GC/MS Analysis of Trace Fatty Acid Methyl Esters (FAME) in Jet Fuel Using Energy Institute Method IP585

Application Note

Fuels

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Abstract

This paper describes the application of IP Method 585 for measuring trace amounts of FAME in jet fuel using the Agilent 5975C GC/MS system. This method uses selective ion monitoring (SIM) to improve FAME selectivity and sensitivity in the complex jet fuel sample matrix. This was demonstrated by running jet fuel samples spiked with known quantities of soybean biodiesel FAMEs. Full recovery of the FAMEs was achieved across a concentration range of 1 to 40 mg/kg total FAME in jet fuel. Analysis precision for these results was shown to be three to ten times better than the method requirements.

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Introduction

Multi-product pipelines (MPP) are used to transport many different types of liquid hydrocarbon fuels. This transport includes jet fuel, which is also known as aviation turbine fuel (AVTUR). Over the years the Joint Inspection Group (JIG), an international consortium of jet fuel producers, has developed guidelines and procedures to assure the quality of MPP transported jet fuel. Recently, the MPP transport of biodiesel fuel has resulted in jet fuel contamination with fatty acid methyl esters (FAME). While the effects of FAMEs in jet fuel are still being studied, the JIG has placed a maximum limit of 5 mg/kg (ppm) total FAME in jet fuel.

Biodiesel fuel contains up to 20 wt% FAMEs mixed with conventional petroleum diesel. The chemical structure of FAMEs consists of a non-polar long chain hydrocarbon coupled to a polar methyl ester group. FAMEs are made from a variety of renewable resources, principally vegetable oils and animal fats. Due to the varied nature of these oils, many different saturated and unsaturated FAMEs can be found in biodiesel. Since it would be difficult to measure every possible FAME in jet fuel, the Energy Institute has identified six FAMEs that represent 95% of the potential sources of jet fuel contamination. These six are shown in Table 1.[1]

The analysis of ppm amounts of FAMEs is difficult due to the chemical complexity of jet fuel. A single capillary GC column cannot sufficiently resolve the six FAMEs from the hydrocarbon matrix. To solve this problem the Energy Institute has developed IP method 585 using gas chromatography/mass spectrometry (GC/MS) to selectively detect and quantify the total FAME content in jet fuel.[1] The electron ionization (EI) mass spectrum of each FAME yields several ions that are somewhat unique to the FAME chemical structure when compared to the typical mass spectra of hydrocarbons. The IP585 method takes advantage of this by using selective ion monitoring (SIM) to detect the FAME peaks as they elute from the GC column. The method also specifies the simultaneous acquisition of full mass spectrum from *m/z* 30 to 330 amu to confirm FAME peak identification if needed. This dual data acquisition technique for mass spectral detection is known as SIM/SCAN.

Experimental

Calibration Standards

Calibration standards were prepared using the instructions described in Section 7 of the method. A Bulk Calibration Solution (BCS) containing 1,000 mg/kg solution of each FAME in n-dodecane was purchased commercially. The internal standard solution containing 1,000 mg/mL of methyl heptadecanoate-d33 (C17:0-d33) was also commercially purchased. These two solutions were used to prepare the Working Calibration Standards (WCS) described in Section 7.3 of the method. Ten individual WCS were prepared in n-dodecane with nominal concentrations of 2, 4, 6, 8, 10, 20, 40, 60, 80, and 100 mg/kg for each FAME and a concentration of 10 mg of the C17:0-d33 internal standard. The five low concentration standards; 2, 4, 6, 8, and 10 mg/kg, were used to construct low level calibration curves. The five high level standards; 20, 40, 60, 80, and 100 mg/kg, were used to construct high level calibration curves.

