Naval Research Laboratory
Washington, DC 20375-5320

NRL/6180/MR—2023/6

Analysis of JP-5 and F-24 Jet Fuel Vapor Composition by Single and Multidimensional Gas Chromatography – Mass Spectrometry

THOMAS LOEGEL

Chemical Sensing and Fuels Technology Branch
Navy Technology Center for Safety & Survivability Division

KATHERINE HINNANT

Combustion and Reacting Transport Branch
Navy Technology Center for Safety & Survivability Division

BRADEN C. GIORDANO

Chemical Sensing and Fuel Technology Section
Chemistry Division

October 23, 2023

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
23-10-2023

2. REPORT TYPE
NRL Memorandum Report

3. DATES COVERED *(From - To)*
6/1/23 – 7/31/23

4. TITLE AND SUBTITLE

Analysis of JP-5 and F-24 Jet Fuel Vapor Composition by Single and Multidimensional Gas Chromatography – Mass Spectrometry

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Thomas N. Loegel, Katherine Hinnant, and Braden C. Giordano

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
1S45

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5320

8. PERFORMING ORGANIZATION REPORT NUMBER

NRL/6180/MR--2023/6

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Strategic Environmental Research and Development Program
4800 Mark Center Drive, Suite 16F16
Alexandria, VA 22350-3605

10. SPONSOR / MONITOR'S ACRONYM(S)

SERDP

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

DISTRIBUTION STATEMENT A: Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Two jet fuels, a JP-5 and F-24, were analyzed via gas chromatography-mass spectrometry (GC-MS), comprehensive multidimensional gas chromatography (GCxGC-MS), and Solid Phase Micro Extraction (SPME) followed by GC-MS analysis. The first two techniques probed the liquid sample while the SPME collected and analyzed the vapor phase above the fuel samples. The combined analysis of the liquid samples via GC-MS and GCxGC-MS show a range of material from C6 to C12 consisting primarily of alkanes, iso alkanes, monocyclic, and single ring aromatics. The material distribution in the total ion chromatograms of both fuels is consistent with the differences in flash point specification for each fuel type. The SPME results add to the analysis by showing the presence of higher boiling material that will likely need to be considered in future foam testing. These results indicate that for the purposes of this program, SPME extracted fuel vapor analysis provides a more accurate representation of the vapor composition.

15. SUBJECT TERMS

Aviation fuel
Gas chromatography - mass spectrometry
Fuel vapor
Solid phase micro extraction

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Thomas Loegel
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	U	21	**19b. TELEPHONE NUMBER** *(include area code)*
U	U	U			(202) 404-1157

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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1.0 Abstract

Two jet fuels, a JP-5 and F-24, were analyzed via gas chromatography-mass spectrometry (GC-MS), comprehensive multidimensional gas chromatography (GCxGC-MS), and Solid Phase Micro Extraction (SPME) followed by GC-MS analysis. The first two techniques probed the liquid sample while the SPME collected and analyzed the vapor phase above the fuel samples. The combined analysis of the liquid samples via GC-MS and GCxGC-MS show a range of material from C_6 to C_{12} consisting primarily of alkanes, iso alkanes, monocyclic, and single ring aromatics. The material distribution in the total ion chromatograms of both fuels is consistent with the differences in flash point specification for each fuel type. The SPME results add to the analysis by showing the presence of higher boiling material that will likely need to be considered in future foam testing. These results indicate that for the purposes of this program, SPME extracted fuel vapor analysis provides a more accurate representation of the vapor composition.

2.0 Background

The goal of this Limited Scope research effort is to develop new foam evaluation tools that will enable a more comprehensive understanding of PFAS-free foam performance under extreme conditions. With the appreciation that fuel vapor composition is dynamic, existing laboratory-based techniques used to evaluate foam performance in the absence of fuel or at a specified fuel temperature do not provide for the systematic understanding of foam failure as a function of vapor composition. As vapor composition is dynamic, and most effected by extreme conditions, it is critical to develop the proper tools to access foam performance. As a proof of concept, this work will focus on identifying the vapor composition of a relevant fuel as a function of temperature, determining the role that fuel composition has on the associated vapor. With that understanding, we will evaluate PFAS-free foam performance as a function of vapor composition, identifying the critical components of fuel vapor that compromise PFAS-free foam performance. By relating vapor composition to novel foam stability metrics, our goal is to realize a tool wherein standard fuel property surveillance will include the ability to determine the most suitable PFAS-free foam formulation for firefighting. This work will provide critical information in support of identifying the most suitable PFAS-free firefighting formulations for a given fuel and firefighting conditions.

The focus of this report is defining vapor composition as a function of temperature and evaluating foam performance as a function of vapor composition. This work has three primary tasks: the determination of the composition of fuel vapor headspace as a function of temperature, the development of a fuel vapor testbed for the quantitative generation of fuel-based vapor streams, and the use of those streams in the generation of PFAS-free foams for laboratory-based evaluation. Briefly, using a combination of Solid Phase Micro Extraction (SPME), direct vapor sampling, and gas chromatography-mass spectrometry (GC-MS), we will identify the primary components of fuel head space as a function of temperature. This will inform the development of a vapor generation testbed that provides quantitative vapor streams of single components and/or mixtures of fuel related vapor.

3.0 Experimental

The two fuels selected for this survey were specification JP-5 (NRL# 21-01) and F-24 (NRL# 21-04) jet fuels

3.1 Gas Chromatography – Mass Spectrometry

An Agilent 6890 GC system was coupled to a 5975C MSD single quadruple mass spectrometer. A 60 m x 250 µm x 0.25 µm RXI-1MS column was used for the separation with a helium carrier gas at a 2 mL min^{-1} constant flow. The oven temperature program began at 40 °C and held for 2 min, then ramped at 5 °C/min

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Manuscript approved October 19, 2023.

to 165 °C, 2.5 °C/min to 265 °C, and finally 10 °C/min to 295 °C for a total run time of 70 min. Samples were analyzed neat and inject via autosampler. A 0.5 µL injection into a split-splitless inlet using a double tapered Agilent ultra inert glass liner with a glass wool operating at a 60:1 split was used. The inlet was kept at a constant 300 °C. The MS transfer line was held at a constant 250 °C. The MSD source and quadrupoles were held at 230 °C and 150 °C, respectively. The MSD had a 5 min solvent delay and used an electron impact source and scanned from m/z 35 to 400. A gain factor of 1.5 was used on the detector.

3.2 Navy Fuel Composition and Screening Tool (FCAST)

The GC-MS data was processed using the FCAST Version 3. Aspects related to fuel property prediction are discussed in the following publication: *Morris, Robert & Cramer, J.A. & Hammond, Mark & Myers, K.M. & Loegel, Thomas. (2013). A fit-for-purpose screening tool based on statistical modeling of fuel composition. 13th International Conference on Stability, Handling and Use of Liquid Fuels 2013. 285-304.*

3.3 Solid phase micro extraction (SPME)

The SPME fiber chosen was a divinylbenzene/carboxen/polydimethylsiloxane (DVB/ CAR/PDMS) blend with a 30 µm CAR/PDMS layer and 50 µm DVB layer manufactured by Supleco. Vapor samples collected on cleaned SPME fibers and were equilibrated for 30 sec at room temperature (~21 °C) over the head space 10 mL of sample in 100 mL amber glass bottle before analysis by GC-MS.

