Analysis of Biodiesel Fatty Acid Methyl Esters (FAME) in Aviation Jet Fuels Using Method IP 585

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Abstract

Accurate analysis of biodiesel FAME in jet fuel is critical for ensuring that contamination levels do not exceed allowable limits. Method IP 585 is commonly used for this analysis and, here, we perform the method using a Stabilwax column and GC-MS in SIM mode. Method calibration curve criteria were met and good recoveries of the total FAME content in jet fuel were obtained.

Introduction

Biodiesel fuel is the most popular type of alternative diesel fuel available today, and it makes up a significant portion of the materials that are routinely transported through multiproduct pipelines. Despite its suitability as an alternative fuel, residual biodiesel remaining in shared pipelines can be a problematic contaminant in other products, such as aviation jet fuel. Biodiesel differs fundamentally from mineral-based diesel in that it is made through the chemical conversion of vegetable oils or animal fats into fatty acid methyl esters (FAME) as shown in Reaction 1. Most naturally occurring fatty acids have an even number of carbon atoms. Fatty acids containing an odd number of carbon atoms, such as methyl heptadecanoate (C17:0), which is included in Method IP 585, are extremely rare.
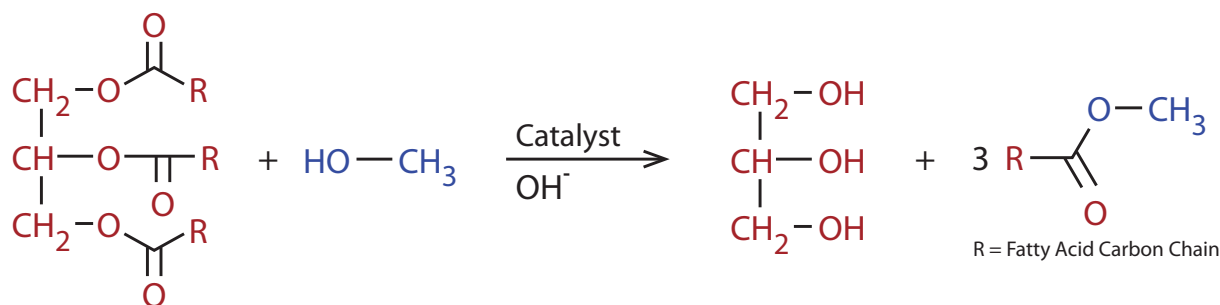
Due to differences in chemical structure, biodiesel fuel has different properties than jet fuel; it has a high freezing point (-5 °C) and poor oxidative stability, characteristics that make it unsafe in jet fuel. At low temperatures, biodiesel forms wax crystals that can clog fuel lines and fuel filters. In addition, because it is hygroscopic, biodiesel fuel requires special handling to prevent high water content and the consequent risk of corrosion and microbial growth. To minimize the potential impact of biodiesel FAME in jet fuel, a contamination limit has been established. The current allowable cross-contamination level of biodiesel FAME in jet fuel A-1 is 50 ppm, an increase from the previous limit of 5.0 ppm (note that 5.0 ppm is still the specification for military grade jet fuels).

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Measuring contamination of biodiesel FAME in jet fuel can be a challenging task due to the chemical complexity of the matrix. A GC-MS method for analysis of biodiesel FAME in jet fuel was developed by the Energy Institute (IP 585: 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) [1]. Due to the high concentration of heavy hydrocarbons in jet fuel, it is not always possible to obtain a complete separation of FAME components from matrix hydrocarbons, and method IP 585 does not require it. The method takes advantage of a polar, wax-type GC column—such as a Stabilwax column—which is much more retentive for the polar FAME compounds than for the less polar fuel hydrocarbon compounds. The polar column maximizes the separation that can be achieved, and it is paired with an MS detector in single ion monitoring (SIM) mode for compound identification. Definitive identifications can be obtained because the chemical structures of FAME, and hence their electron ionization mass spectra, are quite different from the mass spectra of both fuel hydrocarbons and bleed ions from the wax column. By using a polar Stabilwax column and GC-MS in single ion monitoring (SIM) mode, FAME contaminants can be accurately distinguished and quantified relative to the predominant hydrocarbon component of jet fuels.

Experimental

Calibration Standards

Calibration standards were prepared according to Method IP 585 (Section 7). Using individual neat FAME standards (Restek), a bulk calibration solution containing 1,000 mg/kg of each FAME was prepared in *n*-dodecane. The bulk calibration solution was then diluted into a 100 mg/mL working standard solution. The internal standard (methyl heptadecanoate-d33 [C17:0-d33]) was commercially purchased and prepared at 1,000 mg/mL in *n*-dodecane. These two solutions were used to prepare the calibration standards in *n*-dodecane with nominal concentrations of 2, 4, 6, 8, and 10 mg/kg of each FAME (with 10 mg of internal standard methyl heptadecanoate-d33) for the IP 585 low-level calibration curve, as well as 20, 40, 60, 80, and 100 mg/kg of each FAME with IS for the IP 585 high-level calibration curve (Table I).