Table 1.   *Compounds Used to Quantify Total FAME in Jet Fuel. These Six FAMEs are Found in 95% of the Common Feed Stocks Used to Produce Biodiesel*

Chemical name	Common name	Symbol	Molecular formula	Molecular weight
Methyl hexadecanoate	Methyl palmitate	C16:0	$C_{17}H_{34}O_2$	270.45
Methyl heptadecanoate	Methyl margarate	C17:0	$C_{18}H_{36}O_2$	284.45
Methyl octadecanoate	Methyl stearate	C18:0	$C_{19}H_{38}O_2$	298.50
Methyl octadecenoate	Methyl oleate	C18:1	$C_{19}H_{36}O_2$	296.49
Methyl octadecadienaote	Methyl linoleate	C18:2	$C_{19}H_{34}O_2$	294.47
Methyl octadecatrienoate	Methyl linolenate	C18:3	$C_{19}H_{32}O_2$	292.45

Jet Fuel Sample Preparation

A sample of jet fuel was obtained from a local refiner. This sample did not contain any FAME and was used to prepare matrix spikes. Four matrix spikes containing 1, 5, 10, and 40 mg/kg of total FAME were prepared by adding B100 biodiesel derived from soybean oil. Another commercial jet fuel sample was obtained containing an unknown quantity of total FAME. Each sample was prepared by measuring 1 mL of sample into a 2-mL vial followed by the addition of 10 µL of the C17:0-d33 internal standard solution. All samples were prepared in duplicate to measure the repeatability of the method.

GC/MS Analysis of FAME in Jet Fuel

An Agilent 5975C GC/MS system with an Agilent 7693A Automated Liquid Sampler was configured according to the IP585 method. This configuration is described in Table 2 and the instrument operating conditions are shown in Table 3. The mass spectrometer was tuned using the 5975C AUTOTUNE program before running any standards or samples. The calibration standards and a n-dodecane solvent blank were run first and the linear performance of the low level calibration and the high level calibration were measured before running the jet fuel samples. Single GC/MS analyses of each jet fuel sample duplicate were made upon successful calibration. The individual FAME peaks were quantified and the total FAME content in each sample was calculated by summing the individual FAMEs.

Table 2.   *Instrument Configuration for GC/MS Analysis of FAMEs in Jet Fuel*

Component	Description
Agilent 5975C MSD	Mass spectrometer with inert electron ionization source
Agilent 7890A GC	Gas Chromatograph with 100 psi split/splitless inlet and mass spectrometer interface
Agilent 7693A ALS	Automatic liquid injector for 7890A GC with 150-vial tray
G1701EA	MSD Chemstation Software for data acquisition and analysis

Table 3.   *GC/MS Instrument Conditions*

GC Conditions

Inlet temperature	260 °C
Inlet mode	Splitless
Inlet liner	Splitless liner, single taper glass wool (p/n 5062-3587)
Sample volume	1 µL
Column	HP-INNOWAX, 50 m × 0.2 mm id × 0.4 µm film (p/n 19091N-205)
Column flow	Helium at 0.6 mL/min constant flow
Oven program	
Initial temperature	150 °C for 5 min
Oven ramp #1	12 °C/min to 200 °C for 17 min
Oven ramp #2	3 °C/min to 252 °C for 6.5 min
Mass Spec interface	260 °C

Mass Spec Conditions

Ionization source	70 eV electron ionization
Source temperature	230 °C
Quadrupole temperature	150 °C
Data acquisition delay	20 min
Scan range	33 to 320 AMU
SIM ions	See Table 4

Results and Discussion

Calibration

Figure 1 shows an overlay of the Total Ion Chromatograms (TIC) obtained from the 2 mg/kg FAME standard and the n-dodecane solvent blank. These chromatograms established the retention orders and retention times of each FAME as well as the absence of any FAME in the solvent blank. Two calibration curves were constructed from the SIM GC/MS data obtained for each standard. Figures 2 and 3 show the low level and high level calibration curves for the six FAME peaks along with the individual calibration functions and the correlation coefficients (R^2). For each curve, the slopes are calculated using a least-squares linear regression and the y-intercepts are forced through zero. The correlation coefficient of each FAME calibration exceeds the method requirement of 0.985.
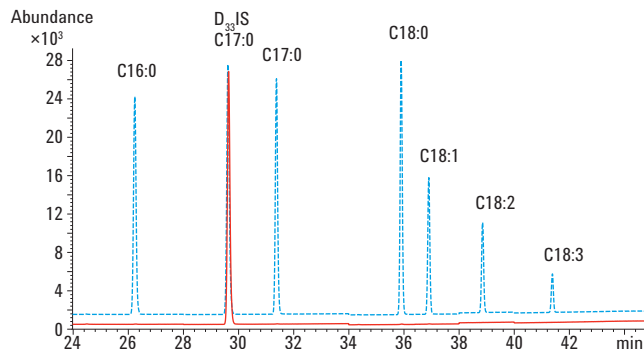

