

Developing a New GCxGC-TOFMS Method for Quantitation of Biofuel Components in Jet Fuel

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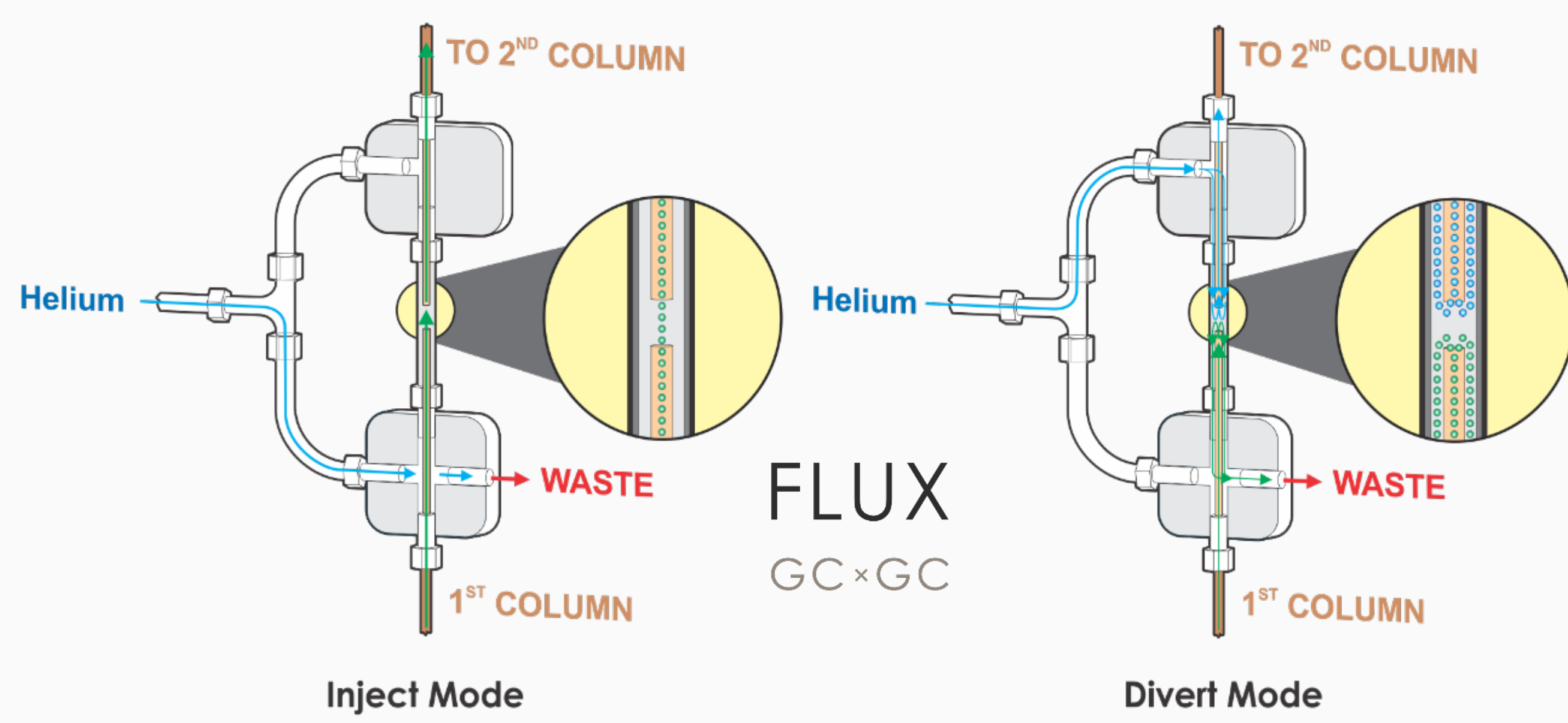
Overview

