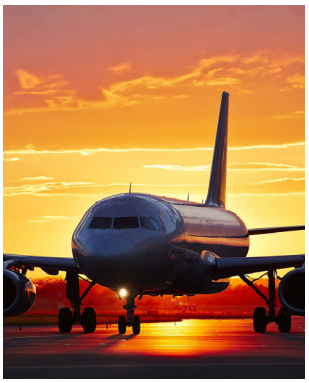
White Paper 058
September 2024

Group-type analysis of hydrocarbons in aviation fuel and other middle distillates (ASTM Method D8396)



This white paper demonstrates the enhancement of productivity and the streamlining of group-type analysis workflows for speciation of hydrocarbons in finished fuels using flow-modulated GC×GC–FID (as outlined in ASTM Method D8396).

Introduction

Finished fuels, such as jet fuel (or aviation turbine fuel, AVTUR) are strictly regulated to ensure the total aromatic content does not exceed specified limits. Aromatics typically burn more slowly than paraffins and produce more soot and particulate matter. This affects combustion properties and environmental emissions.

Traditional specifications mandate that the aromatic content of jet fuel must fall below 25% by volume[1]. The aviation industry's shift towards reducing its carbon footprint, means new sustainable aviation fuels (SAFs) are being developed which contain significantly lower aromatic content. To address this, specifications now require a minimum aromatic content of 8%[2] by volume to ensure the proper swelling of certain O-rings and seals to prevent leaks. SAFs are typically blended with conventional jet fuels to meet the minimum requirements, emphasising the need for rigorous testing of hydrocarbon composition to ensure compliance and safety.

Legacy test methods, such as ASTM Method D2425[3], fail to provide detailed characterisation of hydrocarbon composition, which is crucial for quality control, and assessing product performance and the effects of production processes. To overcome this, ASTM Method D8396[4] has been developed to deliver more accurate quantitative information on hydrocarbon composition through group-

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type analysis using flow-modulated GC×GC–FID. A key advantage of GC×GC is the structured ordering of chromatograms where chemical classes elute together in well-defined bands. These can be easily quantified by drawing stencil regions around the bands of peaks in what is known as group-type analysis.

Additionally, unlike ASTM Method D2425, the use of GC×GC eliminates the need for expensive mass spectrometers, keeping running costs low and simplifying implementation in routine or production labs.

In this study, the use of the INSIGHT®-Flow reverse fill/flush (RFF) flow-modulator for GC×GC–FID is demonstrated alongside automated group-type analysis in ChromSpace® software, to provide fast and accurate quantitative information on hydrocarbon composition. A unique feature of this product package is its ability to analyse two samples simultaneously in a dual-channel configuration, effectively doubling the productivity.

Experimental

Samples: A reference standard and reference blends of both diesel and aviation turbine fuel.

GC×GC: Modulator: INSIGHT®-Flow reverse fill/flush (RFF) flow modulator (SepSolve Analytical); Modulation period (P_M): 7.8 s. Carrier gas: H_2.

Column set: ASTM D8396 reverse phase column set (SepSolve Analytical, PN: OEM-SEP-COLKIT-10)

FID: Total H_2 flow (column and fuel): 50 mL/min; Air flow: 350 mL/min: Makeup gas flow: 5 mL/min; Temperature: 300°C.

Software: ChromSpace® GC×GC software for instrument control and data processing.

Please contact SepSolve for full analytical parameters.

Results and discussion

Optimising the GC×GC separation

The INSIGHT-Flow modulator used in this study has an adjustable sample loop (in the range of 25-250 µL) for greater flexibility in method development. Separation was optimised using a custom column set and larger loop volume, enabling excellent separation of the key chemical classes.

This is evident in the GC×GC–FID colour plot (Figure 1) of a reference standard containing a mix of paraffins, naphthenes and aromatics, used to optimise class separation. In this case, the separation offers excellent distinction between the chemical classes for robust and confident results.