An Agilent 6890 GC system was coupled to a 5975C MSD single quadruple mass spectrometer. A 15 m x 250 µm x 0.25 µm RXI-5MS column was used for the separation with a helium carrier gas at a 2 mL min^{-1} constant flow. The oven temperature program began at 35 °C and held for 0.5 min, then ramped at 5 °C/min to 100 °C, 20 °C/min to 260 °C held for 1 min for a total run time of 23.5 min. A 10:1 split was used. The inlet was kept at a constant 260 °C. The MS transfer line was held at a constant 250 °C. The MSD source and quadrupoles were held at 230 °C and 150 °C, respectively. The MSD had no solvent delay and used an electron impact source and scanned from m/z 35 to 400. A gain factor of 1.0 was used on the detector.

3.4 Comprehensive Two-Dimensional Gas Chromatography Mass Spectrometry GCxGC-MS

Data was collected on a LECO BT system using a liquid nitrogen thermal modulator. The column configuration was a primary column consisting of a 60 m x 250 µm x 0.25 µm Restek Rxi-17 column connected to a 1.1 m x 180 µm x 0.18 µm Restek Rxi-1MS secondary column. A neat sample injection of 0.1 µL was used in a split-splitless inlet held at 300 °C with a split ratio of 75:1. A helium carrier gas was used at a constant flow rate of 2.00 mL min^{-1}. The oven temperature program began at 50 °C with a 1 min hold, then ramped at 3 °C/min to 310 °C. The secondary oven offset was +10 °C and the modulator offset was +15 °C. A 4 s modulation period was used. The time-of-flight mass spectrometer transfer line was held at 250 °C and the source was held at 230 °C throughout the run. Data was collected at a rate of 200 Hz over the mass range of m/z 35-550. Data analysis was performed by LECO ChromaTOF software.

4.0 Data Analysis and Results

4.1 FCAST Analysis

Below are the GC-MS total ion chromatograms (TIC) for the two liquid fuel samples. Visually, the higher flash point limited JP-5 can be noted with lack of material eluting before 15 min relative to the F-24 fuel sample. The final, high boiling material ends at roughly 37.5 min.

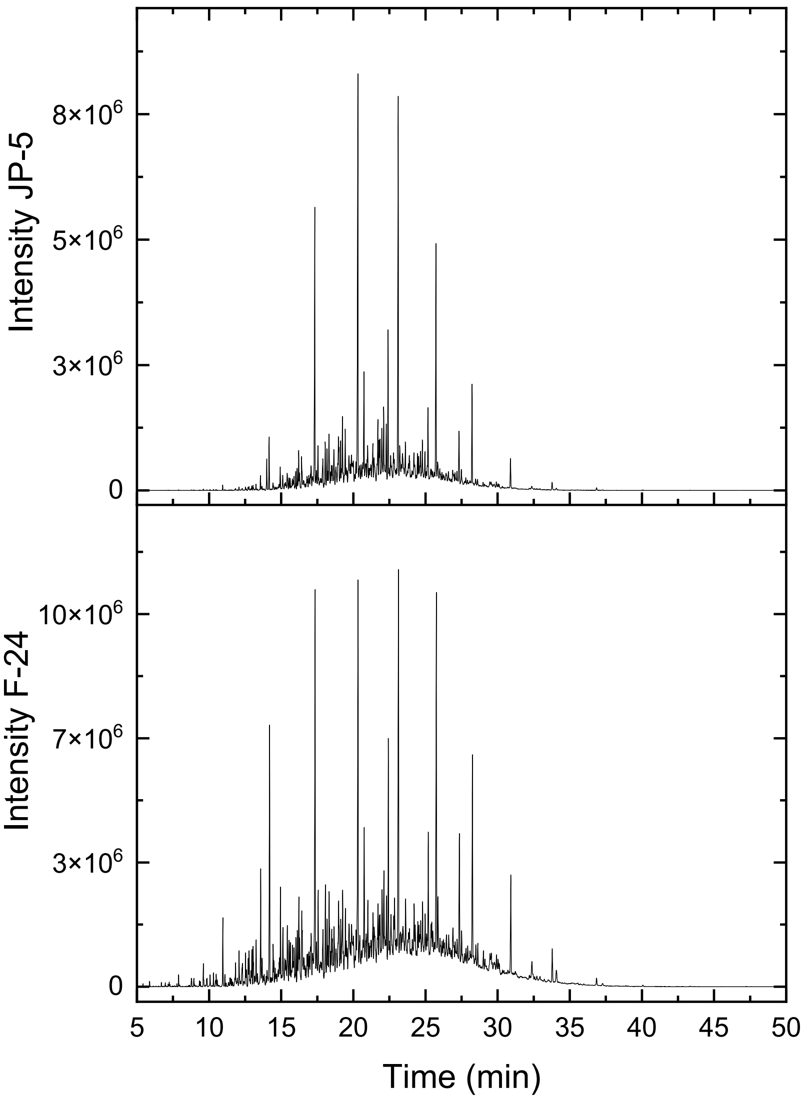

Figure 1: GC-MS total ion chromatograms for the JP-5 sample (top) and F-24 sample (bottom)

From this GC-MS data the FCAST program calculated a distillation plot for the fuels. This is accomplished by using the identified (via mass spectrometry library matching) n-alkane components, using the know boiling points of the n-alkanes to calibrate the time axis to temperature, then using the integrated peak areas to estimate the total precent distilled. This is similar to the ASTM D2887 simulated distillation approach. The distillation curves are found in figure 2.

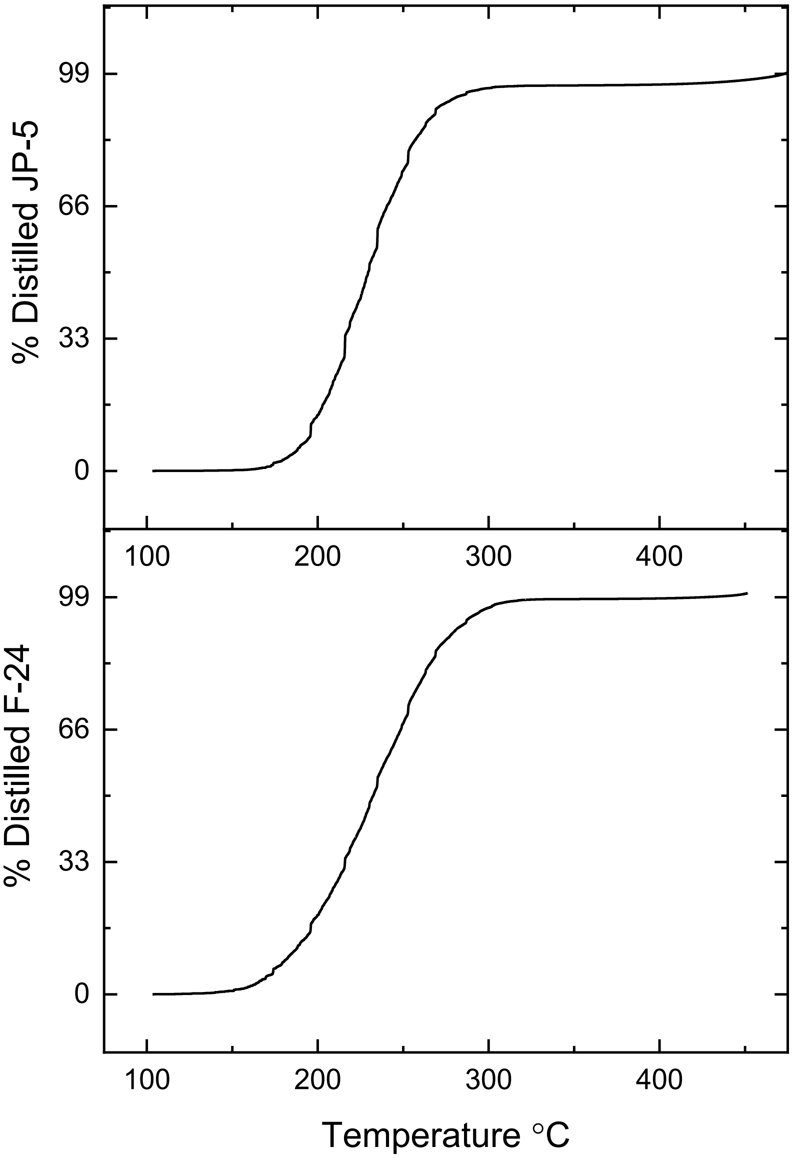

Figure 2. FCAST simulated distillation curves for the JP-5 and F-24 samples.

