Application Note

Instrument: Pegasus® HRT$^+$ 4D with Multi-Mode Source™

Analysis of Heavy Fuel Oil Using Multi-Mode Ionization

LECO Corporation; Saint Joseph, Michigan USA

Key Words: Petroleum, GCxGC, Environmental, Chemical Ionization, Multi-Mode Source (MMS™)

Introduction

Heavy fuel oil, also known as bunker fuel or residual fuel oil, is a complex mixture of petroleum hydrocarbons that is formed as the remnant of the distillation and cracking process. Often combined with distillates and used as fuel by the shipping industry, heavy fuel oils have recently been more stringently regulated by the International Maritime Organization for lower sulfur content due to environmental contamination from sulfur emissions with regulations like the one known as IMO 2020, which limits the sulfur in fuel oil used on board ships operating outside designated emission control areas to 0.5% by mass. With thousands of compounds making up heavy fuel oil, comprehensive two-dimensional gas chromatography (GCxGC) coupled to high-resolution time-of-flight mass spectrometry (HRTOFMS) with multiple modes of ionization provides a full characterization of the volatile and semi-volatile components in this complex mixture. The power of GCxGC provides visually compelling separation of different classes of compounds in a predictably structured nature based on ring-double-bond equivalence (RDBE), allowing for full chromatographic resolution of otherwise coeluting sulfur-containing species from other complex hydrocarbons while the high-resolution MS provides confident formula identification of each peak with differentiation for elemental substitutions like sulfur and nitrogen. The *Multi-Mode Source (MMS)* provides additional opportunities for confident identification of peaks, with well-understood fragmentation patterns that match commercial library spectra formed by electron impact ionization (EI), increased molecular ion formation by positive chemical ionization (PCI), and further selectivity and sensitivity for halogenated species formed by electron capture negative chemical ionization (ECNI).

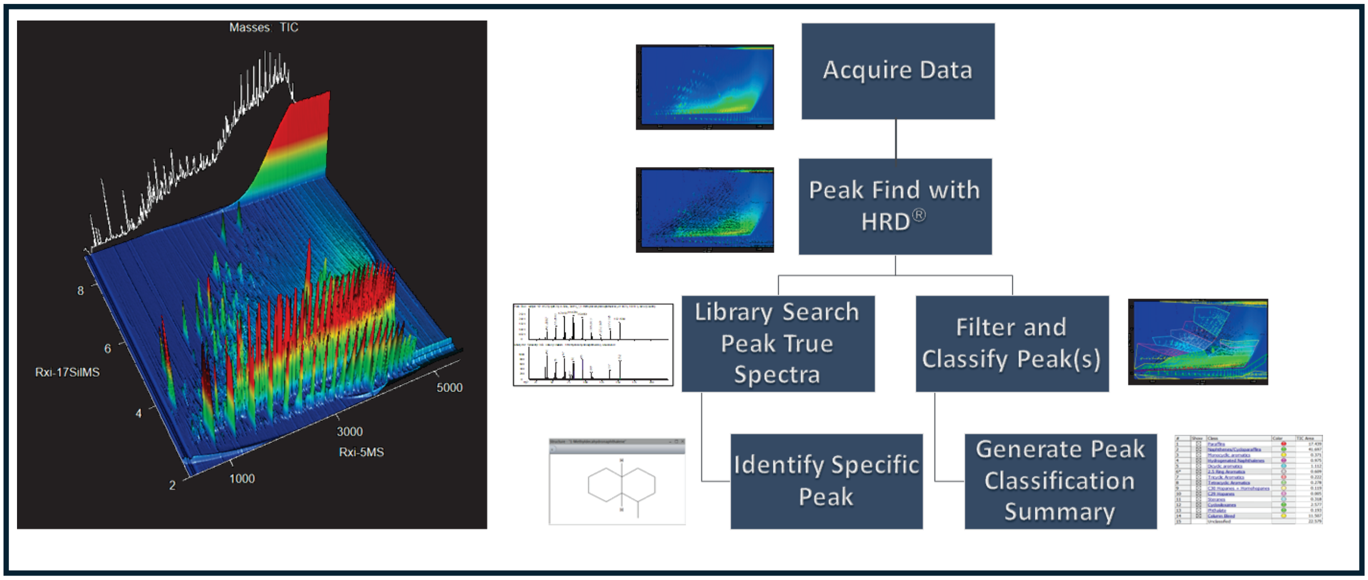


Figure 1. Total Ion Chromatogram Plots of Heavy Fuel Oil Sample: 3D Surface plot of EI acquisition is shown on the left with the white reconstructed chromatogram in the background showing what a single dimension separation would have looked like. The data interrogation workflow for the combination of GCxGC and HRTOFMS data is shown on the right.

