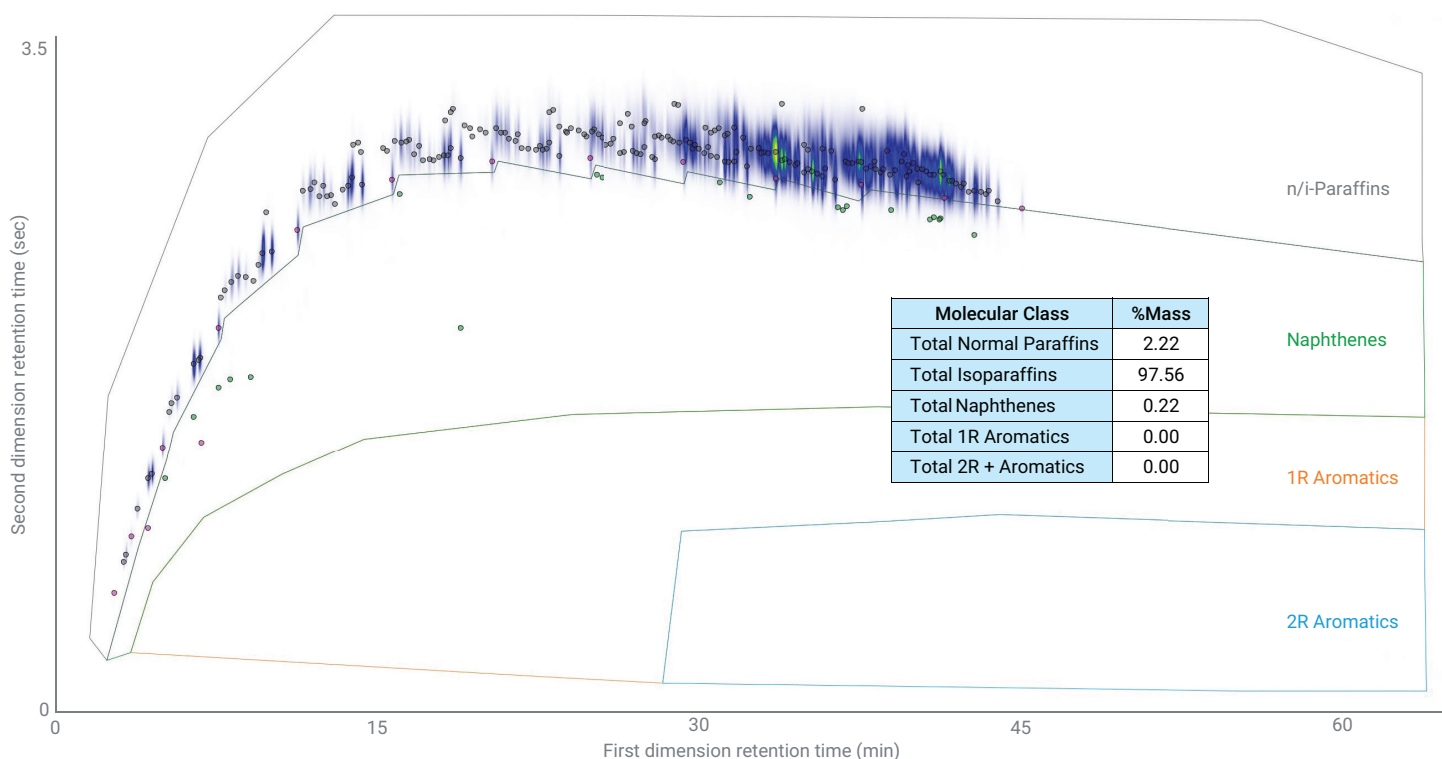| Molecular Class	%Mass
Total Normal Paraffins	2.22
Total Isoparaffins	97.56
Total Naphthenes	0.22
Total 1R Aromatics	0.00
Total 2R + Aromatics	0.00

Figure 9. GCxGC-FID chromatogram of an HEFA-SPK sample.

The NIST 1616b Sulfur in Kerosene standard is slightly heavier than the jet fuel reference standard and trades lower paraffin content for higher aromatic content. The GCxGC-FID chromatogram of the 1616b standard using hydrogen carrier is shown in Figure 10. In addition to the quantitative results by D8396, the GCxGC chromatogram of the 1616b standard reveals the subtle differences of the molecular distribution when compared to the jet fuel reference standard in Figure 5. The 1616b standard has a paraffinic distribution maximum centered around nC_{12} and an aromatic distribution maximum at approximately pentamethylbenzene, compared to the reference jet fuel with maxima at nC_{10} and n-propylbenzene.