Table I: Volumetric Dilutions for 0-100 mg/kg Calibration Standards from the Working Calibration Standard Solution (WSS) and Internal Standard Solution (ISS)

Nominal Standard Concentration (mg/kg)	Volume WSS (μL)	Volume Dodecane (μL)	Volume ISS (μL)
100	1,000	0	10
80	800	200	10
60	600	400	10
40	400	600	10
20	200	800	10
10	100	900	10
8	80	920	10
6	60	940	10
4	40	960	10
2	20	980	10
0	0	1,000	10

Jet Fuel Analysis

To confirm method parameters and performance, jet fuel from a local airport was obtained. An initial analysis was made to determine whether the sample contained FAME impurities. The sample was then fortified at 36, 60, and 120 mg/kg with FAME standard and analyzed according to the method parameters. Additionally, jet fuel and isooctane were fortified with 85 mg/kg soy biodiesel B100 to more accurately mimic sample contamination.

GC-MS Analysis

The standards and samples were analyzed according to Method IP 585 parameters on an Agilent GC-MS 5977A equipped with a capillary split/splitless injector. The MS was used in both SIM and scan modes to identify and quantify FAME impurities in the jet fuel matrix. A Restek Stabilwax column (60 m x 0.25 mm x 0.5 μm, cat.# 10641) was selected for this analysis as it is highly polar and has been shown to perform well for Method IP 585. Instrument parameters are presented in Table II.

Table II: GC/MS Instrument Conditions

GC Conditions	
Inlet Temperature	260 °C
Inlet Mode	Splitless
Inlet Liner	Restek Premium 4.0 mm ID single taper inlet liner w/wool (cat.# 23303.5)
Sample Volume	1 µl splitless for 1 min, then purge flow 100 mL/min
Column	Stabilwax 60 m x 0.25 mm x 0.5 µm (cat.# 10641)
Column Flow	Helium, 0.8 mL/min constant flow
Oven Program	150 °C (hold 5 min), 12 °C/min to 200 °C (hold 17 min), 3 °C/min to 252 °C (hold 3 min)
Mass Spec Interface	260 °C

Mass Spec Conditions	
Source Temperature	300 °C
Quadrupole Temperature	180 °C
Data Acquisition Delay	20 min
Scan Range	33 to 320 amu

Prior to sample analysis, the SIM group start times (Table III) were established by analyzing the lowest concentration calibration standard (2 mg/kg). A solvent blank was also analyzed to demonstrate that no interfering compounds were present. A chromatographic overlay of the blank and 2 mg/mL standard is presented in Figure 1 for easy comparison to the example shown in Annex A of Method IP 585.
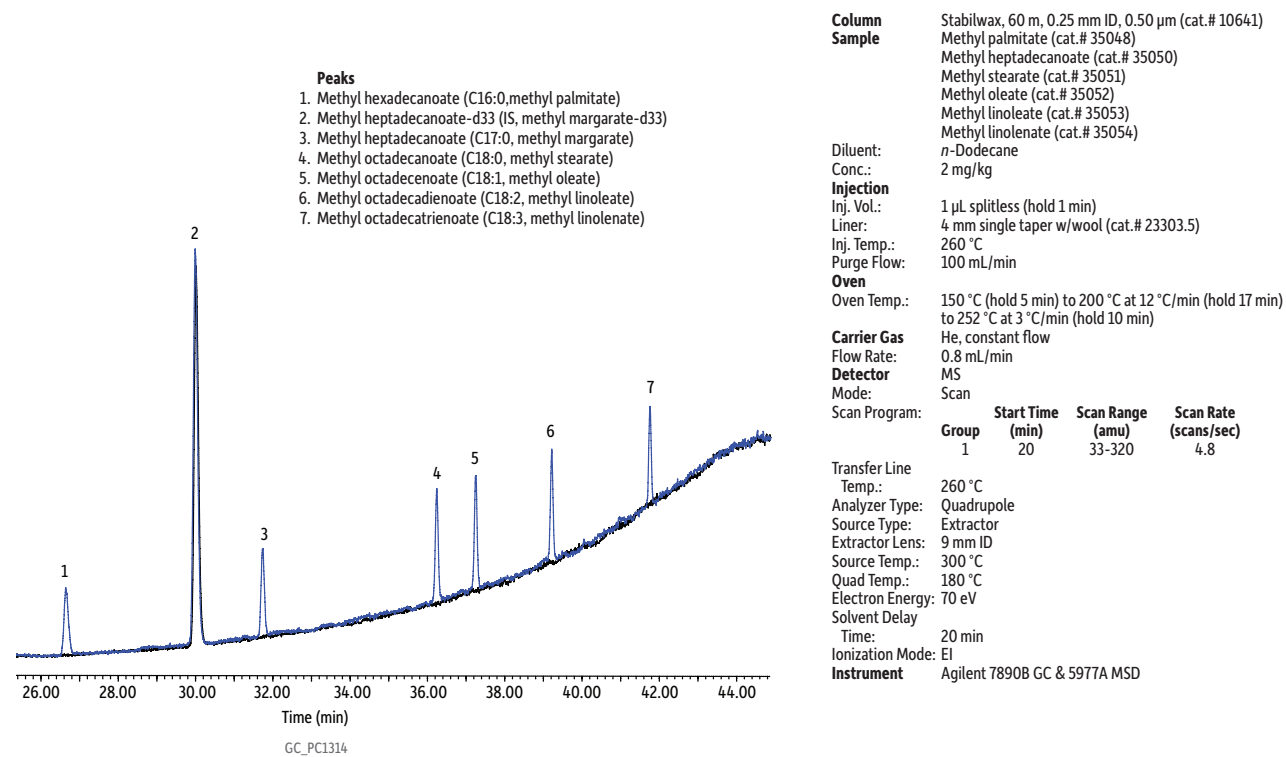
Figure 1: Chromatogram Overlay of 0 (Blank) and 2 mg/kg Standard in Scan Mode