Experimental

A heavy fuel oil sample was diluted in dichloromethane. Analytical parameters for comprehensive two-dimensional gas chromatography high-resolution time-of-flight mass spectrometry (GCxGC-HRTOFMS) equipped with a quad-jet thermal modulator are shown in Table 1 below. Data processing was performed using ChromaTOF® brand software with post-acquisition mass calibration, automatic peak find, and library search. Deconvoluted peaks were compared to the NIST20 spectral library, applying the automated Identification Grading System™ (IGS™) to rank the fitness of library hits based on retention index, spectral match, and expected fragmentation formula mass accuracy. Methane was used as the chemical ionization reagent gas, and flows were optimized using the automated tuning procedure. Use of the *MMS* source allowed for comparison of EI, PCI, and ECNI data with matching retention times, as no column hardware changes were needed to switch between modes.

Table 1. Instrument Parameters for Acquisition of Heavy Fuel Oil Sample Data

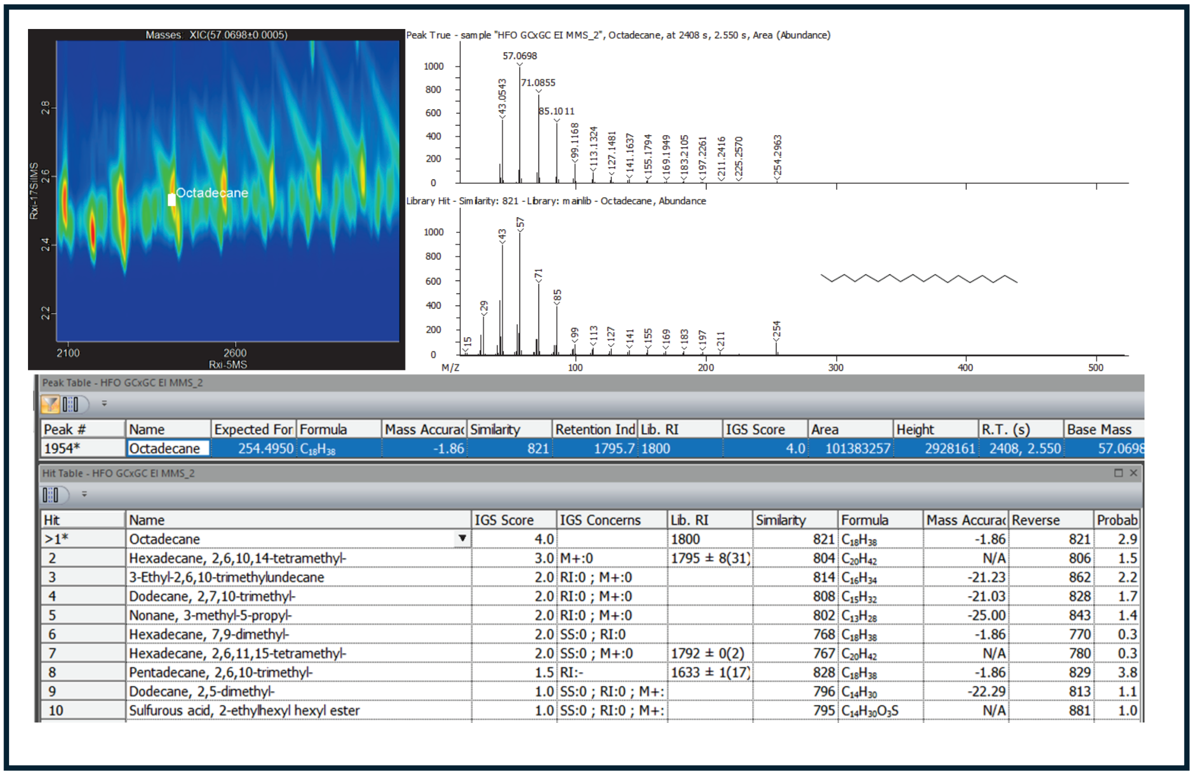
Gas Chromatograph	LECO QuadJet™ Thermal GC×GC
Injection	2 µL liquid injection, pulsed splitless @ 325 °C
Carrier Gas	He @ 1.4 mL/min, constant flow
Column One	Rxi-5MS, 30 m x 0.25 mm i.d. x 0.25 µm coating (Restek, Bellefonte, PA, USA)
Column Two	Rxi-17SilMS, 2.0* m x 0.25 mm x 0.25 µm coating *1.2 m coiled in 2nd oven
Temperature Program	5 min at 40 °C, ramped 4 °C/min to 330 °C, hold for 15 min
Secondary Oven	+15 °C relative to primary oven
Modulator Temperature	+15 °C relative to secondary oven
2nd Dimension Separation Time	7 s
Transfer Line	360 °C
Mass Spectrometer	LECO *Pegasus* HRT$^+$ 4D with *MMS*
Ion Source Temperature	250 °C (EI); 165 °C (PCI and ECNI)
Mass Range	40-1000 m/z (EI and PCI); 30-1000 m/z (ECNI)
Acquisition Rate	200 spectra/s

