Application Note

Instrument: Paradigm™ GCxGC-FID

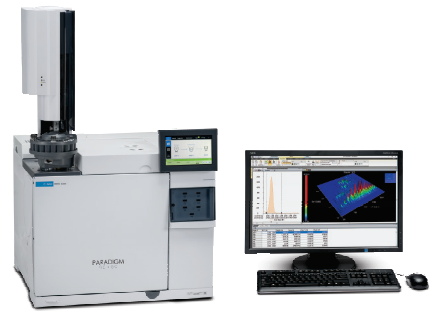
EMPOWERING RESULTS

Elemental Analysis | GC Mass Spectrometry | Metallography

Satisfying ASTM D8396 Requirements

LECO Corporation; Saint Joseph, Michigan USA

Key Words: Petroleum, GCxGC, Flow Modulation, Aviation Fuel, Diesel, Gasoline, Routine



Introduction

In response to the need for standardized compositional characterization of emerging aviation fuels, ASTM Method D8396— "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 GCxGC-FID"— was first approved in 2022. This application note describes how to use a simple workflow with the LECO *Paradigm* system to fulfill the requirements of the ASTM D8396 test method to quantitatively determine mass % of total n-paraffins, iso-paraffins, naphthenes, 1-ring aromatics, and 2-ring aromatics using reverse-fill flush flow modulated comprehensive two-dimensional gas chromatography–flame ionization detection (GCxGC-FID). Understanding of bulk composition is crucial for fast-track certification of synthetic aviation fuels as outlined in ASTM D4054, and the more accurate group-type analysis results provided by GCxGC assist with streamlining the acceptance process. GCxGC clearly resolves aliphatic regions from aromatic ones, creating bands of similar compounds which allow for general classification of chemical components based on structural elements and boiling point behavior with only a single-channel detector. When FID is used, area % values from groups of peaks can be used to quantify mass % composition of a sample.