The F-24 distillation curve is reflective of the greater abundance of higher boiling material which was visually noted in the GC-MS TIC. Running the ASTM D93 flash point test method, small test cup, of the JP-5 and F-24 was 62 °C and 46 °C, respectively.

The top ten identified compounds via mass spectrometry library matching with a match facture of >700 is found in table 1.

Table 1: Top ten FCAST identified compounds eluting before 10 min

	JP-5	F-24

1	octane	octane
2	nonane	nonane
3	2-methyl-octane	2,4-dimethyl-hexane
4	3-ethyl-hexane	3-methyl-heptane
5	1,1,3-trimethyl-cyclohexane	4-ethyl-heptane
6	o-xylene	methylcyclcohexane
7	1-methylethyl-benzene	1,3,5-trimethyl-cyclohexane
8	octahydroindene	Toluene
9	1-ethyl-1-methyl-cyclohexane	p-xylene
10	Butyl-cyclopentane	ethylbenzene

Additionally, figure 3 provides carbon number distribution data for the two fuels. The F-24 sample has a higher abundance of C_7-C_{10} material compared to the JP-5.

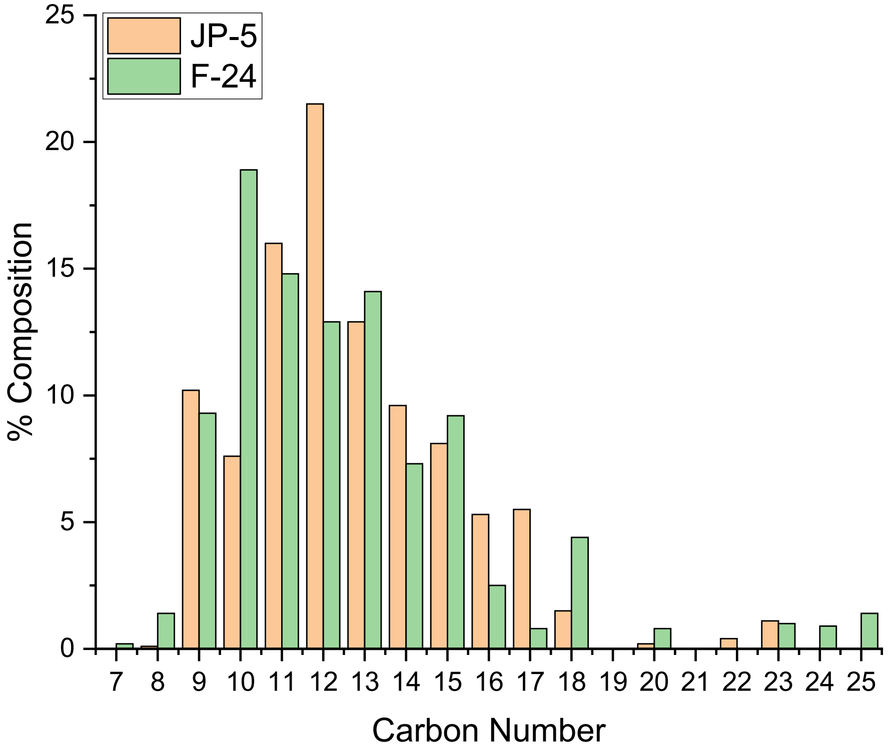

Figure 3. FCAST determined carbon distribution plot for both JP-5 and F-24 samples.

4.2 FCAST survey of previously collected fuel data

Using previously collected GC-MS data process via FCAST, figure 4 shows the range of composition variability for 50 fuel samples collected in the Navy Forensic Fuel Library. This library is comprised of refinery fresh samples retained from every Navy JP-5 procurement.

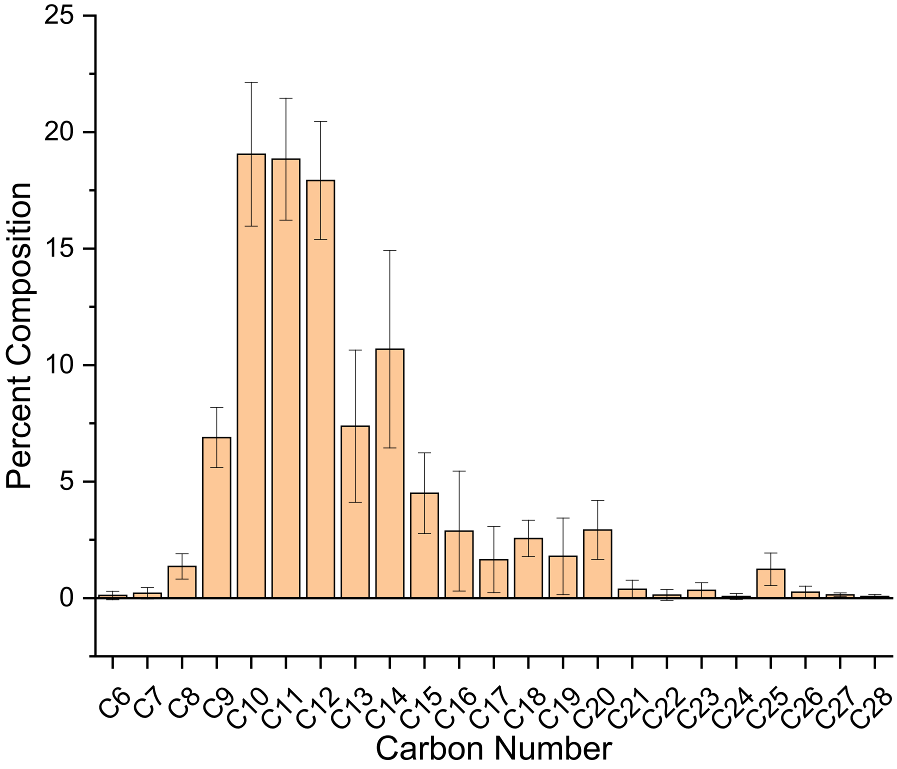

Figure 4. Average composition of fifty JP-5 samples with standard deviation indicated.

4.3 GCxGC-TOF Analysis Results

To confirm the GC-MS results and provide additional clarity to low boiling point species in the samples, GCxGC-Time of flight (TOF) MS was run on the neat liquid samples.