Results and Discussion

A variety of approaches were used to analyze the heavy fuel oil data using tools within *ChromaTOF*, from identification of individual peaks to bulk characterizations of compound classes present in the sample using filtered peak and visualized summary spectral information.

Identification Grading System for Evaluating EI Library Hits

The high-resolution MS spectra produced by the *Pegasus* HRT$^+$ 4D compare very well with the nominal-mass NIST20 spectral database, with tentative identification based on spectral similarity alone for any peaks with scores above 800/1000. However, applying the *Identification Grading System (IGS)* leverages additional information beyond spectral similarity stored within the chromatographic and high-resolution mass spectral data: chromatographic retention index, mass accuracy of the molecular ion, and mass accuracy of fragments based on library hit formula. While the *ChromaTOF* automated Library Search data processing feature automatically generates a user-defined number of library hits that match any given peak's fragmentation pattern with those in the spectral library, using *IGS* allows the library hits to be ranked based on fitness of the hit instead of spectral similarity alone, with higher *IGS* scores correlating to more accurate potential library hits. In cases where there is significant fragmentation and spectra with many similar library spectra matches, the retention index criteria can be especially helpful for bringing more likely matches to the top of the hit list, as in the case of the n-alkane, octadecane.



Peak Table - HFO GCxGC EI MMS_2

Peak #	Name	Expected For	Formula	Mass Accurac	Similarity	Retention Ind	Lib. RI	IGS Score	Area	Height	R.T. (s)	Base Mass
1954*	Octadecane	254.4950	$C_{18}H_{38}$	-1.86	821	1795.7	1800	4.0	101383257	2928161	2408, 2.550	57.0698