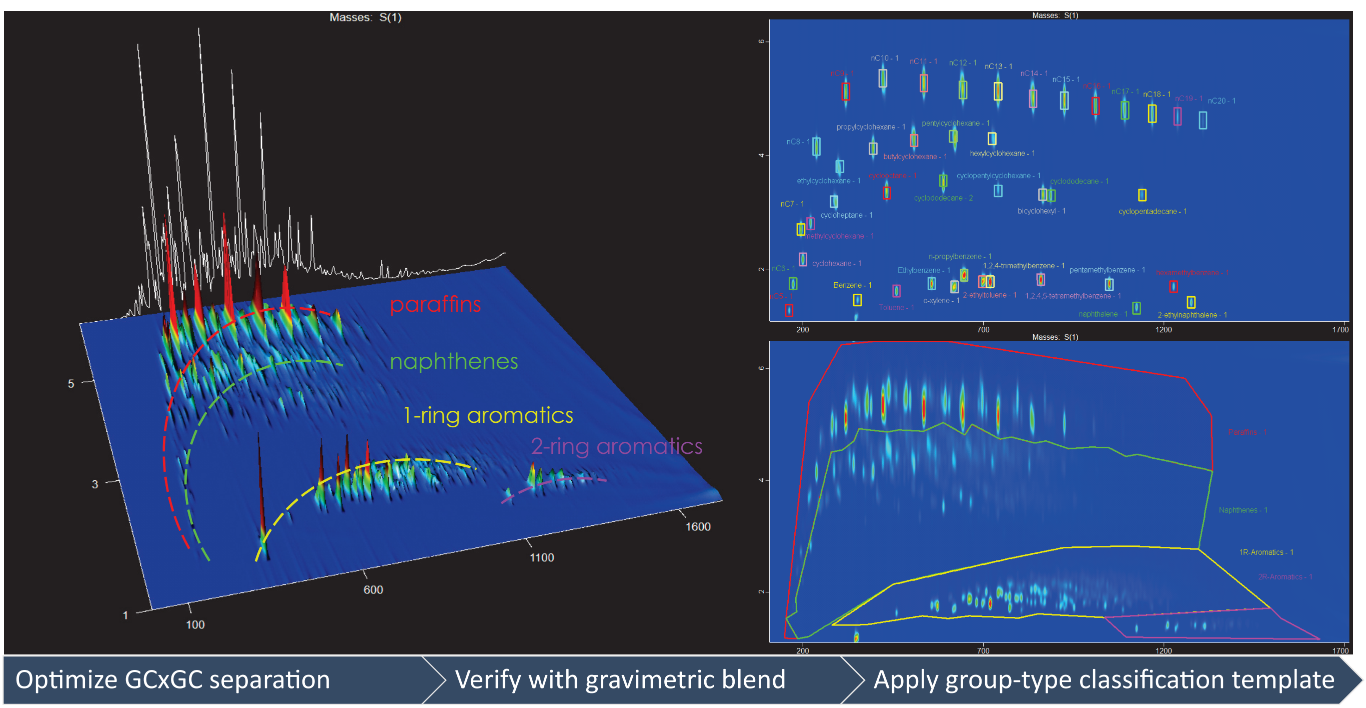


Figure 1. Left: 3D surface plot of aviation fuel showing benefit of GCxGC for improvement of chromatographic resolution, with white reconstructed trace of the 1D GC separation. Compound groups are visually apparent, with the tallest peaks in the back corresponding to paraffins and the short band of analytes at the front corresponding to 2-ring aromatic. Right top: Classification identifying components of the gravimetric standard mix used to verify quantitation method. Right bottom: Contour plot of aviation reference fuel showing classification regions used to generate summary compound class information for ASTM D8396.

Experimental

The LECO *Paradigm* reverse-fill-flush modulated GCxGC system with backpressure regulation is compatible with both Helium and Hydrogen as carrier gas. Native ChromaTOF® software supplies built-in calculations to assist users in developing optimized GCxGC methods that are properly set up using well-understood flow mechanics to ensure full transfer of analytes—an attribute crucial for maintaining accuracy of quantitation throughout the entire chromatogram. Recommendations for acceptable analytical method conditions adapt to allow flexibility for different column sets or carrier gas as desired.

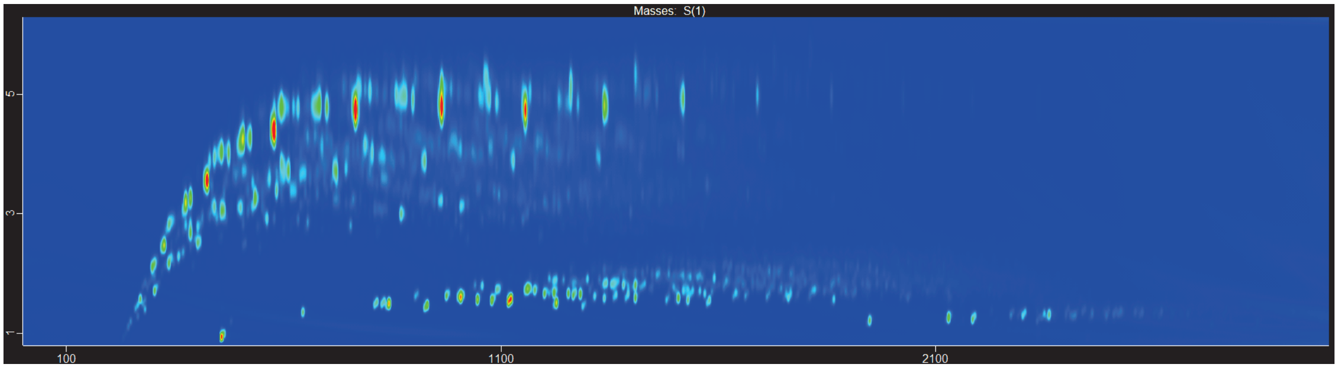


Figure 2. Contour plot of aviation reference fuel acquired using parameters in Table 1 with Helium as carrier gas.

Table 1: Acquisition parameters using Helium as carrier gas.

Gas Chromatograph	**LECO *Paradigm* GC×GC**
Injection	0.1 µL liquid injection, split 100:1 @ 300 °C
Carrier Gas	Helium
Column One	Stabilwax, 20 m x 0.18 mm i.d. x 0.18 µm coating
Column Two	Rxi-5MS, 3.75 m x 0.25 mm x 0.50 µm coating
2nd Dimension Separation Time	5.5 s; Flush factor 1.5
Temperature Program	1.2 min at 40 °C, ramped 2.5 °C/min to 50 °C, ramped 4.5 °C/min to 120 °C, ramped 4.0 °C/min to 280 °C hold for 5 min (Total Runtime: 65.75 min)
FID Data Collection Rate	100 Hz