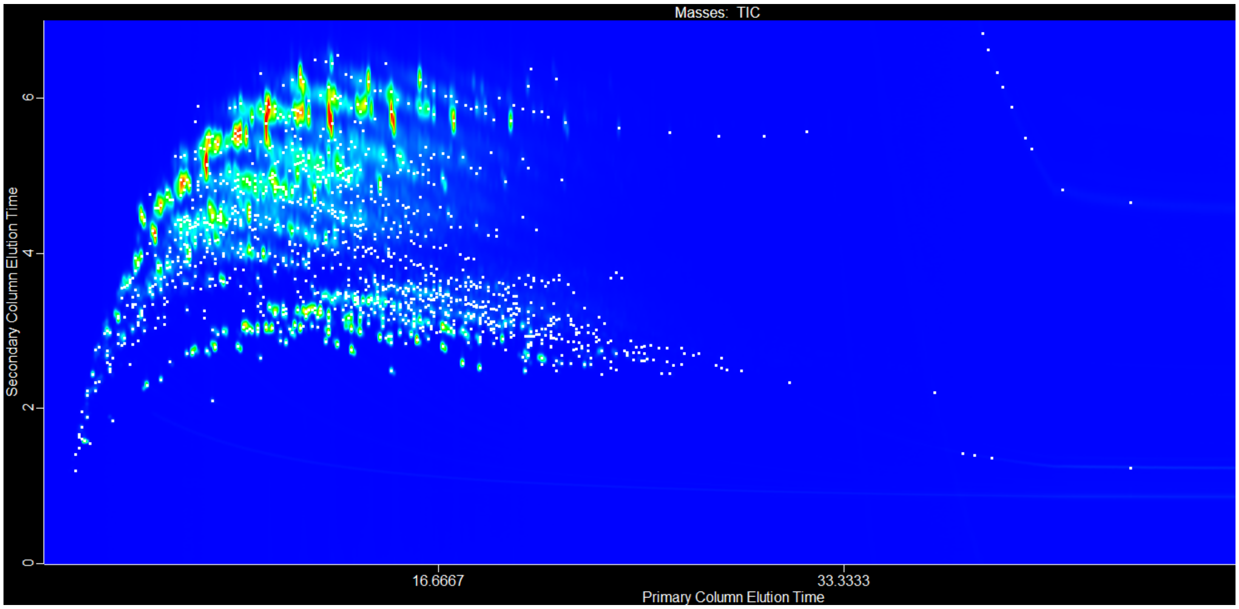

Figure 5. GCxGC-TOF-MS of the JP-5 samples. Each white dot is an identified peak. Intensity in the z-axis scale from green increasing to red.

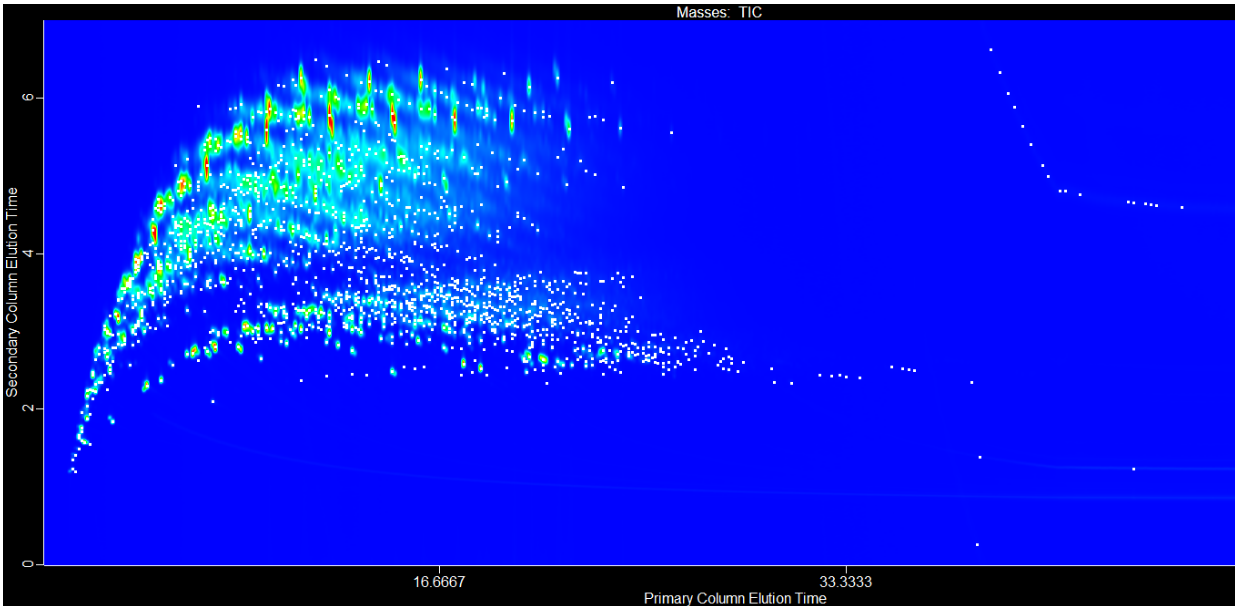

Figure 6. GCxGC-TOF-MS of the F-24 samples. Each white dot is an identified peak. Intensity in the z-axis scale from green increasing to red.

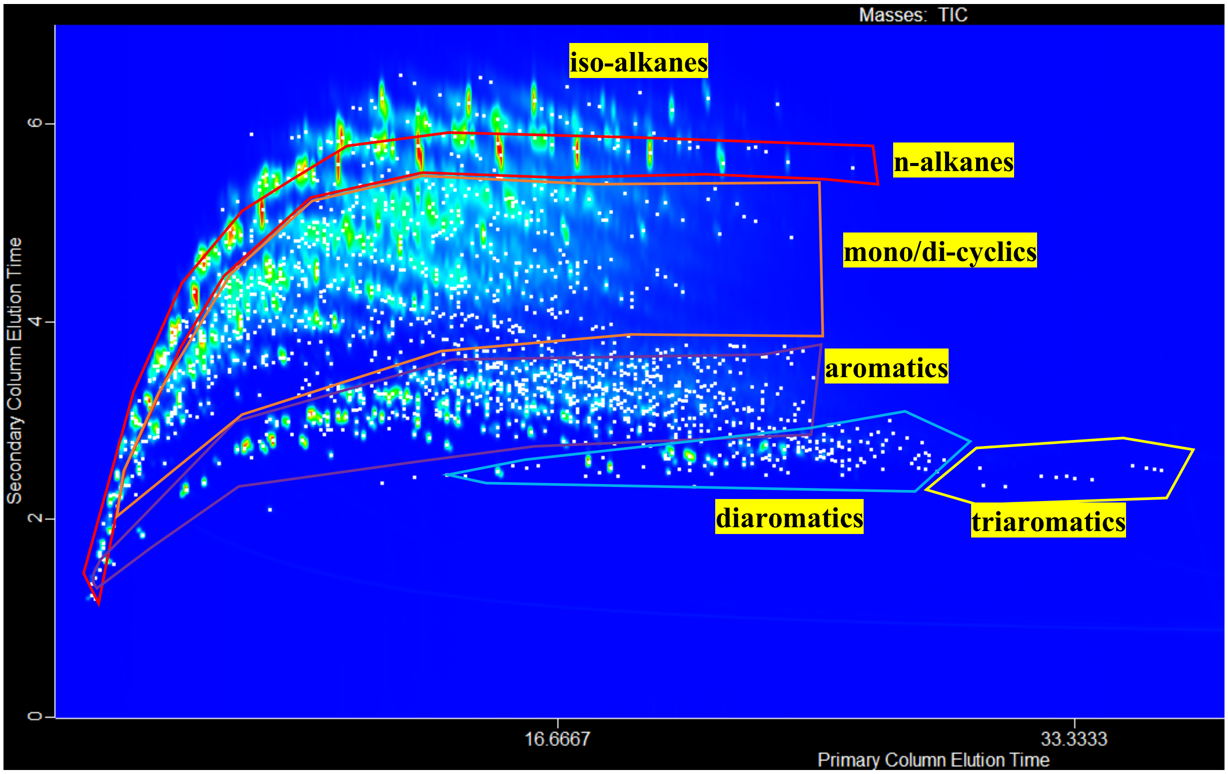

Figure 7. General compound class regions highlighted on the F-24 GCxGC chromatogram.

We can see similar differences in distribution of eluting material as noted in figure 1. However, the more sensitive nature of the system combined with the higher separation resolution allows for detection of over 700 peaks in the first 11 min of the separation. The improved resolution and signal-to-noise allows for improved identification of low boiling point materials.