Hit Table - HFO GCxGC EI MMS_2

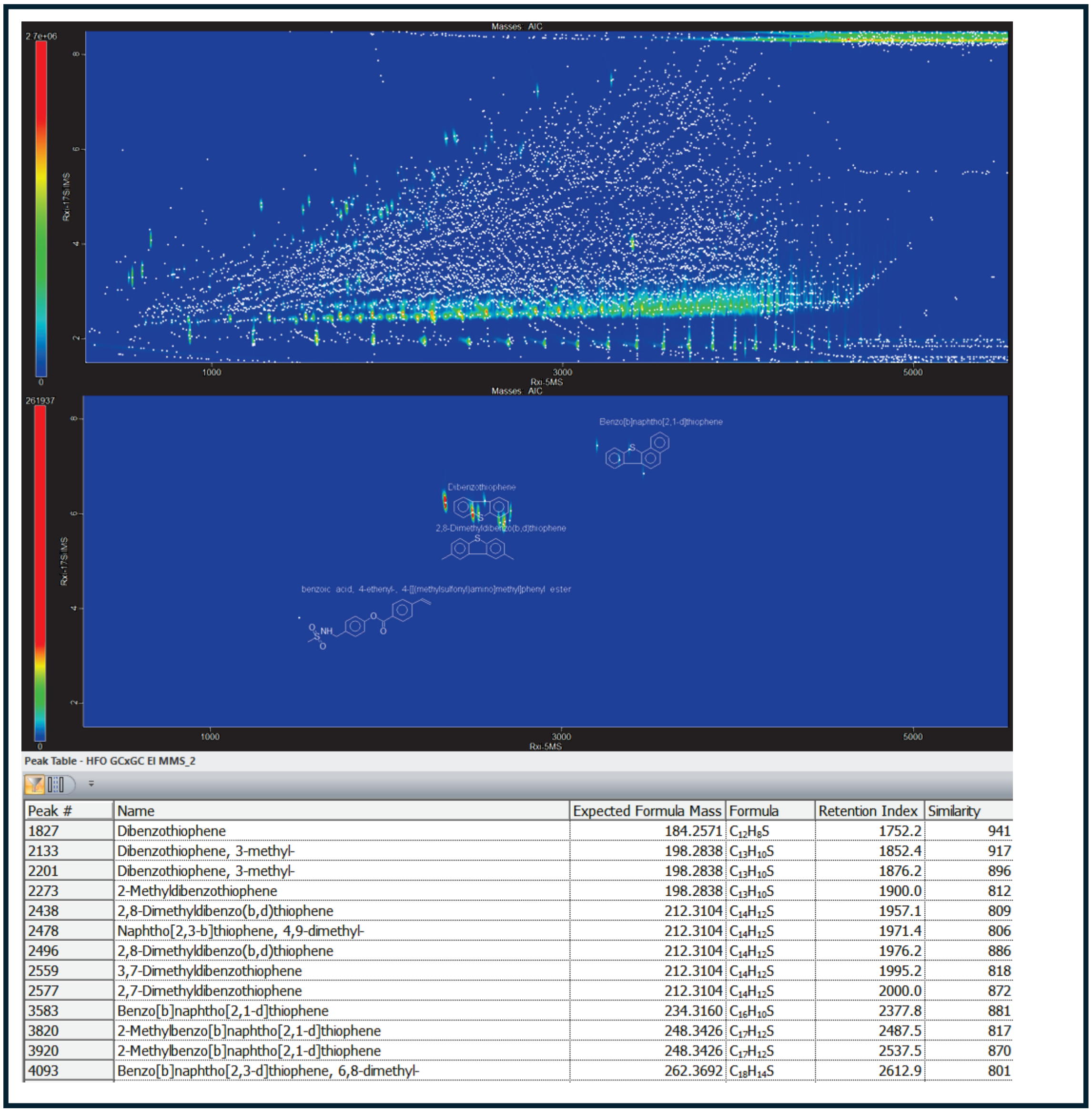
Hit	Name	IGS Score	IGS Concerns	Lib. RI	Similarity	Formula	Mass Accurac	Reverse	Probab
>1*	Octadecane	4.0		1800	821	$C_{18}H_{38}$	-1.86	821	2.9
2	Hexadecane, 2,6,10,14-tetramethyl-	3.0	M+:0	1795 ± 8(31)	804	$C_{20}H_{42}$	N/A	806	1.5
3	3-Ethyl-2,6,10-trimethylundecane	2.0	RI:0 ; M+:0		814	$C_{16}H_{34}$	-21.23	862	2.2
4	Dodecane, 2,7,10-trimethyl-	2.0	RI:0 ; M+:0		808	$C_{15}H_{32}$	-21.03	828	1.7
5	Nonane, 3-methyl-5-propyl-	2.0	RI:0 ; M+:0		802	$C_{13}H_{28}$	-25.00	843	1.4
6	Hexadecane, 7,9-dimethyl-	2.0	SS:0 ; RI:0		768	$C_{18}H_{38}$	-1.86	770	0.3
7	Hexadecane, 2,6,11,15-tetramethyl-	2.0	SS:0 ; M+:0	1792 ± 0(2)	767	$C_{20}H_{42}$	N/A	780	0.3
8	Pentadecane, 2,6,10-trimethyl-	1.5	RI:-	1633 ± 1(17)	828	$C_{18}H_{38}$	-1.86	829	3.8
9	Dodecane, 2,5-dimethyl-	1.0	SS:0 ; RI:0 ; M+:		796	$C_{14}H_{30}$	-22.29	813	1.1
10	Sulfurous acid, 2-ethylhexyl hexyl ester	1.0	SS:0 ; RI:0 ; M+:		795	$C_{14}H_{30}O_3S$	N/A	881	1.0