Figure 1. Chromatographic overlay of a 0 mg/kg standard (red) and 2 mg/kg FAME standard (blue).
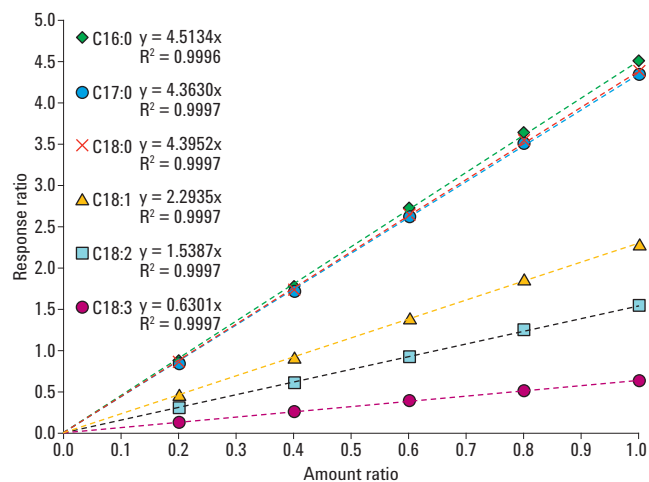

Figure 2. Low level calibration curves for 2, 4, 6, 8, and 10 mg/kg of each FAME in n-dodecane. The calibration curves are forced through zero according to the method's protocol. Each curve exceeds a linearity requirement of $R^2 > 0.985$.
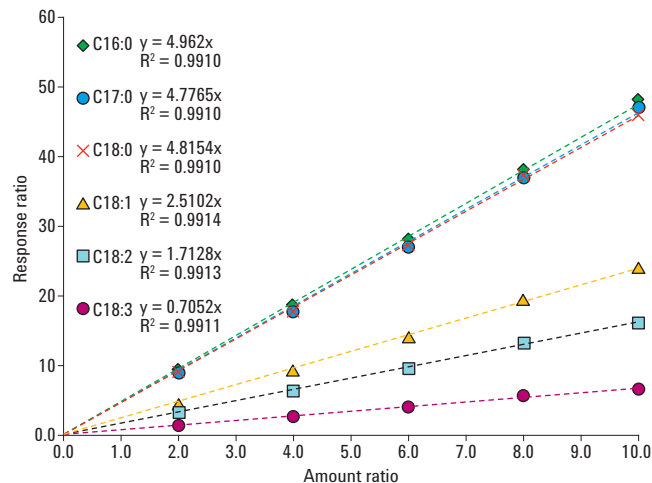

Figure 3. High level calibration curves for 20, 40, 60, 80, and 100 mg/kg of each FAME in n-dodecane. The calibration curves are forced through zero according to the method's protocol. Each curve exceeds the linearity requirement of $R^2 > 0.985$.

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Peak Identification

The large amount of jet fuel injected onto the GC column can shift the FAME peaks to slightly longer retention times as shown in Figure 4. If this matrix effect is present, the retention times of the earlier eluting peaks have a larger shift. As seen in Figure 4, the retention time of methyl palmitate (C16:0) is about 0.3 minutes longer in jet fuel when compared to the retention time n-dodecane. Methyl linolenate (C18:3) has a small shift of 0.025 minutes. Normally, these shifts have no adverse affect on peak identification since the SIM acquisition is designed to selectively detect the FAME peaks and avoid detecting most chromatographic interferences. However, it is a good practice to review the data for correct peak identification prior to generating the final quantitative report. The Agilent Mass Spec Chemstation provides a graphical data review tool called Qedit that allows the user to quickly confirm peak identification and make any necessary corrections.