Table 2. Top 50 compounds in first 11 min of the GCxGC chromatogram sorted by abundance in JP-5 sample

Compound Name	Percent Area	Compound Class	Compound Name	Percent Area	Compound Class
undecane	5.2%	alkane	1-nitroethyl-benzene	1.1%	aromatic
dodecane	4.5%	alkane	3-methyl-nonane	1.1%	iso-alkane
7-methyl-tridecane	3.0%	iso-alkane	methyl-cyclodecane	1.1%	monocyclic
2,5-dimethyl-decane	2.9%	iso-alkane	hexyl-cyclohexane	1.0%	monocyclic
2,2,4,6,6-pentamethyl-heptane	2.5%	iso-alkane	1-methyl-4-(2-methylpropyl)-benzene	1.0%	aromatic
2-methyl-undecane	2.4%	iso-alkane	hexadecane	1.0%	alkane
2-methyl-decane	2.3%	iso-alkane	10-methylnonadecane	0.9%	iso-alkane
2,4-dimethyl- undecane	2.1%	iso-alkane	2-ethyl-1,4-dimethyl-benzene	0.9%	aromatic
5-ethyl-2-methyl-heptane	2.0%	iso-alkane	1-ethyl-2,2,6-trimethylcyclohexane	0.9%	monocyclic

tridecane	2.0%	alkane	1,2,4-trimethyl-benzene	0.9%	aromatic
2-ethyl-1,4-dimethyl-benzene	1.9%	aromatic	2,2,7,7-tetramethyloctane	0.8%	iso-alkane
1-hydroxymethyl-1,3-dimethyl-cyclopentane	1.9%	monocyclic	1-methyl-3-pentyl-cyclohexane	0.8%	monocyclic
pentyl-cyclohexane	1.9%	monocyclic	1,2-diethyl-cyclooctane	0.8%	monocyclic
1-methyl-3-propyl-benzene	1.8%	aromatic	2-methyl- decalin	0.8%	dicyclic
4-methyl-dodecane	1.7%	iso-alkane	4-propyl-heptane	0.8%	iso-alkane
3-methyl-decane	1.6%	iso-alkane	1-ethyl-1,4-dimethyl-cyclohexane	0.8%	monocyclic
3,7-dimethyl-decane	1.6%	iso-alkane	2,6-dimethyl-octane	0.7%	iso-alkane
2,9-dimethyl-decane	1.5%	iso-alkane	3-dodecene	0.7%	
4,6-dimethyl-undecane	1.5%	iso-alkane	o-cymene	0.7%	aromatic
5-methyl-decane	1.5%	iso-alkane	2-methyl-octane	0.7%	iso-alkane
1-ethyl-3-methyl- benzene	1.4%	aromatic	1-ethyl-1-methyl-cyclopentane	0.6%	monocyclic
heptyl-cyclohexane	1.4%	monocyclic	butyl-cyclohexane	0.6%	monocyclic
tetradecane	1.3%	alkane	6,6-dimethyl-undecane	0.6%	iso-alkane
2-methyl-nonane	1.2%	iso-alkane	4-ethyl-decane		iso-alkane

Table 3. Top 50 compounds in first 11 min of the GCxGC chromatogram sorted by abundance in F-24 sample

Compound Name	Percent Area	Compound Class		Percent Area	Compound Class
undecane	3.2%	alkane	2,4-dimethyl-undecane	1.1%	iso-alkane
dodecane	2.6%	alkane	1,2,4,5-tetramethyl- benzene	1.1%	aromatic
2,6-dimethyl-undecane	2.4%	iso-alkane	nonane	1.1%	alkane
2,3,7-trimethyl-octane	2.1%	iso-alkane	tridecane	1.0%	alkane
2,5-dimethyl-decane	1.9%	iso-alkane	3,7-dimethyl-decane	1.0%	iso-alkane
decane	1.6%	alkane	4-ethyl-octane	1.0%	iso-alkane
2-methyl-undecane	1.5%	iso-alkane	2,5-dimethyl-undecane	1.0%	iso-alkane
1-methyl-4-(1-methylethyl)-cyclohexane	1.5%	monocyclic	2-methyl-dodecane	1.0%	iso-alkane
2-methyl-decane	1.5%	iso-alkane	p-xylene	0.9%	aromatic
2,3,5-trimethyl-heptane	1.4%	iso-alkane	2-butyl-1,1,3-trimethyl-cyclohexane	0.9%	monocyclic
1,2,4-trimethyl-benzene	1.4%	aromatic	1-ethyl-3,5-dimethyl-benzene	0.9%	aromatic
1-ethyl-3-methyl-benzene	1.4%	aromatic	1-ethyl-4-methyl-cyclohexane	0.8%	monocyclic
3-methyl-undecane	1.4%	iso-alkane	propyl-benzene	0.8%	aromatic
1-ethyl-2,4-dimethyl-benzene	1.3%	aromatic	1,2-diethyl-cyclohexane	0.8%	monocyclic
Pentane, 2,4-dimethyl-	1.3%	iso-alkane	3-ethyl-2-methyl-heptane	0.8%	iso-alkane
cyclododecane	1.3%	monocyclic	3-methyl-octane	0.8%	iso-alkane

1-methyl-4-propyl-benzene	1.3%	aromatic	o-cymene	0.8%	aromatic
6,6-dimethyl-undecane	1.2%	iso-alkane	1-methylethyl-cyclohexane	0.8%	monocyclic
3-methyl-nonane	1.2%	iso-alkane	6-ethyl-2-methyl-octane	0.7%	iso-alkane
3-ethyl-pentane	1.2%	iso-alkane	1-ethyl-2-methyl-benzene	0.7%	aromatic
methyl-decane	1.2%	iso-alkane	1,3-dimethyl-benzene	0.7%	aromatic
butyl-cyclohexane	1.2%	monocyclic	methyl-cyclodecane	0.7%	monocyclic
1-ethyl-4-methyl-cyclohexane	1.2%	monocyclic	1-methyl-4-(1-methylpropyl)-benzene	0.7%	aromatic

4.4 SPME Results

SPME offers an approach that is able to directly interrogate the vapor phase present above a fuel to give further confirmation on which species are present. While the intensity of each compound should not be relied on as the sorbent chosen can have a dramatic impact on the amount of a particular compound that is collected, we can still get a good understanding of the vapor phase at ambient conditions without speculation based on total sample volatility in a GC inlet. Additionally with less total material injected leads to improved chromatographic clarity in single dimension GC.