Figure 2. Zoomed in contour plot of the heavy fuel oil displays the most abundant mass in the octadecane peak, which is marked with a white peak marker. Notice the grouping of near-eluting branched isomers (top left). The deconvoluted Peak True spectra of the selected octadecane compared to its corresponding Library spectra is shown (top right). A listing of the top ten library hits sorted by IGS score reflects the value of using retention index and molecular ion criteria for determining analyte identification (bottom).

Figure 2 shows the library hit list generated with the use of *IGS*. Although there were hits present with a marginally higher similarity score such as 2,6,10-trimethyl pentadecane (Hit 8), the presence of the molecular ion and correct retention index contributed to a higher *IGS* score, which helped properly identify this particular n-alkane. Using *IGS* allowed for more accurate library assignments by properly ranking the hit list, which in turn populated the automatically generated Peak Table with better quality analyte identifications.

Peak Filtering for Sulfur Speciation

For a sample as complex as heavy fuel oil, hundreds of compounds can be individually identified. To easily highlight peaks of interest, such as those containing sulfur in their associated library formulae, custom Peak Filter sets can be defined using any available Peak Table fields to narrow the focus of the wealth of information available in the automatically generated Peak Table. Figure 3 below shows the comparison of no Peak Filter and a Peak Filter for “peaks containing 'S' in the formula” applied on contour plots displaying the analytical ion chromatogram trace, which shows the summation of signals corresponding to actively displayed peaks in the Peak Table. Isolating compounds of interest for quick study in this way can provide significant time-savings for detailed interrogation of such rich data. As expected, there are not very many sulfur-containing species in this heavy fuel oil sample, which should have less than 0.5% total sulfur by mass. However, there are several groupings of methyldibenzothiophene isomers, which help indicate thermal maturity, as well as even higher aromaticity species like benzonaphthothiophenes.



Peak Table - HFO GCxGC EI MMS_2

Peak #	Name	Expected Formula Mass	Formula	Retention Index	Similarity
1827	Dibenzothiophene	184.2571	$C_{12}H_8S$	1752.2	941
2133	Dibenzothiophene, 3-methyl-	198.2838	$C_{13}H_{10}S$	1852.4	917
2201	Dibenzothiophene, 3-methyl-	198.2838	$C_{13}H_{10}S$	1876.2	896
2273	2-Methyldibenzothiophene	198.2838	$C_{13}H_{10}S$	1900.0	812
2438	2,8-Dimethyldibenzo(b,d)thiophene	212.3104	$C_{14}H_{12}S$	1957.1	809
2478	Naphtho[2,3-b]thiophene, 4,9-dimethyl-	212.3104	$C_{14}H_{12}S$	1971.4	806
2496	2,8-Dimethyldibenzo(b,d)thiophene	212.3104	$C_{14}H_{12}S$	1976.2	886
2559	3,7-Dimethyldibenzothiophene	212.3104	$C_{14}H_{12}S$	1995.2	818
2577	2,7-Dimethyldibenzothiophene	212.3104	$C_{14}H_{12}S$	2000.0	872
3583	Benzo[b]naphtho[2,1-d]thiophene	234.3160	$C_{16}H_{10}S$	2377.8	881
3820	2-Methylbenzo[b]naphtho[2,1-d]thiophene	248.3426	$C_{17}H_{12}S$	2487.5	817
3920	2-Methylbenzo[b]naphtho[2,1-d]thiophene	248.3426	$C_{17}H_{12}S$	2537.5	870
4093	Benzo[b]naphtho[2,3-d]thiophene, 6,8-dimethyl-	262.3692	$C_{18}H_{14}S$	2612.9	801