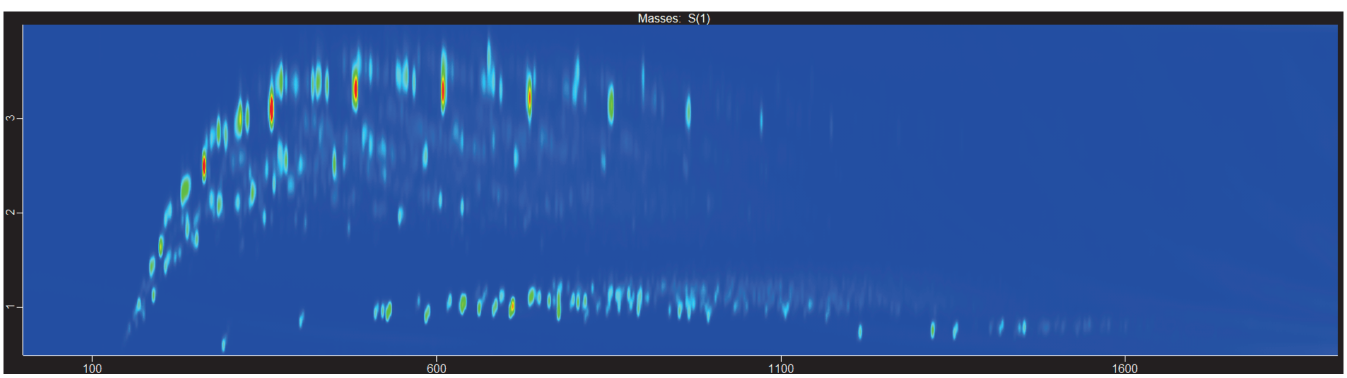


Figure 3. Contour plot of aviation reference fuel acquired using parameters in Table 2 with Hydrogen as carrier gas.

Table 2: Acquisition parameters using Hydrogen as carrier gas.

Gas Chromatograph	**LECO *Paradigm* GC×GC**
Injection	0.1 µL liquid injection, split 200:1 @ 280 °C
Carrier Gas	Hydrogen
Column One	Heavywax, 20 m x 0.18 mm i.d. x 0.18 µm coating
Column Two	Rxi-5MS, 3.5 m x 0.25 mm x 0.20 µm coating
2nd Dimension Separation Time	3.5 s; Flush factor 1.75
Temperature Program	0.6 min at 40 °C, ramped 3.4 °C/min to 50 °C, ramped 7.0 °C/min to 200 °C, ramped 6.0 °C/min to 280 °C hold for 5 min (Total Runtime: 43.3 min)
FID Data Collection Rate	100 Hz

Results and Discussion

ASTM D8396 requires that a gravimetric reference blend be used to make sure that the system accurately reports quantitative information for both individual species within 0.3 mass % as well as the total class within 1.0 mass %. Figure 4 below shows the identified peaks from a gravimetric blend that contains a mix of n-alkanes, cycloparaffins, and aromatic compounds.