As the trend toward “greener,” renewable biofuels becomes more prevalent in the petroleum marketplace, concerns over pipeline cross-contamination and mixing are being addressed through more rigorous analytical testing. For jet fuels, especially, regulated methods like IP585 and ASTM D7974, respectively, address the accurate quantitation of fatty acid methyl esters (FAMES), which impact jet fuel freezing points and can cause fuel gelling to occur, and determination of specific hydrocarbons in synthesized iso-paraffins (SIP) that are used for blending with jet fuel. Utilizing two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GCxGC-TOFMS), methods for the analysis of jet fuel for determination of FAMES and SIP hydrocarbons using a new diverting flow modulator have been developed. Leveraging the increased chromatographic resolution that comes with GCxGC, more accurate quantitation for these specific analytes can be achieved, as FAME peaks are pulled away from other jet fuel matrix peaks. Hydrocarbons present in SIP, such as farnesane—quantitatively used for synthetic blend specifications—are separated from the aromatic species present in jet fuel. With TOFMS as the detector, identification of other potential non-targeted contaminants or analytes of interest, such as sulfur- or nitrogen-substituted species, can be determined by matching full mass range spectra to commercially available libraries. Taking advantage of the benefits of both multidimensional gas chromatography and fast spectral acquisition with TOFMS, a more comprehensive characterization of jet fuels and the contributions made from shared pipelines or biofuel blending is achieved.

Analytical Parameters

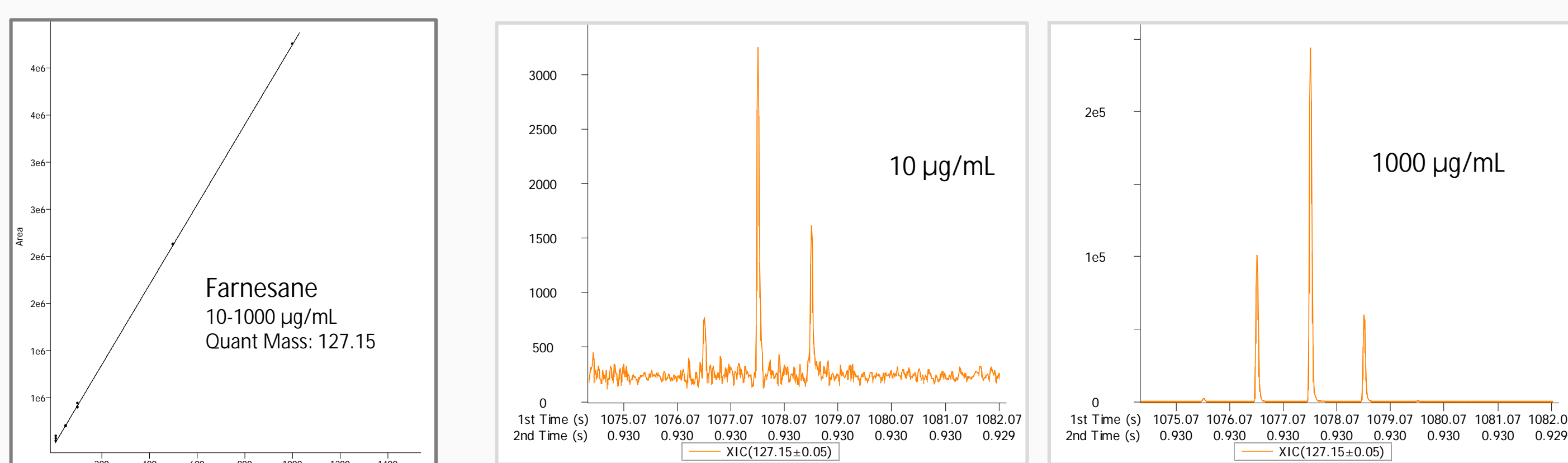
Gas Chromatograph	LECO FLUX GCxGC
Injection	1µL liquid injection, (Split Ratios 10:1, 20:1, and 100:1)
Carrier Gas	He @ 1.4 mL/min, Corrected Constant Flow
Primary Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 µm coating
Secondary Column	Rxi-17Silms, 0.77 m x 0.10 mm x 0.10 µm coating
Temperature Program	60 °C, hold for 5 min, then ramp 8 °C/min to 300 °C, hold for 4 min Secondary oven maintained +40 °C relative to primary oven
Modulation Period	1.0 second
Transfer Line	300 °C
Mass Spectrometer	LECO Pegasus BT
Ion Source Temperature	250 °C
Mass Range	50-550 m/z
Acquisition Rate	200 spectra/s