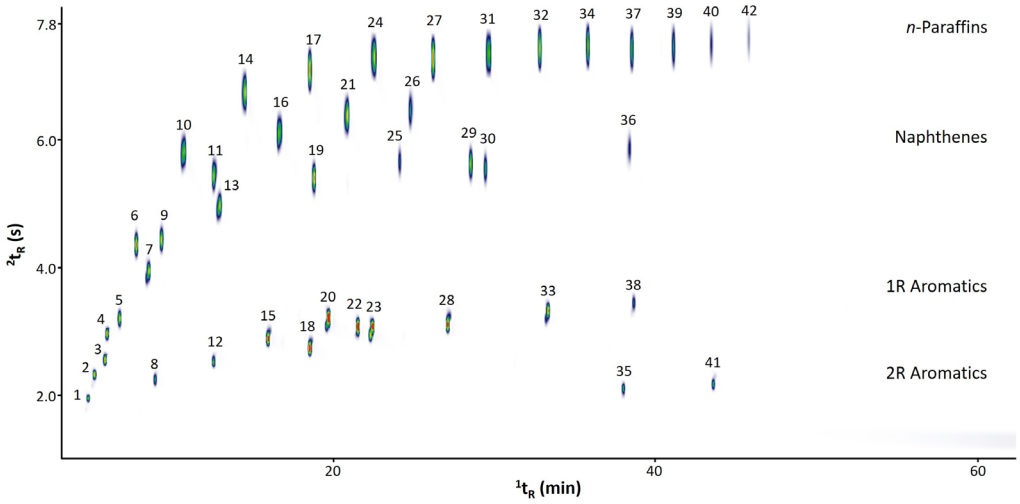

Figure 1

GC×GC–FID colour plot for the separation of a reference standard containing chemical classes of interest.

The reference standard was analysed in replicate (n=10) to assess method repeatability and precision. The results shown in Table 1 demonstrate excellent repeatability, with the relative standard deviation (RSD) of the raw peak areas consistently within 2%. Figure 2 further illustrates method precision, showing that the calculated mass percent values were consistently within 0.5% of the known composition.

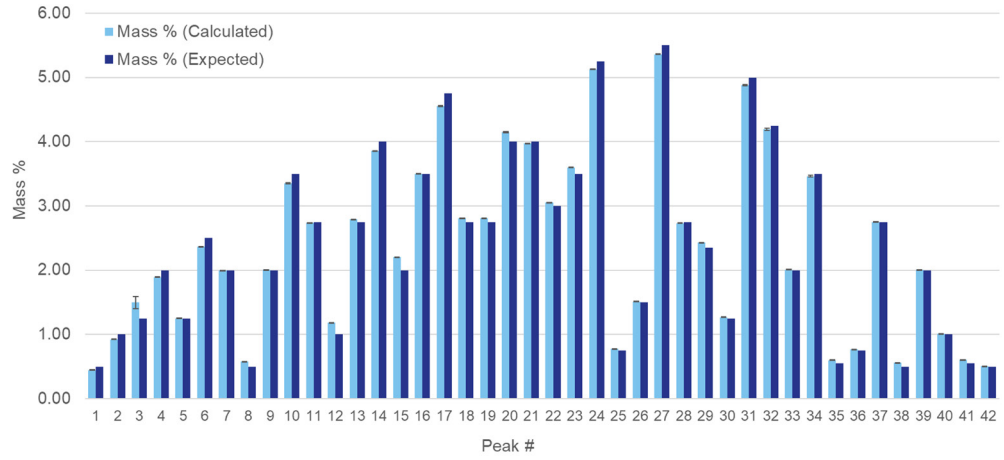

Figure 2

Comparison of the known mass % values for the reference standard with those calculated across 10 replicate injections. Peak identities are provided in Table 1.