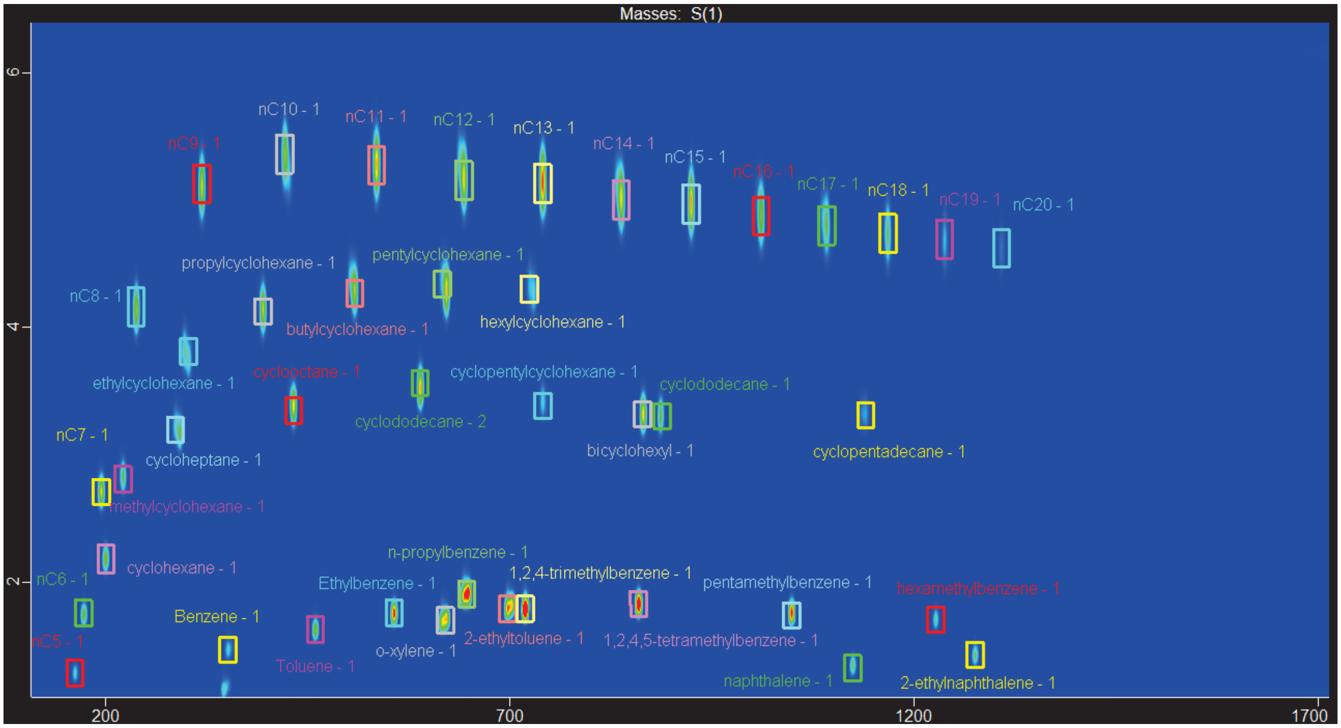


Figure 4. Contour plot of gravimetric blend acquired with Hydrogen as carrier gas.