Diverting Flow Modulation

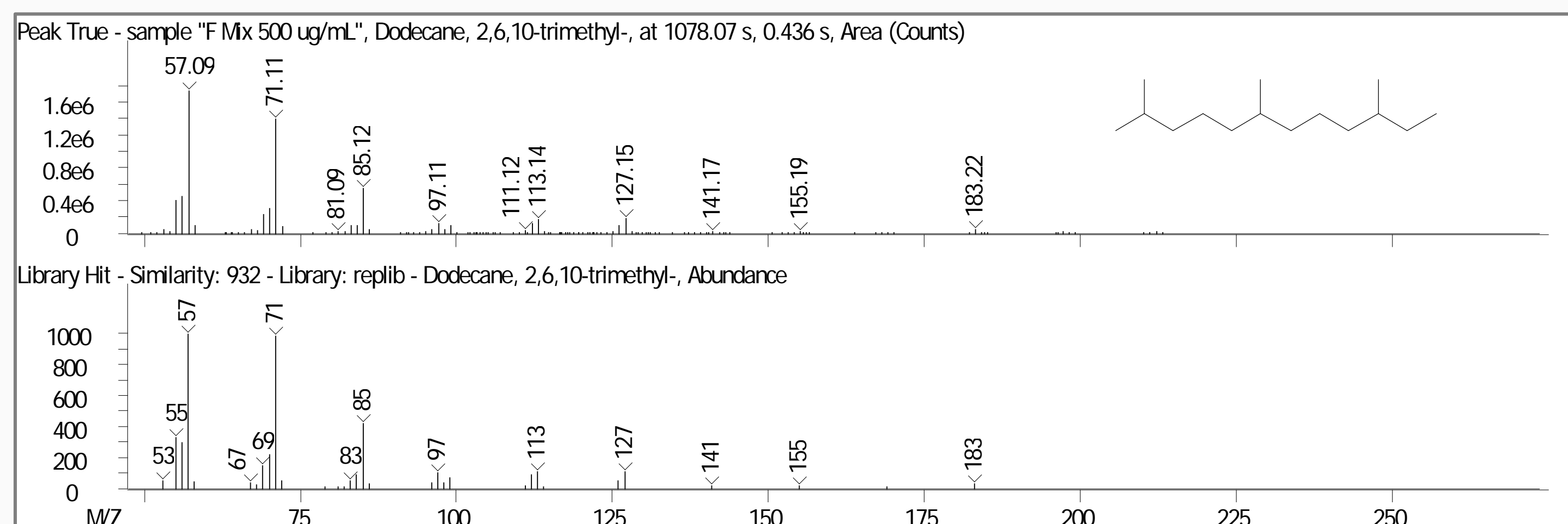


Diverting flow modulation works by sampling a representative portion of analyte eluting from the end of the primary GC column and injecting onto a second, shorter GC column for fast GC separation in a complementary phase, allowing for separations based on different column phase affinities. The LECO FLUX modulator operates using a valve in two states—inject mode and divert mode. During the inject mode, the analyte stream from the primary GC column is forced into the secondary column with an auxiliary flow of 3.0 mL/min. During the divert mode, the auxiliary flow switches and forces the eluting stream from the primary column to waste. One cycle of inject and divert makes up the second dimension separation time, also known as modulation period.