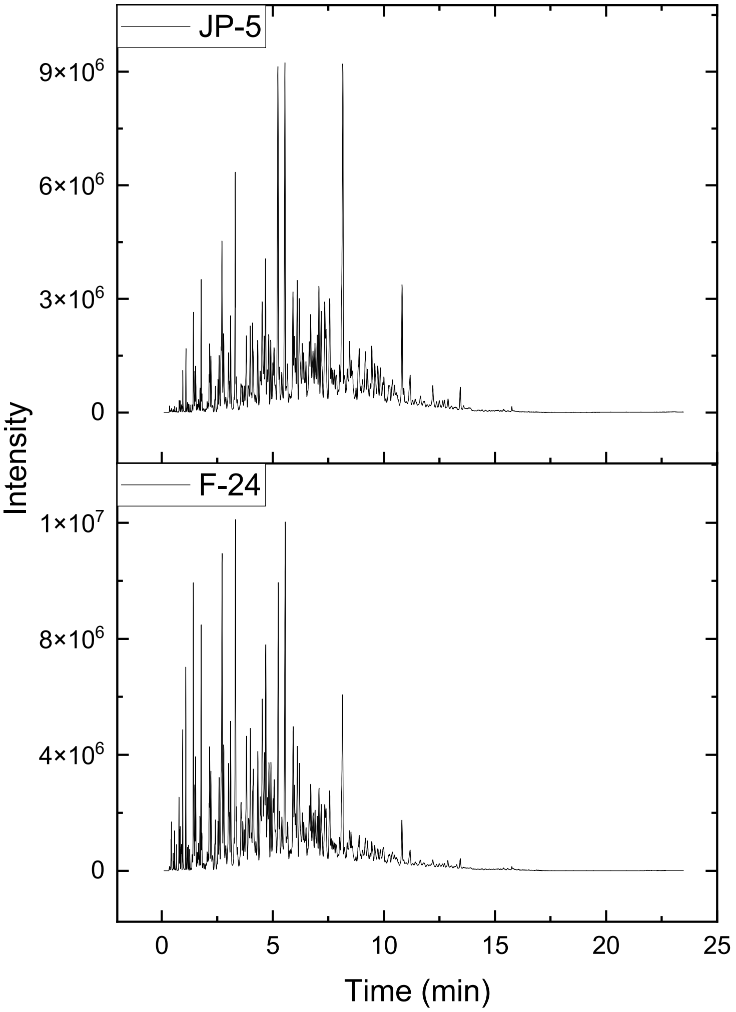

Figure 8. SPME GC-MS TIC plots of JP-5 (top) and F-24 (bottom)

Comparing figure 1 and figure 8 we can see a difference in chromatographic profile yet the trend of a greater number and potentially abundance of early eluting, low boiling material in the F-24 sample remains. In both bases the majority of material has eluted from the GC system before the column temperature reaches 100 °C. Figure 9 and 10 shows that this low boiling material does not comprise a significant amount of the bulk fuel as measure by distillation. Additionally, using distillation profiles may not yield actionable information for the purpose of fuel vapor distribution.

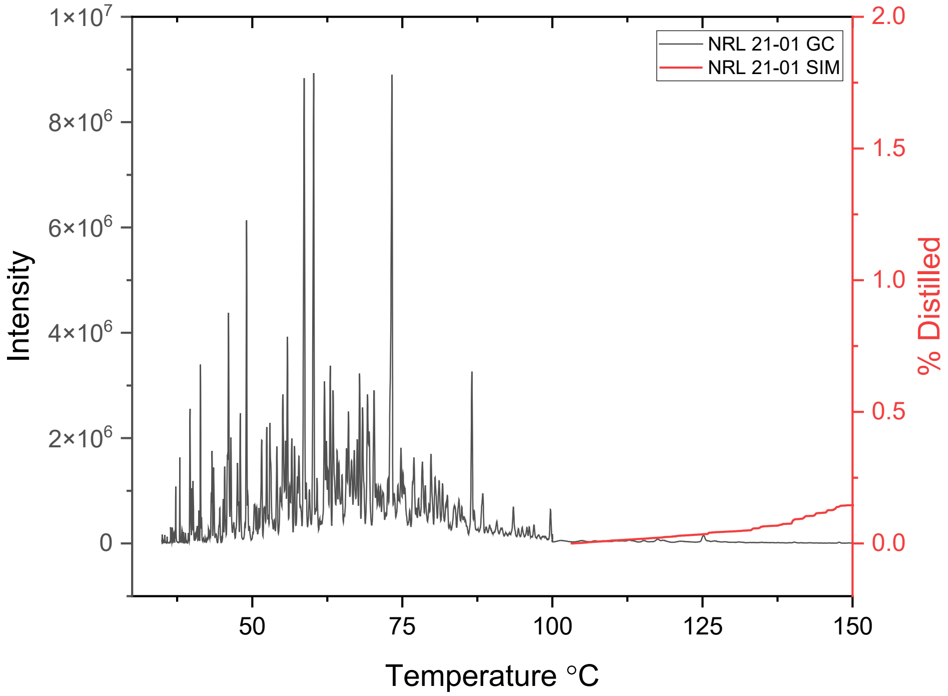

Figure 9. Double y-plot depicting the SPME GC TIC combined with the simulated distillation data from figure 2 of the JP-5 fuel sample on the same temperature axis

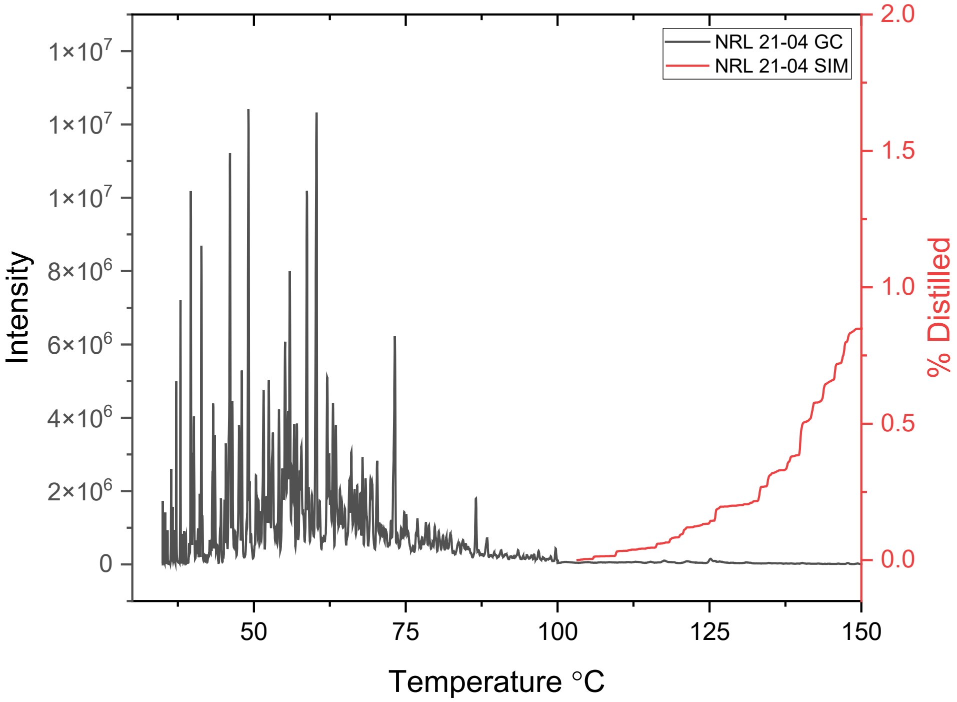

Figure 10. Double y-plot depicting the SPME GC TIC combined with the simulated distillation data from figure 2 of the F-24 fuel s sample on the same temperature axis

Using the same integration and MS library matching procedure used in the FCAST analysis a table of identified species with match factors greater than 700 are found for both samples below.

Table 4. SPME GC-MS compound hit list for the JP-5 sample sorted by compound class, retention times are in min, precent represent total peak area of the chromatogram.