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Peak #	Component	Average peak area (n=10)	RSD (%)	Relative response factor (RRF)	Average calculated mass % (n=10)	Expected mass %
1	Pentane	6.07E+07	1.72	1.0080	0.44	0.50
2	Hexane	1.26E+08	1.72	1.0034	0.92	1.00
3	Cyclohexane*	1.99E+08	8.26	0.9799	1.50	1.25
4	Heptane	2.57E+08	1.67	1.0000	1.89	2.00
5	Methylcyclohexane	1.66E+08	1.59	0.9799	1.25	1.25
6	Octane	3.20E+08	1.72	0.9975	2.36	2.50
7	Cycloheptane	2.66E+08	1.66	0.9799	1.99	2.00
8	Benzene	7.10E+07	1.66	0.9095	0.57	0.50
9	Ethylcyclohexane	2.66E+08	1.80	0.9799	2.00	2.00
10	Nonane	4.54E+08	1.69	0.9955	3.35	3.50
11	Propylcyclohexane	3.64E+08	1.70	0.9799	2.73	2.75
12	Toluene	1.47E+08	1.70	0.9195	1.18	1.00
13	Cyclooctane	3.72E+08	1.70	0.9799	2.79	2.75
14	Decane	5.21E+08	1.74	0.9940	3.85	4.00
15	Ethylbenzene	2.77E+08	1.71	0.9271	2.20	2.00
16	Butylcyclohexane	4.66E+08	1.72	0.9799	3.50	3.50
17	Undecane	6.14E+08	1.70	0.9927	4.55	4.75
18	o-Xylene	3.53E+08	1.70	0.9271	2.81	2.75
19	Decaline	3.69E+08	1.70	0.9658	2.81	2.75
20	Propylbenzene	5.26E+08	1.71	0.9329	4.15	4.00
21	Pentylcyclohexane	5.29E+08	1.71	0.9799	3.97	4.00
22	2-Ethyltoluene	3.87E+08	1.72	0.9329	3.05	3.00
23	1,2,4-Trimethylbenzene	4.56E+08	1.69	0.9329	3.60	3.50
24	Dodecane	6.91E+08	1.71	0.9916	5.13	5.25
25	Cyclopentylcyclohexane	1.01E+08	1.67	0.9671	0.77	0.75
26	Hexylcyclohexane	2.01E+08	1.77	0.9799	1.51	1.50
27	Tridecane	7.22E+08	1.69	0.9907	5.36	5.50
28	1,2,4,5-Tetramethylbenzene	3.48E+08	1.70	0.9376	2.73	2.75
29	Bicyclohexyl	3.19E+08	1.68	0.9681	2.43	2.35
30	Cyclododecane	1.69E+08	1.66	0.9799	1.27	1.25
31	Tetradecane	6.56E+08	1.65	0.9899	4.88	5.00
32	Pentadecane	5.63E+08	1.95	0.9893	4.19	4.25
33	Pentamethylbenzene	2.57E+08	1.65	0.9415	2.01	2.00
34	Hexadecane	4.65E+08	1.81	0.9887	3.46	3.50
35	Naphthalene	7.29E+07	1.63	0.8954	0.60	0.55
36	Cyclopentadecane	1.02E+08	1.65	0.9799	0.77	0.75
37	Heptadecane	3.69E+08	1.73	0.9882	2.75	2.75
38	Hexamethylbenzene	7.13E+07	1.63	0.9447	0.56	0.50
39	Octadecane	2.69E+08	1.73	0.9877	2.00	2.00
40	Nonadecane	1.36E+08	1.76	0.9873	1.01	1.00
41	Ethylnaphthalene	7.32E+07	1.60	0.8919	0.60	0.55
42	Eicosane	6.76E+07	1.81	0.9869	0.50	0.50

Table 1

Evaluation of method repeatability and precision via replicate analysis (n=10) of the reference standard shown in Figure 1.