Farnesane Quantitation

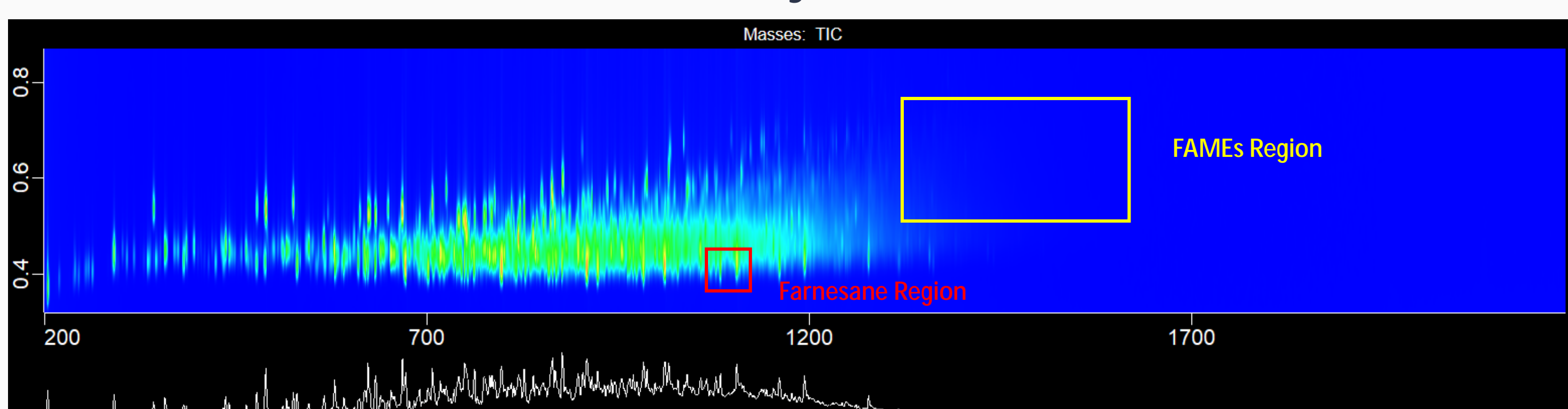


Two zoomed-in linear traces of the farnesane at the highest and lowest concentrations for quantitation are shown above, demonstrating narrow peaks of less than 50 ms FWHH in the second dimension, and the proper sampling of at least three slices over the first dimension representation of the peak.



The deconvoluted Peak True spectra for the farnesane (also known as 2,6,10-trimethyldodecane) peak at 500 µg/mL is shown above compared to the NIST library hit with an excellent similarity score of 937/1000.

GCxGC Analysis of Jet Fuel



GCxGC contour plot of the total ion chromatogram (TIC) for a commercial jet fuel sample is shown above, along with a reconstructed summation of the primary GC separation. This view clearly demonstrates the ability of the second dimension to pull apart compounds that would otherwise coelute in a one-dimensional GC analysis. Regions where farnesane and the FAMES of interest elute are marked in yellow and red, respectively.

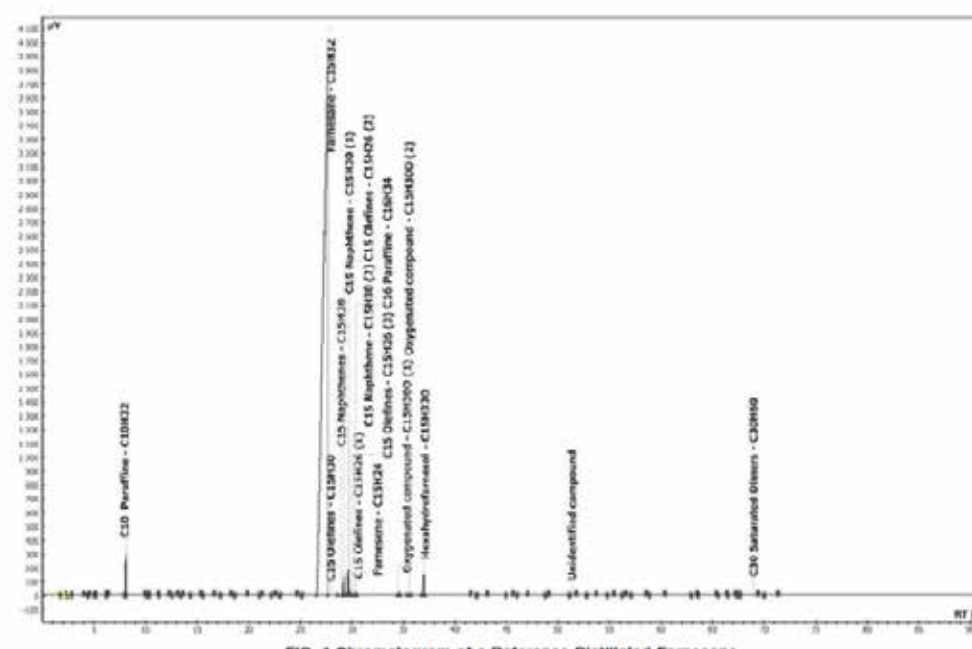
Current Standard Methods

Two current standard test methods for biofuel components in jet fuel are ASTM D7974 and IP 585.



Designation: D7974 - 15

Standard Test Method for Determination of Farnesane, Saturated Hydrocarbons, and Hexahydrofarnesol Content of Synthesized Iso-Paraffins (SIP) Fuel for Blending with Jet Fuel by Gas Chromatography¹



ASTM D7974 is a GC-FID method quantitating farnesane, saturated hydrocarbons, and hexahydrofarnesol. Potential for coelution of compounds leading to overestimation of these compounds is high.