Quantitative Results and Analysis Precision

Figure 5 shows typical SIM/SCAN total ion chromatograms for a jet fuel sample containing 5 mg/kg of total FAME. Four jet fuel samples spiked with soybean biodiesel were prepared and run in duplicate. For each run, the concentration of individual FAMEs detected in the sample was determined using the appropriate calibration curve. The total FAME content was then calculated by summing the individual FAME results. A density correction was finally applied to the total FAME concentration to account for the difference in density between n-dodecane and the jet fuel. Table 5 shows the results from this analysis. Full recoveries of total FAME were observed for each of the four jet fuel spikes across the full quantification range of the method.

The single user precision of the method was measured and expressed as repeatability (r). Repeatability is the absolute difference between duplicate test results obtained by the same operator, using the same apparatus on identical test material in a single day. Table 5 shows the calculated repeatability for each of the jet fuel sample spikes along with a comparison to the repeatability specification of the method. The duplicate analysis of all four samples showed precision that was three to ten times better than the method requirements.
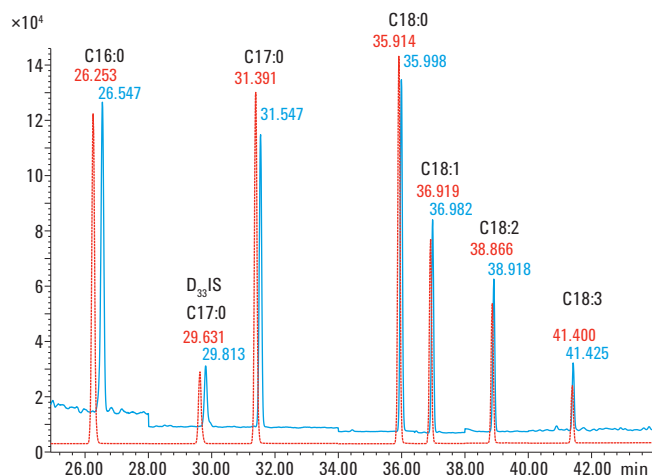

Figure 4. Overlay of a 2 mg/kg FAME standard in n-dodecane (red TIC) and a jet fuel sample spiked with FAME (blue TIC). The jet fuel matrix causes shifts to longer retention times.
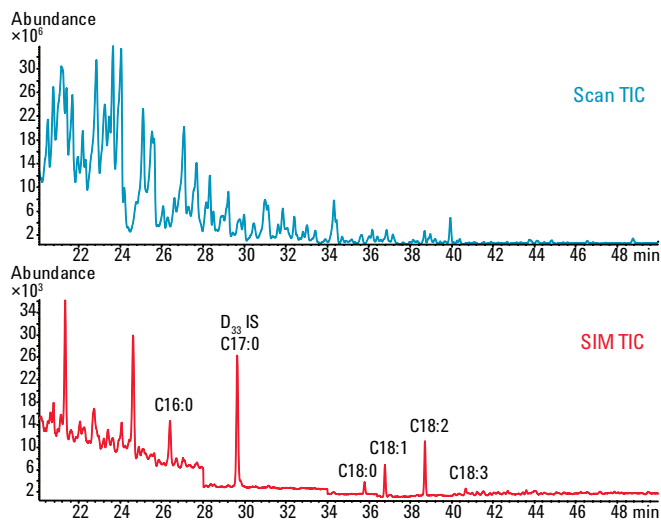

Figure 5. A SIM/SCAN result obtained from a jet fuel sample spiked with 5 mg/kg total FAME from soybean-derived biodiesel.

Table 4. SIM group table for FAMEs in jet fuel. A dwell time of 50 msec was used for each SIM ion.

Detected FAME	SIM ions	SIM group start
C16:0	227, 239, 270, 271	20.0 min
C17:0	317	28.0 min
C17:0-d33 (IS)	241, 253, 284	28.0 min
C18:0	255, 267, 298	34.0 min
C18:1	264, 265, 296	36.5 min
C18:2	262, 263, 264, 294, 295	38.0 min
C18:3	236, 263, 292, 293	40.0 min

A commercial jet fuel sample containing an unknown quantity of total FAME was also prepared and run in duplicate. The resulting SIM total ion chromatogram for this sample is shown in Figure 6 and the quantitative results are listed in Table 6. Repeatability for this sample was calculated using the duplicate results and was found to be much better than the method specification.