Figure 3. Full analytical ion contour plot of heavy fuel oil with all peaks and peak markers is shown (top). The same heavy fuel oil sample is filtered so that only signal contributions from peaks that contain "S" in their identified formula are shown, with automatically generated name and structure displayed on the contour plot; note the clustered bands of benzothiophene isomers based on structural similarity (middle). The filtered peak table shows data used to populate the filtered contour plot, with information on each peak that meets the Peak Filter Criteria (bottom).

PCI for Molecular Ion Confirmation

Using the *MMS* allows for convenient changes between ionization modes without venting the source or any additional manual hardware intervention. Because there is no venting or moving of the GC columns, the retention times of peaks generated between ionization modes align from run to run, as can be seen in Figure 4. This is especially useful when complementary information from a softer ionization mode provides additional information for confirming the identity of a given peak.

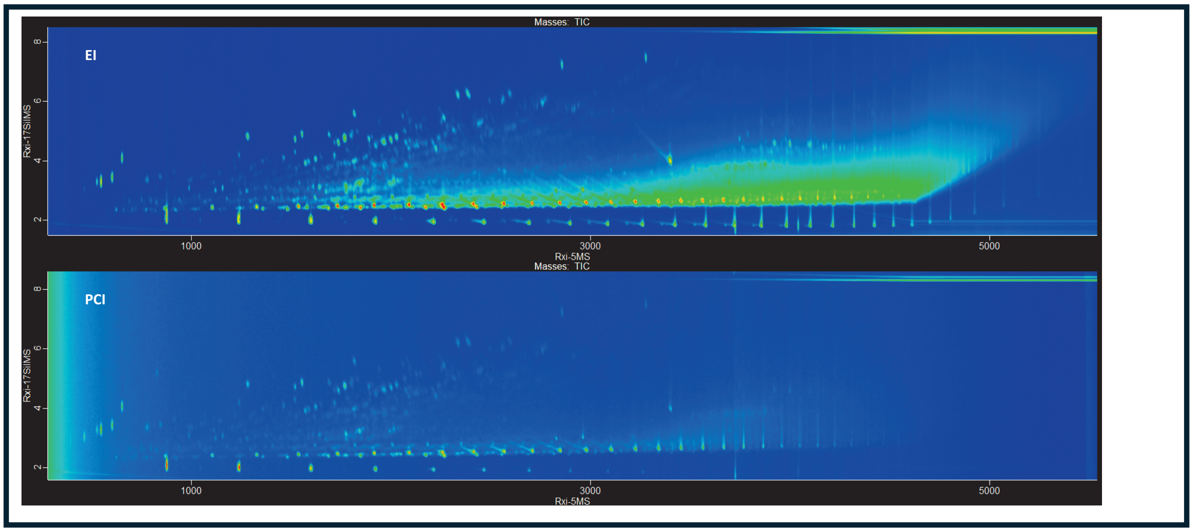
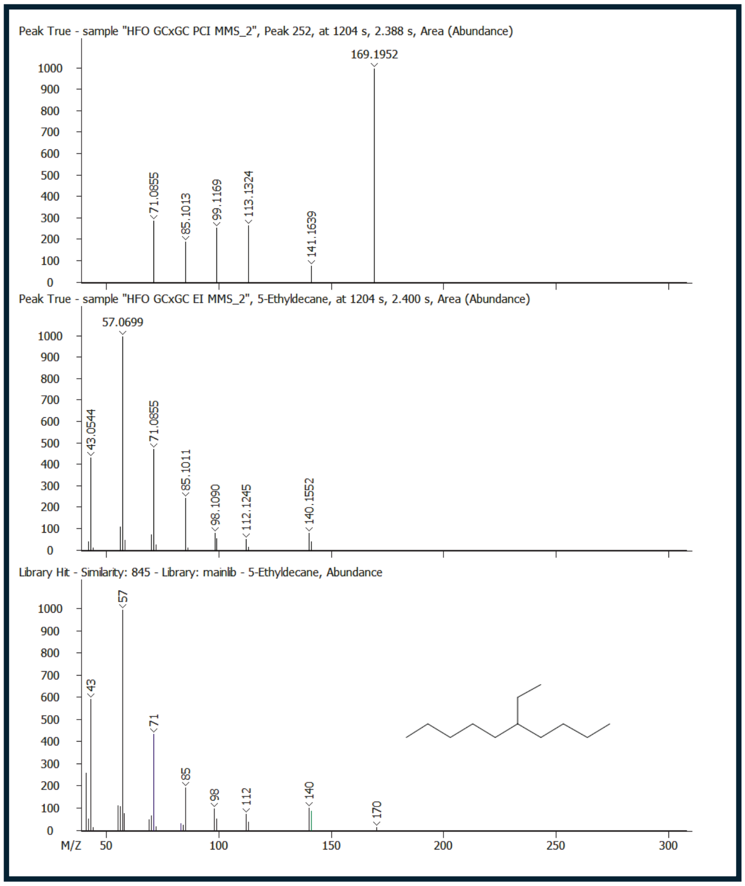