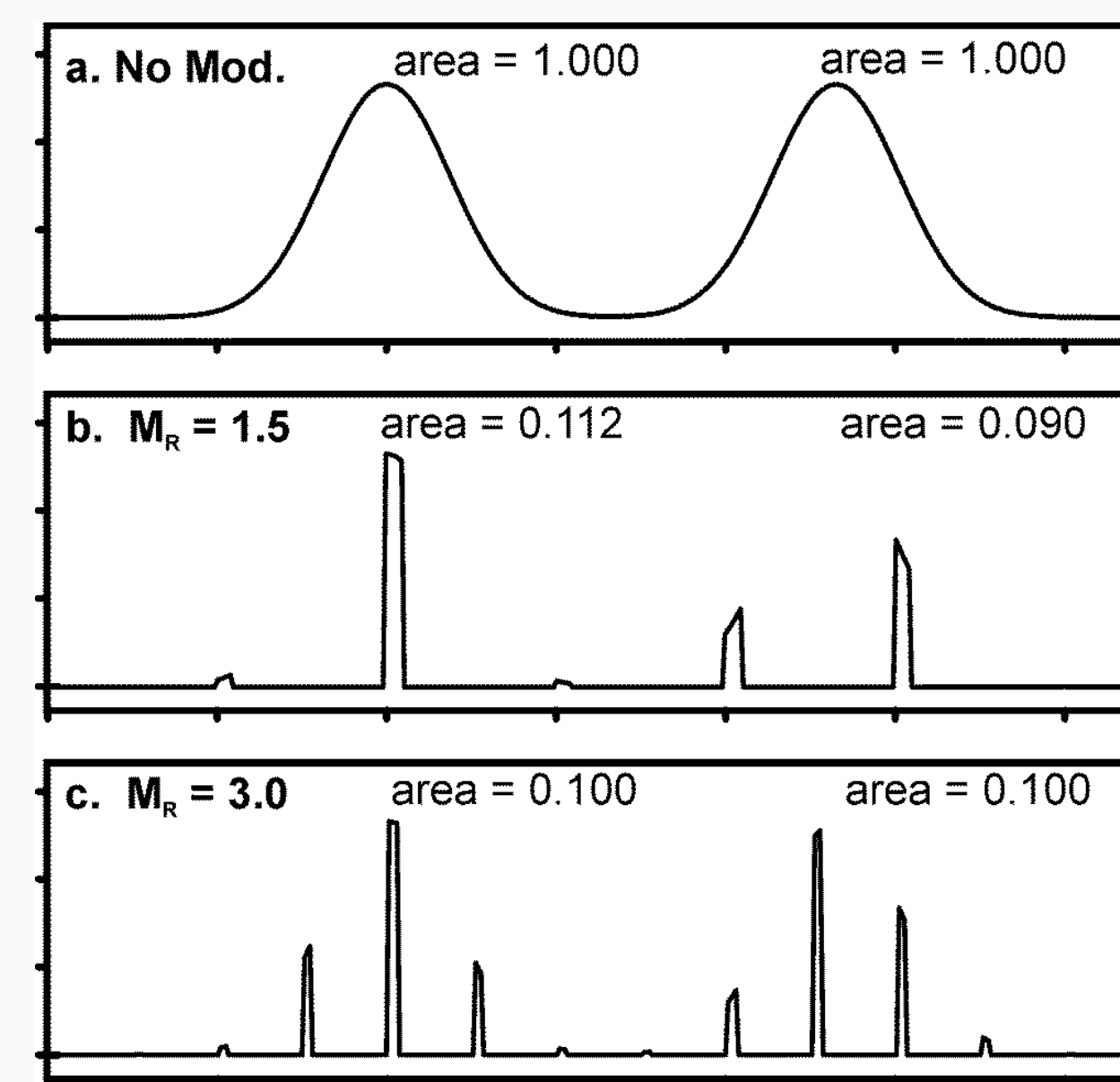
Determination of fatty acid methyl esters (FAME), derived from bio-diesel fuel, in aviation turbine fuel – GC-MS with selective ion monitoring/scan detection method