Normal Alkanes			
Retention Time	Match Factor	Name	Percent
8.15	923	Undecane	9.8%
5.55	936	Decane	7.6%
3.31	913	Nonane	4.0%
10.82	920	Dodecane	2.9%
1.77	944	Octane	1.6%
13.43	893	Tridecane	0.6%
0.95	932	Heptane	0.5%
0.59	906	n-Hexane	<0.1%
15.76	823	Tetradecane	<0.1%
0.44	821	Pentane	<0.1%
Iso Alkanes			

Retention Time	Match Factor	Name	Percent
4.82	884	Octane, 2,6-dimethyl-	2.8%
7.18	832	Decane, 2-methyl-	2.5%
6.10	858	Decane, 4-methyl-	2.2%
7.00	800	Decane, 5-methyl-	1.6%
4.61	850	Nonane, 4-methyl-	1.4%
2.79	822	Heptane, 2,5-dimethyl-	1.4%
2.68	853	Octane, 2-methyl-	1.2%
9.84	823	Undecane, 2-methyl-	1.1%
11.18	791	Undecane, 2,6-dimethyl-	1.1%
6.49	820	Nonane, 3,7-dimethyl-	1.0%
1.49	857	Heptane, 3-methyl-	0.4%
8.84	794	Tetracontane, 3,5,24-trimethyl-	0.4%
2.53	914	Heptane, 2,3-dimethyl-	0.4%
12.73	767	Tetradecane, 2,6,10-trimethyl-	0.3%
2.04	903	Heptane, 2,4-dimethyl-	0.1%
1.37	910	Hexane, 2,3-dimethyl-	0.1%
3.52	790	Octane, 4-ethyl-	0.1%
0.83	920	Hexane, 3-methyl-	<0.1%
0.79	794	Hexane, 2-methyl-	<0.1%
1.95	815	Hexane, 3-ethyl-	<0.1%
1.99	869	Heptane, 2,2-dimethyl-	<0.1%
0.52	853	Pentane, 2-methyl-	<0.1%
0.42	834	Butane, 2-methyl-	<0.1%
1.32	806	Pentane, 2,3,3-trimethyl-	<0.1%
Alkyl Monocyclo Alkanes			
Retention Time	Match Factor	Name	Percent
5.05	814	Cyclopentane, 1-methyl-3-(2-methylpropyl)-	3.1%
6.19	775	Cyclohexane, butyl-	2.8%
3.81	852	Cyclohexane, propyl-	1.6%
3.01	892	Cyclohexane, 1-ethyl-2-methyl-	1.4%
7.70	756	Cyclopentane, 1,2-dipropyl-	1.1%
2.21	896	Cyclohexane, 1,1,3-trimethyl-	0.8%
2.16	929	Cyclohexane, ethyl-	0.8%
5.30	781	Cyclohexane, 1-methyl-2-propyl-	0.8%
5.00	885	m-Menthane, (1S,3R)-(+)-	0.8%
1.53	905	Cyclohexane, 1,3-dimethyl-, cis-	0.6%
1.09	940	Cyclohexane, methyl-	0.5%
5.11	844	Cyclooctane, 1,2-diethyl-	0.5%
3.59	766	Cyclohexane, (1-methylethyl)-	0.4%
2.88	808	Cyclohexane, 1,1,2-trimethyl-	0.4%

3.04	915	Cyclohexane, 1-ethyl-4-methyl-, trans-	0.4%
2.42	925	Cyclohexane, 1,2,4-trimethyl-, (1α,2β,4β)-	0.3%
3.92	820	Cyclopentane, butyl-	0.3%
4.04	811	Cyclohexane, 1-ethyl-2,3-dimethyl-	0.3%
3.40	852	Cyclohexane, 1-ethyl-4-methyl-, cis-	0.3%
1.72	929	Cyclohexane, 1,2-dimethyl-, trans-	0.3%
1.67	869	Cyclopentane, 1-ethyl-3-methyl-, cis-	0.3%
1.81	900	Cyclohexane, 1,4-dimethyl-, cis-	0.2%
2.30	841	trans-1,2-Diethyl cyclopentane	0.2%
2.39	813	Cyclohexane, 1,2,3-trimethyl-	0.1%
2.10	859	Cyclohexane, 1,2-dimethyl-, cis-	0.1%
1.27	894	Cyclopentane, 1,2,3-trimethyl-, (1α,2α,3β)-	<0.1%
2.96	808	Cyclohexane, 1,1,3,5-tetramethyl-, cis-	<0.1%
1.60	852	Cyclohexane, 1,1-dimethyl-	<0.1%
1.21	905	Cyclopentane, 1,2,4-trimethyl-	<0.1%
0.90	909	Cyclopentane, 1,2-dimethyl-, cis-	<0.1%
2.49	851	Cyclohexane, 1,2,4-trimethyl-	<0.1%
1.88	759	Cyclopentane, (1-methylethyl)-	<0.1%
0.67	901	Cyclopentane, methyl-	<0.1%
0.46	841	Cyclopropane, 1,1-dimethyl-	<0.1%
0.87	915	Cyclopentane, 1,3-dimethyl-, cis-	<0.1%
Dicyclo Alkanes			
Retention Time	Match Factor	Name	Percent
6.64	830	Naphthalene, decahydro-, trans-	1.6%
Alkyl Dicyclo Alkanes			
Retention Time	Match Factor	Name	Percent
8.52	841	Naphthalene, decahydro-2-methyl-	0.9%
3.57	852	Pentalene, octahydro-2-methyl-	0.4%
Acyclic Alkenes			
Retention Time	Match Factor	Name	Percent
4.46	757	1-Octene, 2,6-dimethyl-	0.3%
5.62	766	3-Heptene, 2,2,3,5,5,6,6-heptamethyl-	0.3%
0.89	838	1-Hexene, 3,5-dimethyl-	<0.1%
Alkyl Benzenes			
Retention Time	Match Factor	Name	Percent
7.56	824	p-Cymene	4.5%
2.71	955	p-Xylene	3.5%
4.52	945	Benzene, 1-ethyl-3-methyl-	2.0%
6.71	808	Benzene, 1-methyl-3-propyl-	1.6%
6.90	856	Benzene, 2-ethyl-1,4-dimethyl-	1.4%
8.45	808	Benzene, 1,2,3,4-tetramethyl-	1.2%

1.43	812	Toluene	1.1%
4.91	888	Benzene, 1-ethyl-2-methyl-	1.1%
8.36	779	Benzene, 1-ethyl-2,3-dimethyl-	0.9%
5.66	806	Benzene, (1-methylpropyl)-	0.7%
2.58	935	Ethylbenzene	0.7%
3.72	868	Benzene, (1-methylethyl)-	0.3%
Indans and Tetralins			
Retention Time	Match Factor	Name	Percent
9.46	791	Naphthalene, 1,2,3,4-tetrahydro-	1.5%
12.20	781	Naphthalene, 1,2,3,4-tetrahydro-5-methyl-	0.7%
12.89	781	Naphthalene, 1,2,3,4-tetrahydro-6-methyl-	0.3%
13.59	780	Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl-	0.1%
15.42	757	Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	<0.1%
Oxygen-Bound			
Retention Time	Match Factor	Name	Percent
6.39	810	1-Decanol, 2-methyl-	1.5%
4.43	777	1-Octanol, 2-butyl-	1.3%
6.33	808	Oxirane, tetradecyl-	1.2%
7.85	799	Cyclododecanemethanol	1.0%
7.77	760	13-Octadecenal, (Z)-	0.7%
8.75	791	Phytol	0.6%
9.05	772	4-Chloro-3-n-hexyltetrahydropyran	0.5%
9.04	790	n-Nonadecanol-1	0.4%
3.65	764	1-Decanol, 2-hexyl-	0.3%
1.16	785	1-Nonanol	0.1%
11.53	777	1,2-15,16-Diepoxyhexadecane	<0.1%

Table 5. SPME GC-MS compound hit list for the F-24 sample sorted by compound class, retention times are in min, precent represent total peak area of the chromatogram.