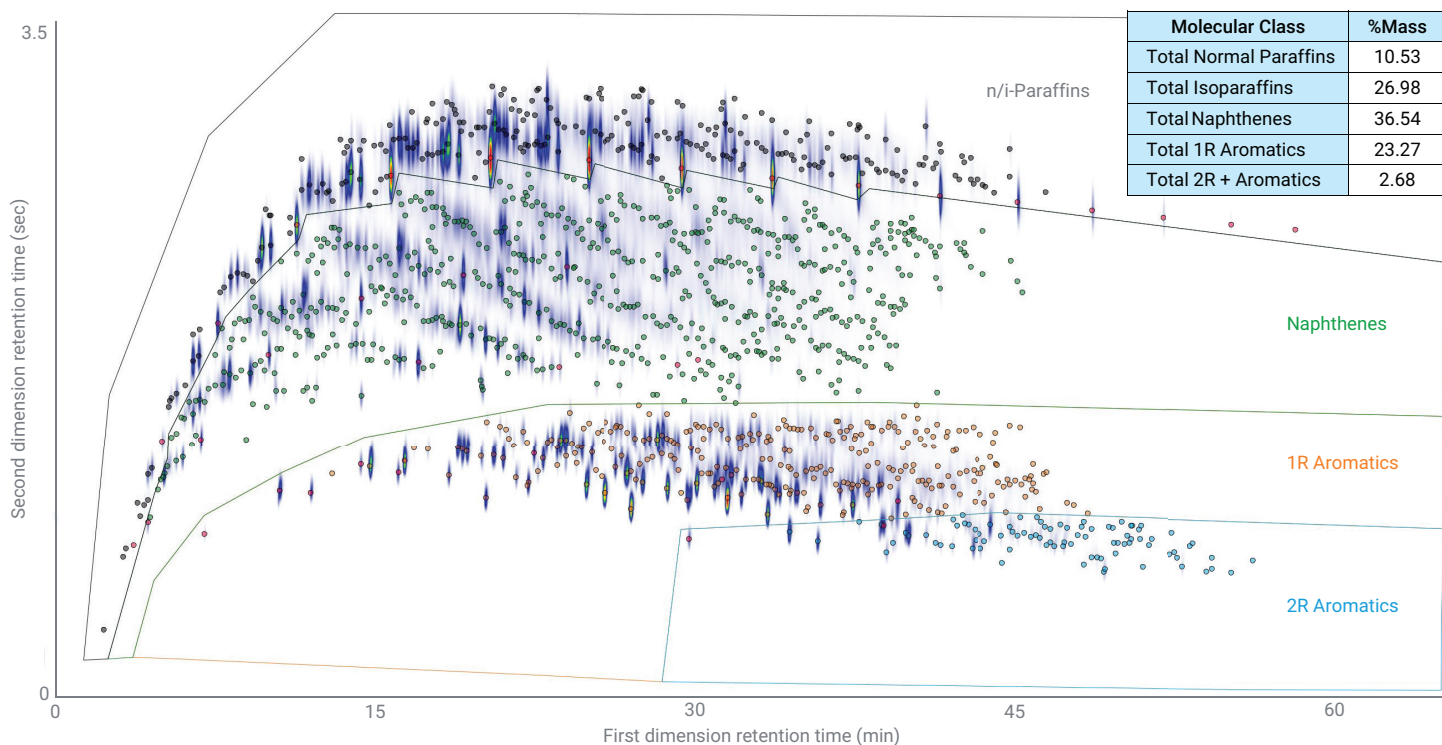| Molecular Class	%Mass
Total Normal Paraffins	10.53
Total Isoparaffins	26.98
Total Naphthenes	36.54
Total 1R Aromatics	23.27
Total 2R + Aromatics	2.68

Figure 10. GCxGC-FID chromatogram of the NIST 1616b Sulfur in Kerosene standard reference material.