Fatty acid methyl ester	Molecular formula	Symbol used
methyl hexadecanoate (methyl palmitate)	C ₁₆ H ₃₂ O ₂	C16:0
methyl heptadecanoate (methyl margarate)	C ₁₇ H ₃₄ O ₂	C17:0
methyl octadecanoate (methyl stearate)	C ₁₈ H ₃₆ O ₂	C18:0
methyl octadecanoate (methyl oleate)	C ₁₈ H ₃₄ O ₂	C18:1
methyl octadecanoate (linoleate)	C ₁₈ H ₃₂ O ₂	C18:2
methyl octadecanoate (linolenate)	C ₁₈ H ₃₀ O ₂	C18:3

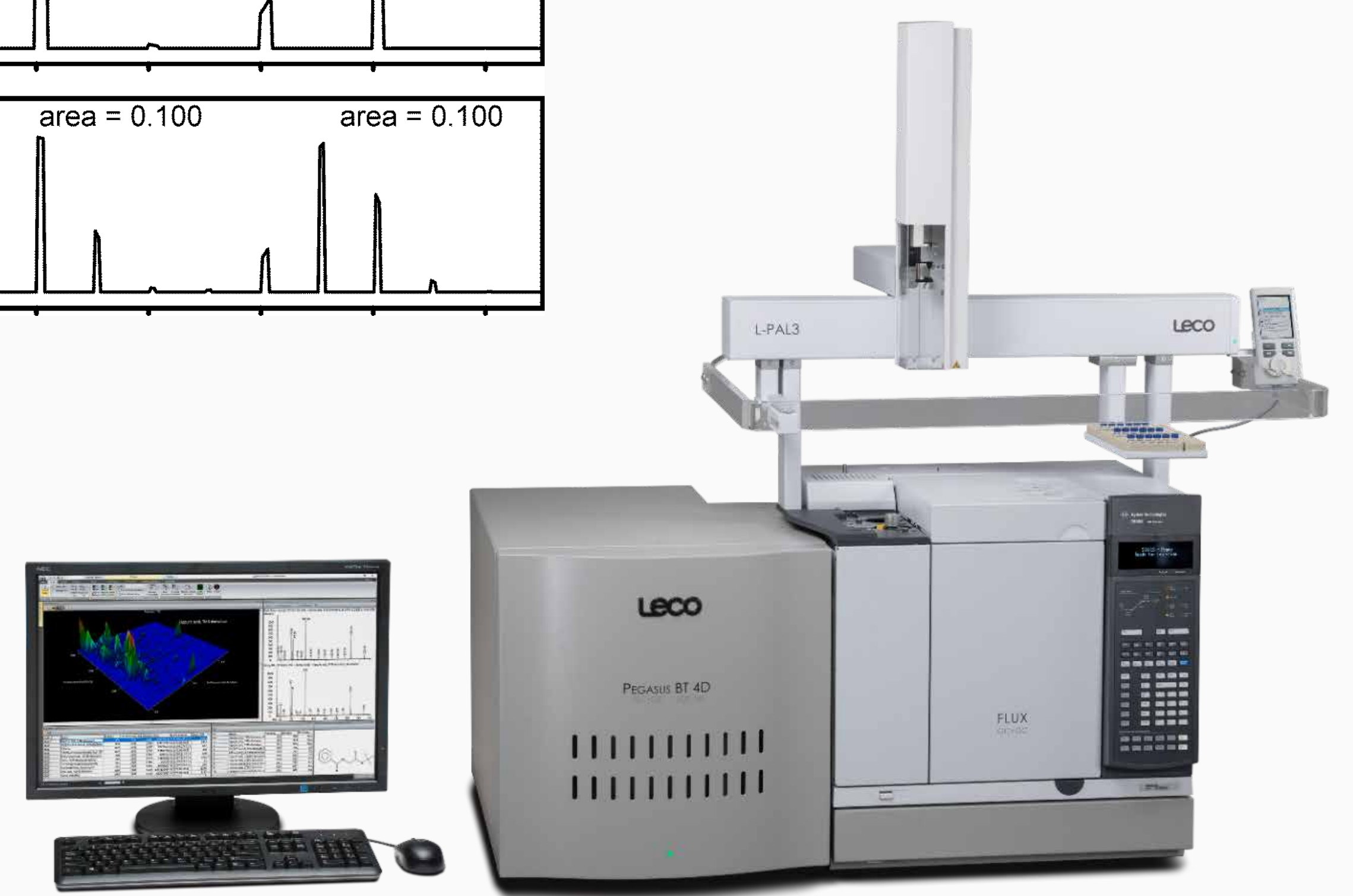
6 FAMES commonly found in 95% of feedstocks are quantitated with two separate calibration curves.