**Note that cyclohexane was used as the wash solvent, thus impacting repeatability for this component.*

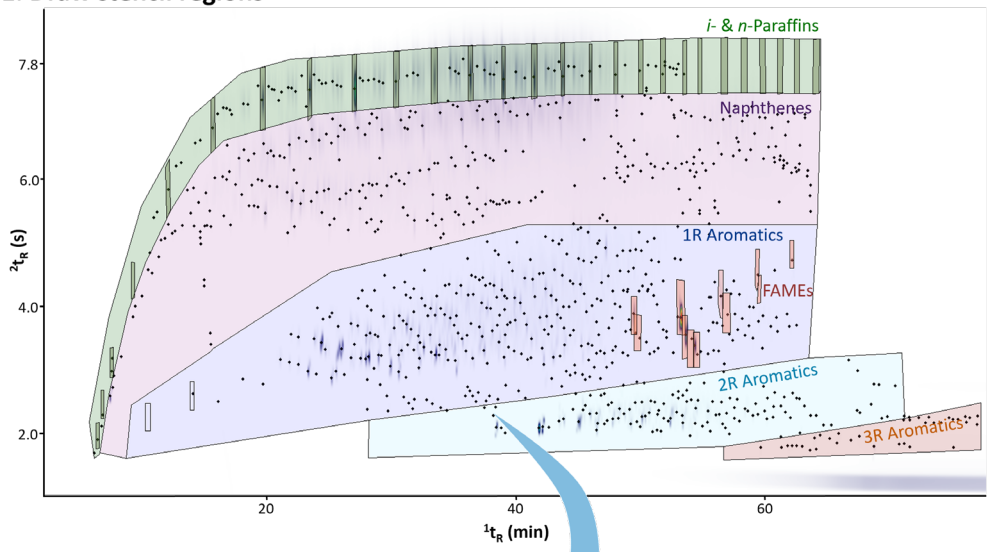
Group-type classifications

Once the separation was optimised, reference blends of jet fuel and diesel were analysed to enable stencil boundaries to be defined around the key chemical classes – namely, n-paraffins, iso-paraffins, naphthenes, fatty acid methyl esters (FAMEs) and aromatics (further sub-divided as 1R, 2R or 3R, based on the number of aromatic rings present).

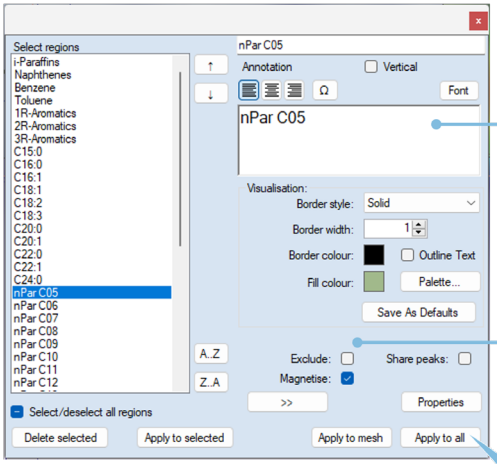
Figure 3 shows the group-type workflow in ChromSpace software as applied to a reference diesel blend. Stencil regions are easily customised and configured to suit user preferences (Figure 3, middle). After integration of each stencil region, the areas are translated into an area percent table (Figure 3, bottom) providing a fast and robust overview of sample composition.

Stencils can be saved and applied to multiple data files in an automated batch sequence to generate area percent reports, enabling the method to be scalable across multiple GC×GC–FID platforms for fast classification. This proven workflow has already gained accredited status in several high-throughput contract labs for the analysis of total petroleum hydrocarbons (TPH).