The CRMU-DEKR sample from LGC is a reference material for density testing and is made of sweetened kerosene, a common term for a jet fuel precursor or blend component. The GCxGC-FID chromatogram for the sweetened kerosene is shown in Figure 11 and has a similar composition to that of the jet fuel reference standard shown in Figure 5. GC Image has several built-in tools for comparing sample data, and Figure 12 shows the side-by-side comparison of the DEKR sweetened kerosene (red) with the 1616b low-sulfur kerosene (blue). In addition to the visual comparison, differences between individual compound peaks (called "blobs" in GC Image) are tabulated for both retention and detector response for a more-granular analysis. The comparison functionality also includes the affine transformation capability shown in Figure 7 to align and enable comparison of samples that may be slightly shifted due to column aging, sample data that was generated years prior, or even samples run on a different instrument.
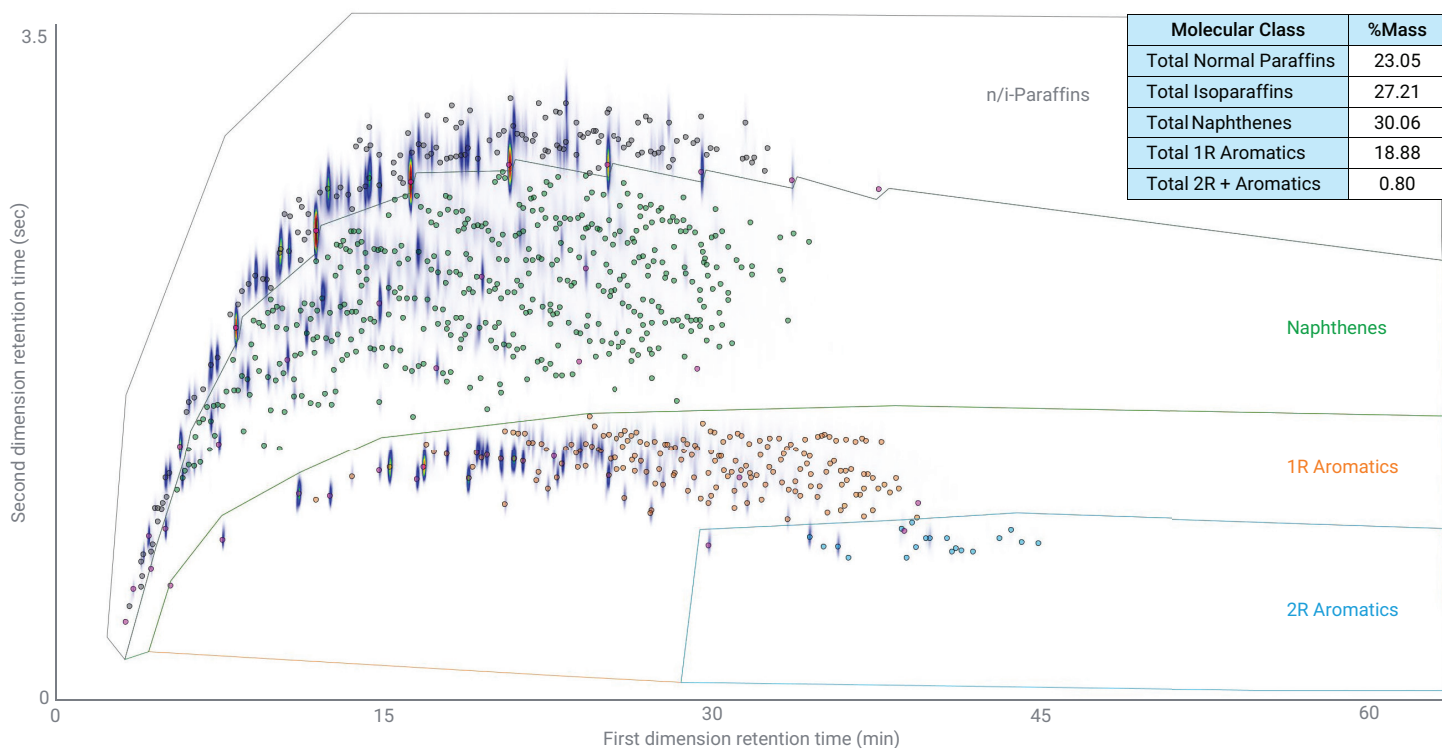

Molecular Class	%Mass
Total Normal Paraffins	23.05
Total Isoparaffins	27.21
Total Naphthenes	30.06
Total 1R Aromatics	18.88
Total 2R + Aromatics	0.80