Figure 4. Comparison of full TIC chromatogram of heavy fuel oil acquired in EI and PCI modes, illustrating the excellent retention time correlation between acquisitions where no manual hardware intervention or venting was required.

Where no molecular ion was present in the EI spectra, chemical formulae calculated from the molecular ion formed in PCI mode were used to confirm peak identities suggested by comparison matches of EI mode spectra to library spectra, such as in the example of 5-ethyldecane shown in Figure 5. Due to the excellent mass accuracies present, the only possible chemical formula within 2 ppm for the expected [M-H] molecular ion due to the fully saturated structure was $C_{12}H_{25}$. Mass accuracies of the fragments only further confirm the identity of the chemical compound, with less than 2 ppm for each major mass contributor in the PCI spectra for the peak as can be seen in Table 2.


Peak True - sample "HFO GCxGC PCI MMS_2", Peak 252, at 1204 s, 2.388 s, Area (Abundance)

Peak True - sample "HFO GCxGC EI MMS_2", 5-Ethyldecane, at 1204 s, 2.400 s, Area (Abundance)

Library Hit - Similarity: 845 - Library: mainlib - 5-Ethyldecane, Abundance

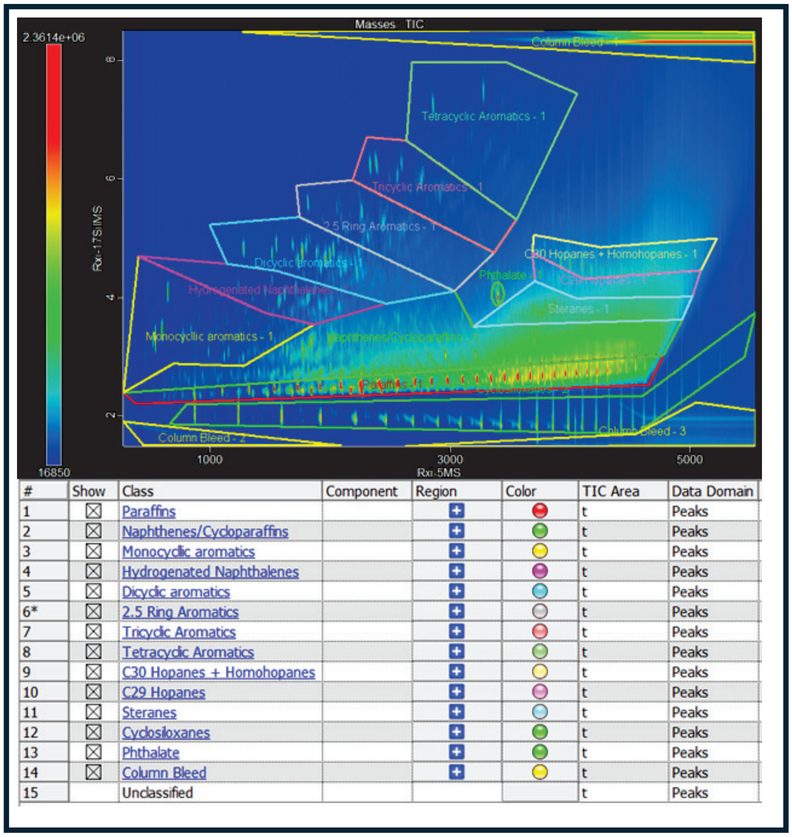
Figure 5. Peak True Spectra from PCI (top), EI (middle), and the NIST20 library spectra (bottom) for the 5-ethyldecane peak.