1. Draw stencil regions



2. Customise stencil regions



Stencil regions can be named and ranked in a user-defined order, and customised in terms of style

Regions can easily be excluded, e.g. column bleed

3. Integrate to generate area percent report

Area Percent

Peak #	Source	Area	Area %	Status
Group 48	Total Paraffins	5.1834E+09	44.99	Include
Group 47	Total FAMEs	8.42453E+08	7.31	Included
Group 46	Total Aromatics	1.84676E+09	16.03	Included
Group 3	Benzene	0	0	Included
Group 4	Toluene	9.20147E+05	0.01	Included
Group 5	1R-Aromatics	1.62108E+09	14.07	Included
Group 6	2R-Aromatics	1.75288E+08	1.52	Included
Group 7	3R-Aromatics	4.94728E+07	0.43	Included
Group 49	n-Paraffins	2.37882E+09	20.65	Included
Group 1	i-Paraffins	2.80458E+09	24.34	Included
Group 2	Naphthenes	3.64944E+09	31.67	Included

Figure 3

Group-type analysis workflow in ChromSpace software.

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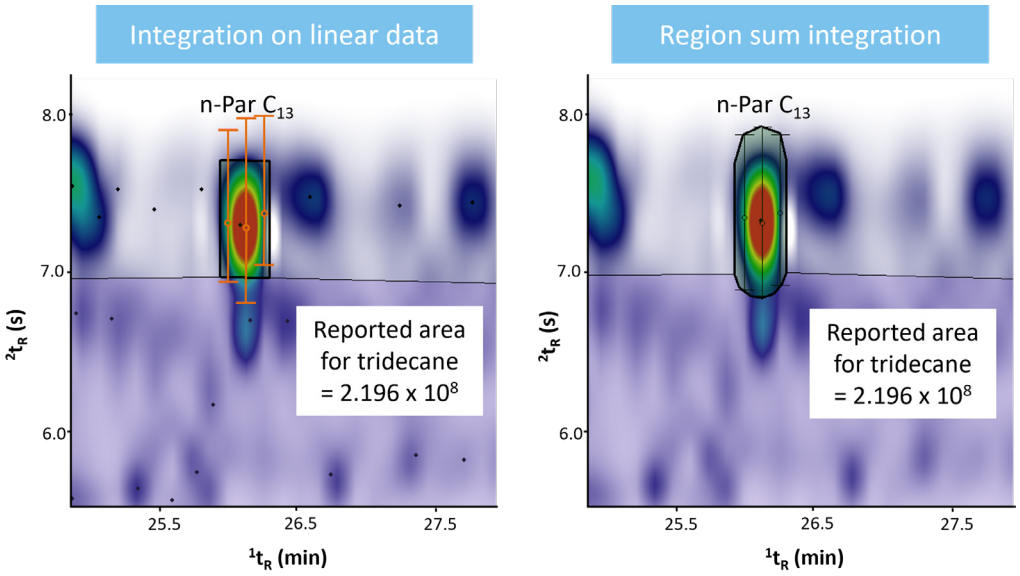

Figure 4

A close-up of stencils integrated using two different approaches. Note that both integration methods report the same values, but greater care must be taken when defining stencil boundaries when using 'region sum.'

Alternative integration methods for group-type reporting

Unlike other GC×GC software platforms, ChromSpace offers the flexibility to employ different integration methods for group-type reporting, catering to user preference.

The first method involves a two-step process where peak integration is initially applied to the linear data, followed by merging the modulated sub-peaks to determine peak areas. In this approach, if a peak apex falls within a stencil region, the entire peak area is reported, even if the tail extends beyond the region (Figure 4, left), meaning stencil boundaries do not have to be drawn carefully around each individual peak. Alternatively, integration can be carried out by summing the total signal within a region, known as 'region sum.' However, in this approach it is crucial to accurately define the stencil boundaries to avoid inaccurate reporting (Figure 4, right). It is important to note that some software packages only offer this approach, which is often more laborious because the stencils must be drawn precisely and reviewed regularly.

In this study, the 'peak based' approach has been applied for faster stencil development and reduced risk of reporting errors when applying the stencil to varied sample types.