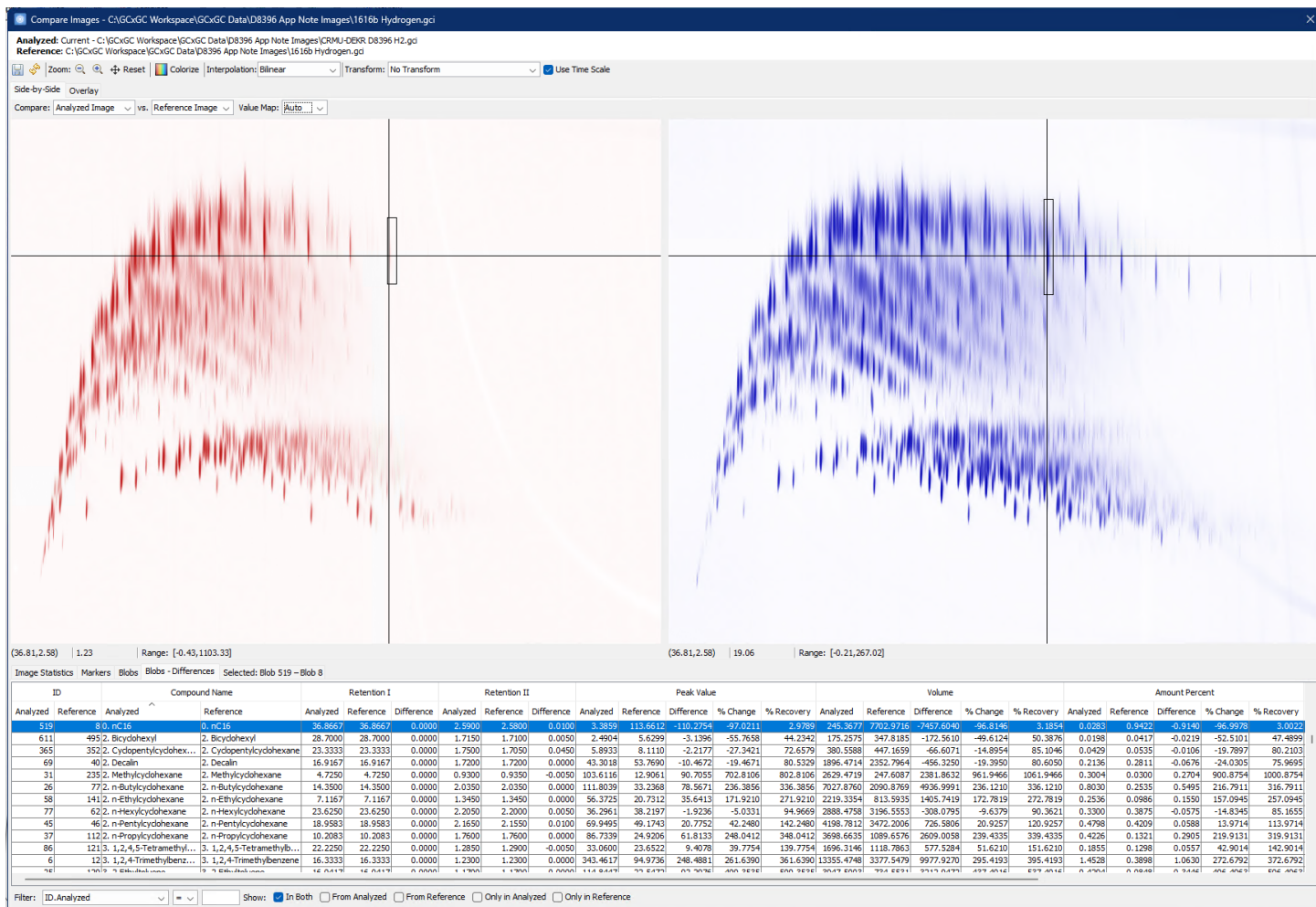**Figure 11.** GCxGC-FID chromatogram of the CRMU-DEKR sweetened kerosene sample.

Figure 12. Comparison of the CRMU-DEKR sweetened kerosene (red) with the 1616b low-sulfur kerosene (blue) using the GC Image Compare Images tool.