Normal Alkanes			
Retention Time	Match Factor	Name	Percent
5.56	936	Decane	6.7%
3.32	899	Nonane	5.3%
8.14	892	Undecane	3.9%
1.77	939	Octane	2.5%
0.95	944	Heptane	1.2%
10.81	873	Dodecane	1.0%
0.43	959	Pentane	0.4%
0.58	963	n-Hexane	0.3%
13.43	843	Tridecane	0.2%

0.38	822	Butane	<0.1%
15.76	800	Tetradecane	<0.1%
16.89	758	Nonadecane	<0.1%
Iso Alkanes			
Retention Time	Match Factor	Name	Percent
3.99	885	Octane, 2,6-dimethyl-	3.4%
4.13	863	Heptane, 3-ethyl-2-methyl-	2.4%
4.63	850	Nonane, 4-methyl-	2.0%
2.79	819	Octane, 3-methyl-	1.7%
6.11	840	Decane, 4-methyl-	1.7%
1.49	866	Heptane, 3-methyl-	0.7%
2.53	907	Heptane, 2,3-dimethyl-	0.5%
2.13	811	Octane, 2-methyl-	0.4%
11.18	754	Tetracontane, 3,5,24-trimethyl-	0.4%
0.83	925	Hexane, 3-methyl-	0.3%
0.79	836	Hexane, 2-methyl-	0.3%
2.04	894	Heptane, 2,4-dimethyl-	0.2%
0.42	947	Butane, 2-methyl-	0.2%
1.37	936	Hexane, 2,3-dimethyl-	0.2%
0.52	922	Pentane, 2-methyl-	0.1%
1.94	779	Hexane, 3-ethyl-	<0.1%
0.55	925	Pentane, 3-methyl-	<0.1%
1.99	840	Heptane, 2,2-dimethyl-	<0.1%
1.31	804	Pentane, 3-ethyl-2-methyl-	<0.1%
Alkyl Monocyclo Alkanes			
Retention Time	Match Factor	Name	Percent
5.07	839	Cyclopentane, 1-methyl-3-(2-methylpropyl)-	2.5%
3.82	876	Cyclohexane, propyl-	2.2%
3.01	894	Cyclohexane, 1-ethyl-2-methyl-	2.0%
6.20	751	Cyclohexane, butyl-	2.0%
5.41	773	Cyclopentane, 1,2-dipropyl-	1.7%
1.09	947	Cyclohexane, methyl-	1.3%
2.16	913	Cyclohexane, ethyl-	1.2%
2.21	899	Cyclohexane, 1,1,3-trimethyl-	1.1%
3.92	818	Cyclopentane, butyl-	1.1%
1.53	910	Cyclohexane, 1,4-dimethyl-, trans-	1.1%
5.01	873	Cyclohexane, 1-methyl-4-(1-methylethyl)-, cis-	0.9%
5.30	781	Cyclohexane, 1-methyl-2-propyl-	0.8%
2.42	914	Cyclohexane, 1,2,4-trimethyl-	0.6%

3.05	916	Cyclohexane, 1-ethyl-4-methyl-, cis-	0.6%
5.12	848	Cyclooctane, 1,2-diethyl-	0.5%
2.88	824	Cyclohexane, 1,1,2-trimethyl-	0.5%
1.72	934	Cyclohexane, 1,2-dimethyl-, trans-	0.5%
0.89	930	Cyclopentane, 1,3-dimethyl-, cis-	0.4%
3.41	879	Cyclohexane, 1-ethyl-4-methyl-, trans-	0.4%
4.04	815	Cyclohexane, 2-ethyl-1,3-dimethyl-	0.4%
1.81	911	Cyclohexane, 1,4-dimethyl-, cis-	0.3%
1.66	891	Cyclopentane, 1-ethyl-2-methyl-, cis-	0.3%
1.16	792	Cyclopentane, ethyl-	0.3%
2.29	864	trans-1,2-Diethyl cyclopentane	0.3%
2.39	836	Cyclohexane, 1,2,3-trimethyl-	0.2%
0.66	950	Cyclopentane, methyl-	0.2%
1.60	860	Cyclohexane, 1,1-dimethyl-	0.2%
1.27	936	Cyclopentane, 1,2,3-trimethyl-, (1α,2α,3β)-	0.2%
1.21	912	Cyclopentane, 1,2,4-trimethyl-	0.2%
2.10	882	Cyclohexane, 1,2-dimethyl-, cis-	0.1%
1.63	871	Cyclopentane, 1-ethyl-3-methyl-, cis-	0.1%
1.86	778	Cyclopentane, 1,1,3,4-tetramethyl-, cis-	<0.1%
2.01	849	1-Ethyl-2-(4-methylpentyl)cyclopentane	<0.1%
Dicyclo Alkanes			
Retention Time	Match Factor	Name	Percent
6.65	811	Naphthalene, decahydro-, trans-	1.1%
Acyclic Alkenes			
Retention Time	Match Factor	Name	Percent
3.59	771	1-Cyclohexylnonene	0.3%
3.26	762	Tridecane, 7-methylene-	0.3%
5.62	759	3-Heptene, 2,2,3,5,5,6,6-heptamethyl-	0.3%
Alkyl Benzenes			
Retention Time	Match Factor	Name	Percent
5.25	877	Mesitylene	5.3%
2.72	975	Benzene, 1,3-dimethyl-	4.1%
7.56	807	p-Cymene	3.1%
4.53	942	Benzene, 1-ethyl-3-methyl-	2.4%
1.42	826	Toluene	2.3%
3.10	927	p-Xylene	1.5%
4.92	885	Benzene, 1-ethyl-2-methyl-	1.2%
6.71	800	Benzene, 1-methyl-3-propyl-	1.1%
2.58	920	Ethylbenzene	1.0%

6.90	836	Benzene, 2-ethyl-1,4-dimethyl-	0.9%
5.67	752	Benzene, (1-methylpropyl)-	0.6%
8.45	789	Benzene, 1,2,3,4-tetramethyl-	0.5%
3.72	853	Benzene, (1-methylethyl)-	0.5%
Oxygen-Bound			
Retention Time	Match Factor	Name	Percent
5.98	758	trans-p-mentha-1(7),8-dien-2-ol	1.4%
7.00	788	1-Decanol, 2-hexyl-	1.3%
7.84	776	Cyclododecanemethanol	0.9%
6.40	803	1-Decanol, 2-methyl-	0.9%
8.52	842	Bicyclo[4.1.0]heptan-3-one, 4,7,7-trimethyl-, [1R-(1α,4β,6α)]-	0.8%
11.30	760	Naphth[1,2-b]oxirene, decahydro-1a,7-dimethyl-	0.7%
8.58	762	7-Hexadecenal, (Z)-	0.6%
9.04	773	Undec-10-ynoic acid, dodecyl ester	0.5%
7.77	769	13-Octadecenal, (Z)-	0.3%
11.70	763	2(1H)-Naphthalenone, octahydro-4a,5-dimethyl-, (4aα,5α,8aβ)-	<0.1%
0.74	774	1-Penten-3-ol, 2-methyl-	<0.1%

Reviewing tables 4 and 5, the biggest distinction is the presents of material like naphthalenes and other material C_{13}-C_{20}.

5.0 Conclusions

The combined analysis of the liquid samples via GC-MS and GCxGC-MS show a range of material from C_6 to C_{12} consisting primarily of alkanes, iso alkanes, monocyclic, and single ring aromatics. The material distribution in the total ion chromatograms of both fuels is consistent with the differences in flash point specification for each fuel type. The SPME results add to the analysis by showing the presence of higher boiling material that will likely need to be considered in future foam testing. These results indicate that for the purposes of this program, SPME extracted fuel vapor analysis provides a more accurate representation of the vapor composition.

6.0 Future Work

The next experimental work to further improve our more detailed understanding on fuel headspace composition would be to better characterize SPME performance. The SPME sorbent likely impacts relative ratios of material present in the vapor phase. Additionally, only room temperature was tested. An experiment that tested various common SPME sorbent chemistries and conditions would provide a more complete picture with a higher degree of accuracy.