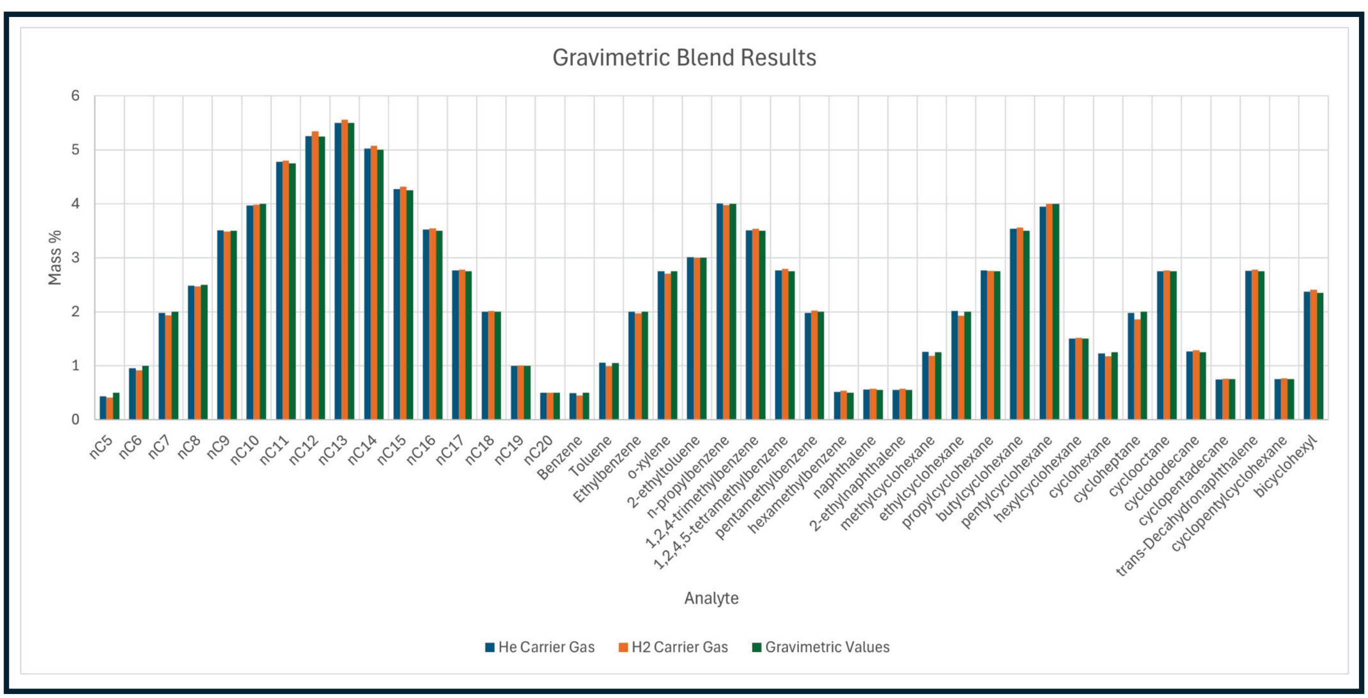


Figure 5. Plot of experimental mass % values for both Hydrogen and Helium carrier gas analyses compared to the expected values for each analyte in the gravimetric blend.

Once the system demonstrated accurate mass % values from the gravimetric blend of individual components, a real sample of aviation fuel was analyzed and used to develop the bulk group-type classification template, as shown in Figure 6 below.

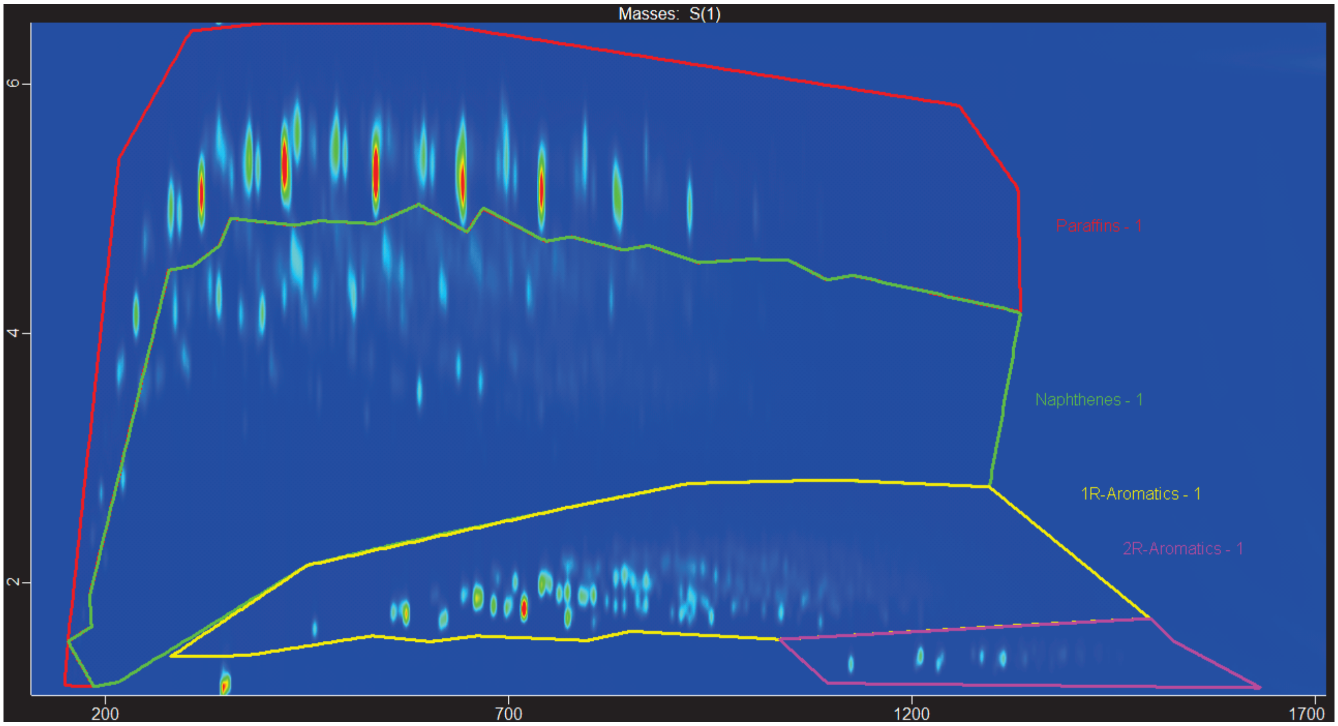


Figure 6. Contour plot of an aviation fuel with rich distribution of diverse compounds used to draw classification templates for group-type analysis with regions for paraffins, naphthenes, 1R-aromatics, and 2R-aromatics.