Current jet fuel regulations set maximum total FAME level at 5 mg/kg, so only the lower calibration range is necessary. There is a possibility of coelution of fuel matrix compounds that could interfere with accurate quantitation.

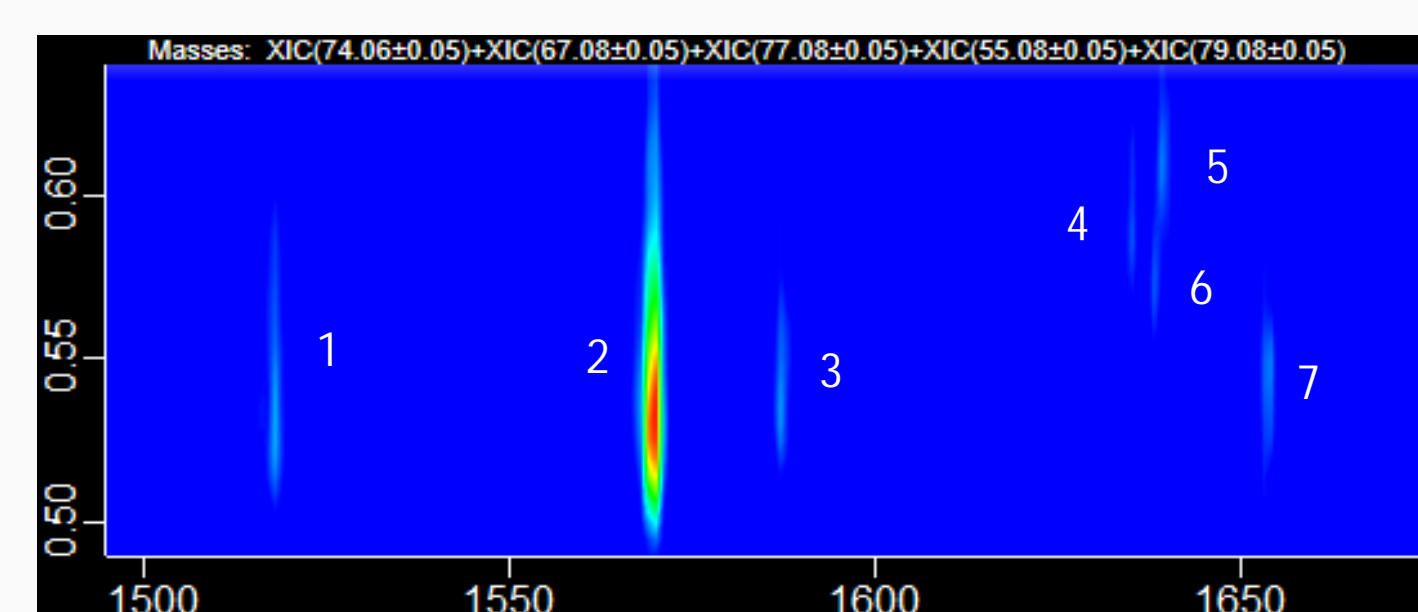
Ensuring Accurate Quantitation



Getting a representative sampling of any peak is necessary to ensure accurate quantitation. For diverting flow modulation, at least three sampled “slices” per peak are required, so the second dimension separation time (modulation period) needs to be set shorter than 1/3 the expected first dimension peak width. The figure to the left shows the importance of properly sampling a peak so that representative relative peak areas are conserved.