Expanding the method to diesel

Though out-of-scope of ASTM D8396, this configuration can accommodate diesel samples simply by extending the final oven temperature from 230 to 300 °C, which is the maximum temperature of the DB-17 column. This allows polyaromatic species containing three and four aromatic rings to elute from the system, as well as the separation of FAMEs present in biodiesel. Figure 13 shows a biodiesel blend analyzed using the hydrogen carrier method by increasing the final oven temperature to 300 °C. The FAMEs content can be seen in the monoaromatic region indicated by magenta annotations.
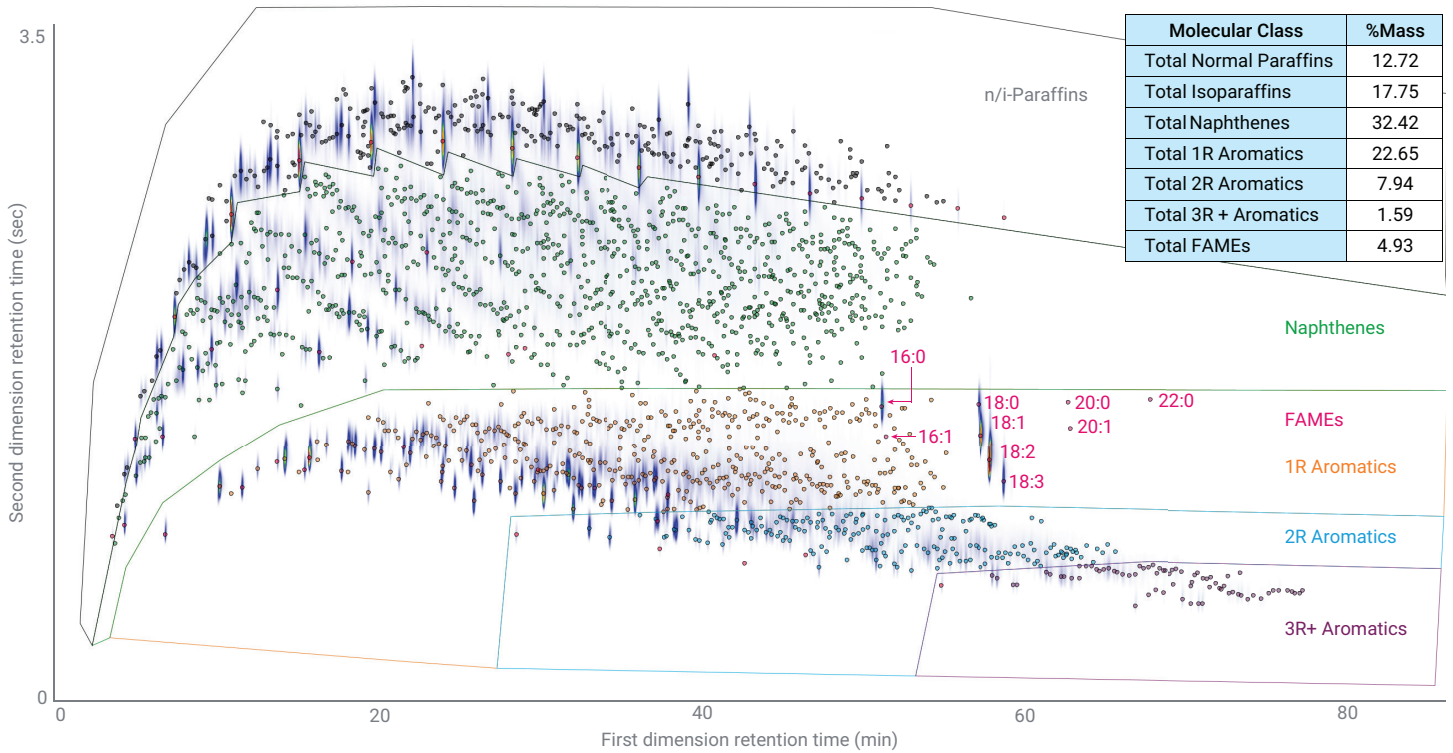

Molecular Class	%Mass
Total Normal Paraffins	12.72
Total Isoparaffins	17.75
Total Naphthenes	32.42
Total 1R Aromatics	22.65
Total 2R Aromatics	7.94
Total 3R + Aromatics	1.59
Total FAMEs	4.93

Figure 13. GCxGC chromatogram of a blended diesel sample with FAMEs content.

Conclusion

An Agilent 8890 GC configured with an Agilent Reversed Flow Modulator has been demonstrated as a simple, precise, and robust GCxGC flow modulator through the application of ASTM D8396 using both hydrogen and helium carrier. Identification of marker compounds and delineation between molecular classes was achieved using the template-based identification protocol within GC Image. Group-based quantification was demonstrated for conventional jet fuel, SATF as FT-SPK and HEFA-SPK, kerosene, and a diesel-FAME blend. A precision study was conducted with 10 consecutive replicate injections of a gravimetric mixture and showed quantitative precision of less than 1.0 %RSD for practically all 42 compounds over a concentration range of 0.50 to 5.50% mass. The exceptional retention time repeatability from Agilent's 6th-generation EPC technology combined with GC Image's advanced and intuitive image transformation capabilities establishes the foundation for long-term success with D8396 and future GCxGC test methods.

Acknowledgements

References

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