Figure 6. SIM TIC of a commercial jet fuel sample containing 3.3 mg/kg total FAME.

Table 5. Quantification of Soybean Biodiesel FAME (mg/kg) Spikes in Jet Fuel

1 mg/kg Jet fuel spike

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total*
Run 1	0.6	0.0	0.1	0.3	0.1	0.0	1.0
Run 2	0.6	0.0	0.1	0.3	0.1	0.0	1.0
						Avg	**1.0**
						r (exp)	**0.0**
						r (IP585)	**0.7**

5 mg/kg Jet fuel spike

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total*
Run 1	0.6	0.0	0.2	0.9	2.6	0.6	4.6
Run 2	0.7	0.0	0.2	1.0	2.6	0.6	4.7
						Avg	**4.7**
						r (exp)	**0.1**
						r (IP585)	**1.2**

10 mg/kg Jet fuel spike

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total*
Run 1	1.1	0.0	0.4	2.1	5.7	1.1	9.7
Run 2	1.1	0.0	0.4	1.9	5.6	1.2	9.5
						Avg	**9.6**
						r (exp)	**0.2**
						r (IP585)	**2.1**

40 mg/kg Jet fuel spike

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total*
Run 1	4.8	0.0	1.8	8.3	25.4	4.2	41.4
Run 2	4.3	0.0	1.7	7.9	24.0	4.1	39.1
						Avg	**40.2**
						r (exp)	**2.3**
						r (IP585)	**7.1**

*Reproducibility (r) was calculated using sample duplicates and compared to the IP 585 method reproducibility specifications. *The total FAME results have been corrected for the density difference between n-dodecane and the jet fuel.*
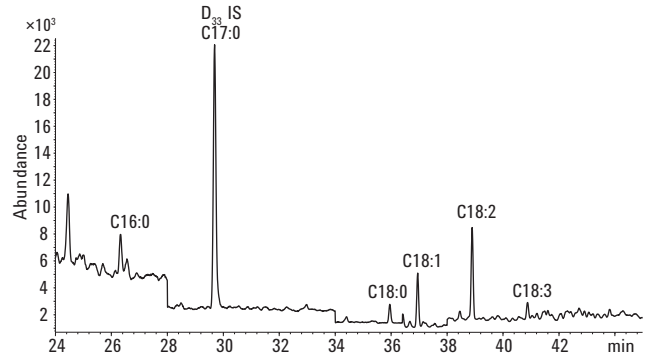
Table 6. Quantification of FAMEs (mg/kg) in a Commercial Jet Fuel Sample

mg/kg

	C16:0	C17:0	C18:0	C18:1	C18:2	C18:3	Total*
Run 1	0.4	0.0	0.1	0.7	1.8	0.3	3.3
Run 2	0.4	0.0	0.1	0.7	1.8	0.3	3.3
						Avg	**3.3**
						r (exp)	**0.0**
						r (IP585)	**1.0**

*Reproducibility (r) was calculated using sample duplicates and compared to the IP 585 method reproducibility specifications. *The total FAME results have been corrected for the density difference between n-dodecane and the jet fuel.*

Conclusion

The Agilent 5975C GC/MS system is shown to be an excellent platform for the measurement of trace FAME in jet fuel using Energy Institute Method IP585. The system is easily set-up for simultaneous SIM/SCAM data acquisition to maximize sensitivity and selectivity as well as provide full spectra for qualitative analysis. Using the calibration procedure described in the method, the 5975C exceeded the linearity requirements at both the low and high concentration ranges. Four matrix spikes prepared in a commercial jet fuel sample ranging from 1 mg/kg to 40 mg/kg were analyzed in duplicate after successful calibration. The analysis results showed complete recovery of the total FAME content in each sample along with greater precision than the method requirements. Similar outstanding results were observed for a commercial jet fuel sample containing and unknown amount of FAME contamination.

Reference

1. IP 585/10 "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", The Energy Institute, London, UK.

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