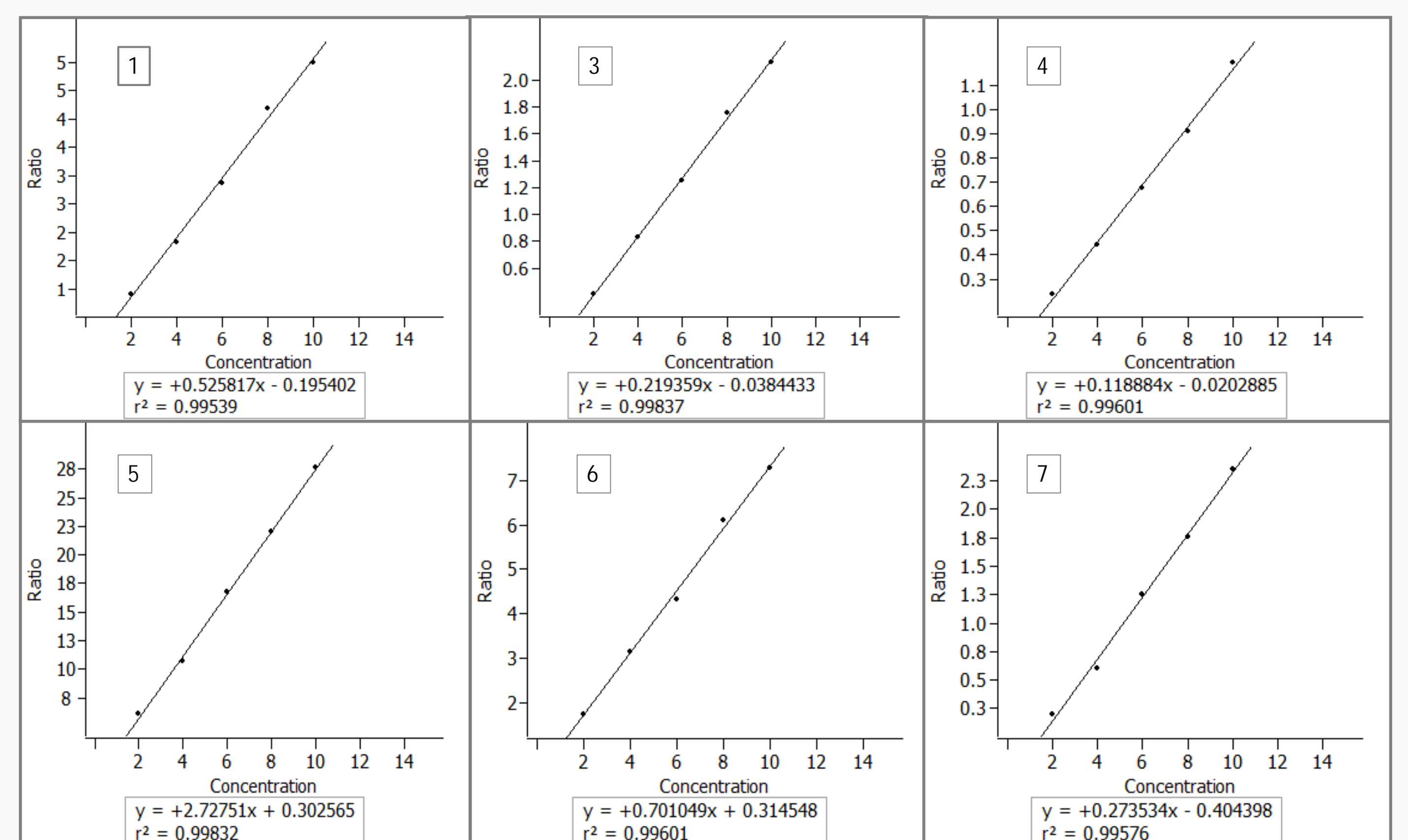


FAME Quantitation



A zoomed section of the GCxGC contour plot displaying representative FAME masses with each analyte at a concentration of 2 mg/kg is shown above.

Peak #	Name	Symbol
1	methyl hexadecanoate	C16:0
2	methyl heptadecanoate-d33	IS
3	methyl heptadecanoate	C17:0
4	methyl linoleate	C18:0
5	methyl linolenate	C18:1
6	methyl oleate	C18:2
7	methyl stearate	C18:3



Calibration curves generated from 0 mg/kg to 10 mg/kg are shown for each of the 6 calibration FAME analytes above. Methyl heptadecanoate-d33 was spiked in at 10 mg/kg as the internal standard. Excellent linearity was demonstrated, with R² values of greater than 0.995 for each analyte.

Conclusions

The new LECO FLUX diverting flow modulator creates narrow second dimension peaks (~50 ms FWHH), allowing for not only excellent peak capacity for comprehensive two-dimensional gas chromatography separation of a complex sample, but also quantitation of farnesane and low-concentration FAMES in jet fuel. A variety of new GCxGC methods were developed to overcome the inherent limitations of existing current methods, enhancing the potential for coelutions and inaccurate quantitation. This was accomplished by utilizing the enhanced chromatographic resolution of GCxGC and improved specificity in quantitation with a better-than-nominal mass spectrometer, the LECO Pegasus BT.