Table 2. Major fragments of 5-ethyldecane peak from the PCI spectra with calculated mass accuracies shown.

Mass	Abundance	Formula	Species	Mass Accuracy (ppm)
169.1952	1000	$C_{12}H_{25}$	$[M-H]^+$	0.56
71.0855	287	C_5H_{11}	fragment	-0.12
113.1324	268	C_8H_{17}	fragment	-0.69
99.1169	256	C_7H_{15}	fragment	0.88
85.1013	190	C_6H_{13}	fragment	1.20
141.1639	79	$C_{10}H_{21}$	fragment	1.16

Using Classifications for Bulk Characterization

In addition to individual peak identifications, bulk characterization of the sample was performed using the Classifications feature, which utilizes the structured nature of GCxGC contour plots in conjunction with Peak Filters. First, regions that correspond to elution bands of similarly structured compounds were drawn on the contour plot, shown in Figure 7. Then, Peak Filters were applied to each region so that only peaks that met criteria for definition of each chemical class were counted as belonging to the specified class.



#	Show	Class	Component	Region	Color	TIC Area	Data Domain
1	☒	Paraffins		⊞	●	t	Peaks
2	☒	Naphthenes/Cycloparaffins		⊞	●	t	Peaks
3	☒	Monocyclic aromatics		⊞	●	t	Peaks
4	☒	Hydrogenated Naphthalenes		⊞	●	t	Peaks
5	☒	Dicyclic aromatics		⊞	●	t	Peaks
6*	☒	2.5 Ring Aromatics		⊞	●	t	Peaks
7	☒	Tricyclic Aromatics		⊞	●	t	Peaks
8	☒	Tetracyclic Aromatics		⊞	●	t	Peaks
9	☒	C30 Hopanes + Homohopanes		⊞	●	t	Peaks
10	☒	C29 Hopanes		⊞	●	t	Peaks
11	☒	Steranes		⊞	●	t	Peaks
12	☒	Cyclosiloxanes		⊞	●	t	Peaks
13	☒	Phthalate		⊞	●	t	Peaks
14	☒	Column Bleed		⊞	●	t	Peaks
15		Unclassified				t	Peaks

Figure 6. Total Ion Chromatogram Plot of Heavy Fuel Oil Sample with Classifications Regions overlay (top). Classification method view defines the color and type of data summarized (bottom).

Table 3. Classification summary results of total ion chromatogram signal peak area percent by class for heavy fuel oil sample

Class	TIC Area %
Paraffins	17.44
Naphthenes/Cycloparaffins	41.70
Monocyllic aromatics	0.37
Hydrogenated Naphthalenes	0.98
Dicyclic aromatics	1.11
2.5 Ring Aromatics	0.61
Tricyclic Aromatics	0.22
Tetracyclic Aromatics	0.28
C30 Hopanes + Homohopanes	0.12
C29 Hopanes	0.01
Steranes	0.32
Cyclosiloxanes	2.58
Phthalate	0.19
Column Bleed	11.51
Unclassified	22.58
Total	**100.00**

An example of the resulting Classification Summary based on the EI signal is shown in Table 3, summarizing the area percent based on the total ion chromatogram signals belonging into each class.

Conclusion

The combination of multiple modes of ionization, GCxGC, and high-resolution mass spectra provides unparalleled power for not only confident identification of individual compounds like the important sulfur-containing species within a complex mixture, but also bulk characterization of the types of compound classes present for drawing insights into components of heavy fuel oil.

LECO Corporation | 3000 Lakeview Avenue | St. Joseph, MI 49085 | Phone: 800-292-6141 | 269-985-5496
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