The completed stencil was applied to numerous reference blends of diesel and jet fuel to ensure that the calculated mass percent values aligned well with the known concentrations (Figure 5).

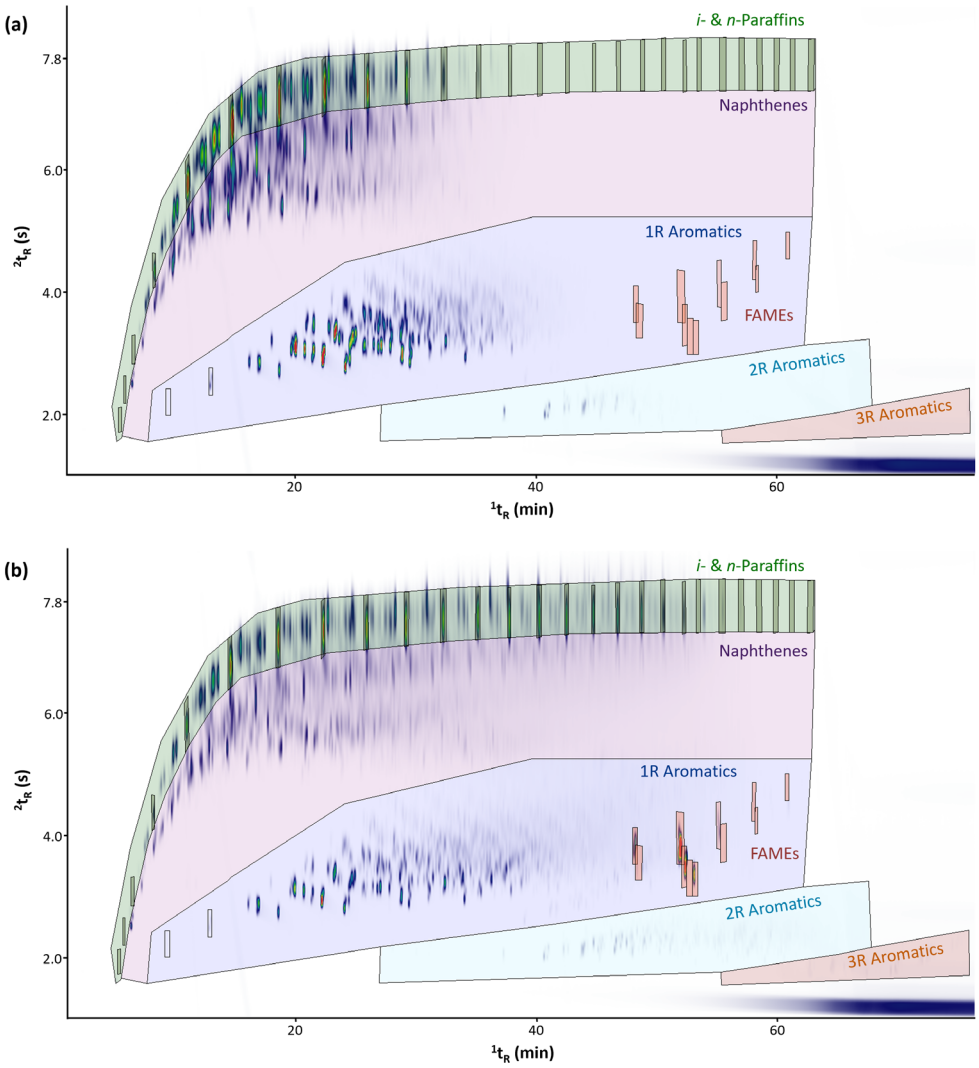

Figure 5

GC×GC–FID colour plots for (a) jet fuel reference blend and (b) diesel reference blend with a comparison of the calculated and expected mass percent values for the aromatic regions.