The same classification template could then be applied to any fuel analyzed using the same acquisition parameters for the summed areas of any peaks within a given region because GCxGC retention times are consistent from run to run. Used in conjunction with the classification template for the gravimetric blend that showed individual analyte results, the total n-paraffin class values were calculated and then subtracted from general "paraffin" class to generate the iso-paraffin class values. The table and figures below show the application of these classification templates to the following types of fuels: traditional aviation turbine fuel (AVTUR), Jet A, synthetic aviation turbine fuel (SATF), high-temperature Fischer-Tropsch synthetic paraffinic kerosene (FT-SPK), high-temperature Fischer-Tropsch synthetic paraffinic kerosene with aromatics (FT-SPK/A), and hydroprocessed esters and fatty acids synthetic paraffinic kerosene (HEFA-SPK).

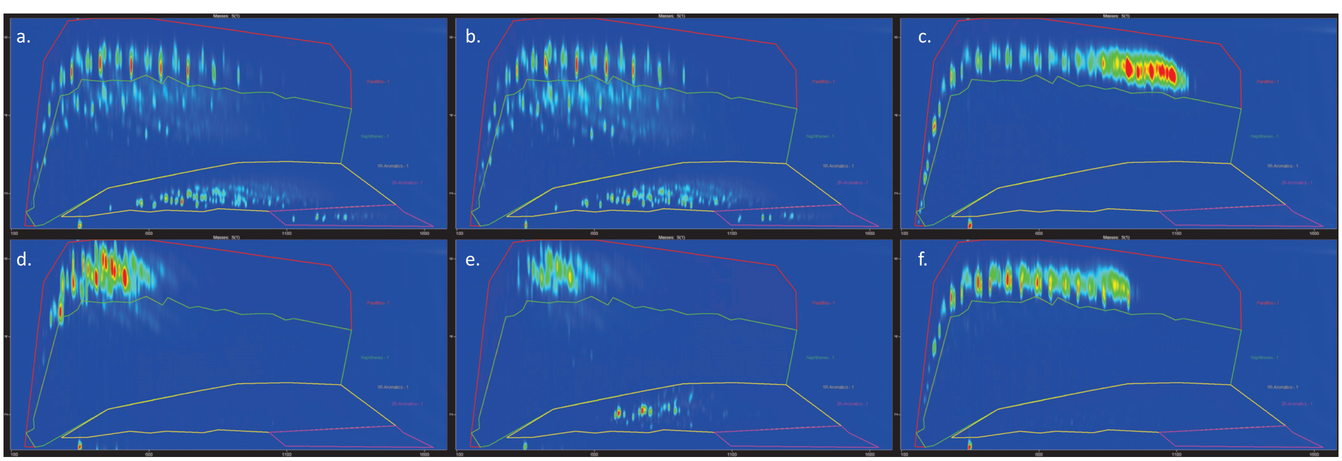


Figure 7. Contour plots from a variety of aviation fuels with hydrocarbon group-type analysis classification templates applied. a) AVTUR; b) Jet A; c) SATF; d) FT-SPK; e) FT-SPK/A; f) HEFA-SPK.

Table 3: Results of GCxGC group-type analysis for n-paraffins, isoparaffins, naphthenes, 1-ring aromatics, and 2-ring aromatics by mass% for a variety of fuels using the same classification templates shown in Figure 7 above.

Mass % per Hydrocarbon Group-type Class by FID						
	AVTUR	**Jet A**	**SATF**	**HTFT-SPK**	**HTFT-SPK/A**	**HEFA-SPK**
n-Paraffins	21.0	18.0	34.0	2.2	5.6	22.3
Iso-Paraffins	26.1	25.2	64.7	92.7	69.1	74.6
Naphthenes	31.8	37.3	0.8	4.4	6.8	2.1
1-Ring Aromatics	19.0	17.7	0.3	0.4	18.3	0.7
2-Ring Aromatics	2.1	1.8	0.2	0.2	0.2	0.3

Conclusion

LECO *Paradigm* provides a complete solution for ASTM D8396 from method development to final sample composition results. Fully integrated hardware control with software guidelines assist with optimizing acquisition methods that ensure full transfer flow modulation and accurate quantitation. User-friendly guidance for setting up methods and flexibility in software tools for creating classification templates and peak finding provide simple data processing and accurate results.

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