Group	(a) Jet fuel reference blend		(b) Diesel reference blend	
	Calculated mass %	Expected mass %	Calculated mass %	Expected mass %
1R-Aromatics	24.69	24.30	18.18	18.38
2R-Aromatics	0.31	0.03	0.85	0.90
3R Aromatics	0.00	*No value reported*	0.49	0.11
Total Aromatics	25.00	24.60	19.52	19.31

Improving productivity with dual channel GC×GC–FID

A unique feature of SepSolve's product package for ASTM Method D8396 is the ability to double productivity via dual-channel GC×GC–FID. Here, two INSIGHT-Flow modulators are configured within the same GC oven (Figure 6) to enable simultaneous analysis of two samples in a dual-channel mode.The dual-channel system is fully controlled using ChromSpace, with reporting of data from both channels performed in automated sequences.

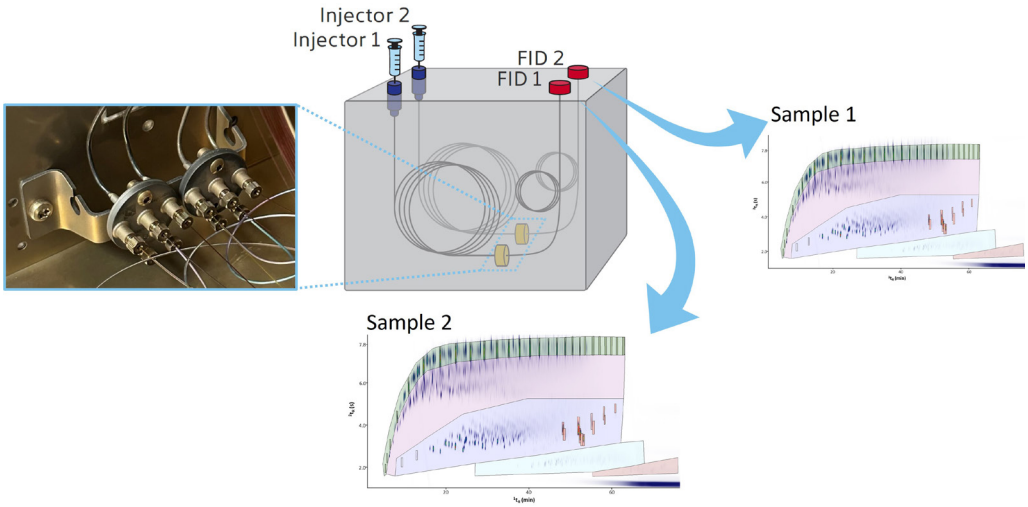

Figure 6

Diagram and photo of a dual injection system with two INSIGHT-Flow modulators mounted on a single bracket within the GC oven.

Conclusions

This white paper has shown SepSolve's GC×GC–FID product package for ASTM Method D8396 to be a versatile and powerful approach to the group-type analysis of hydrocarbons in finished fuels. Key features are:

- INSIGHT-Flow is a proven reverse fill/flush modulator in operation in numerous high-throughput labs across the world.
- Training requirements are minimised using a single software platform (ChromSpace) to control the GC×GC–FID system and perform data processing.
- ChromSpace provides automated data processing with easy-to-use stencils and simple area percent tables.
- INSIGHT-Flow modulators are retrofittable to all popular GCs, allowing existing systems to be upgraded to GC×GC capability.
- Optional dual-channel GC×GC–FID further increases productivity by allowing two samples to be run simultaneously.

For more information on this application, or any of the techniques or products used, please contact SepSolve.

References

[1] ASTM D1655-22, Standard Specification for Aviation Turbine Fuels. https://www.astm.org/d1655-22.html

[2] ASTM D7566-21, Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons. https://www.astm.org/d7566-21.html

[3] ASTM D2425-21, Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry

[4] ASTM D8396-22, Standard Test Method for Group Types Quantification of Hydrocarbons in Hydrocarbon Liquids with a Boiling Point between 36°C and 343°C by Flow Modulated GC×GC–FID. https://www.astm.org/d8396-22.html

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