Peaks
1. Methyl hexadecanoate (C16:0, methyl palmitate)
2. Methyl heptadecanoate-d33 (IS, methyl margarate-d33)
3. Methyl heptadecanoate (C17:0, methyl margarate)
4. Methyl octadecanoate (C18:0, methyl stearate)
5. Methyl octadecenoate (C18:1, methyl oleate)
6. Methyl octadecadienoate (C18:2, methyl linoleate)
7. Methyl octadecatrienoate (C18:3, methyl linolenate)

Column: Stabilwax, 60 m, 0.25 mm ID, 0.50 µm (cat.# 10641)
Sample: Methyl palmitate (cat.# 35048)
Methyl heptadecanoate (cat.# 35050)
Methyl stearate (cat.# 35051)
Methyl oleate (cat.# 35052)
Methyl linoleate (cat.# 35053)
Methyl linolenate (cat.# 35054)
Diluent: *n*-Dodecane
Conc.: 2 mg/kg
Injection
Inj. Vol.: 1 µL splitless (hold 1 min)
Liner: 4 mm single taper w/wool (cat.# 23303.5)
Inj. Temp.: 260 °C
Purge Flow: 100 mL/min
Oven
Oven Temp.: 150 °C (hold 5 min) to 200 °C at 12 °C/min (hold 17 min) to 252 °C at 3 °C/min (hold 10 min)
Carrier Gas He, constant flow
Flow Rate: 0.8 mL/min
Detector MS
Mode: Scan

Scan Program:			
Group	Start Time (min)	Scan Range (amu)	Scan Rate (scans/sec)
1	20	33-320	4.8

Transfer Line
Temp.: 260 °C
Analyzer Type: Quadrupole
Source Type: Extractor
Extractor Lens: 9 mm ID
Source Temp.: 300 °C
Quad Temp.: 180 °C
Electron Energy: 70 eV
Solvent Delay
Time: 20 min
Ionization Mode: EI
Instrument Agilent 7890B GC & 5977A MSD

GC_PC1314

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Table III: SIM Group Targeted Compounds and Start Times

Target FAME Compounds	Symbol	SIM Ions for Quantification	SIM Group Start Time
Methyl hexadecanoate (methyl palmitate)	C16:0	227, 239, 270, 271	20 min
Methyl heptadecanoate-d33 (methyl margarate-d33)	C17:0-d33 (IS)	317	28 min
Methyl heptadecanoate (methyl margarate)	C17:0	241, 253, 284	29 min
Methyl octadecanoate (methyl stearate)	C18:0	255, 267, 298	35 min
Methyl octadecenoate (methyl oleate)	C18:1	264, 265, 296,	36.6 min
Methyl octadecadienoate (linoleate)	C18:2	262, 263, 264, 294, 295	38.5 min
Methyl octadecatrienoate (linolenate)	C18:3	236, 263, 292, 293	40.5 min

Results and Discussion

Linearity

Calibration standards were analyzed and the resulting calibration curves for each FAME were forced through zero according to Method IP 585. Each curve exceeds the method linearity requirement of R>0.985 (R²>0.970), as shown in Figure 2 and Table IV.
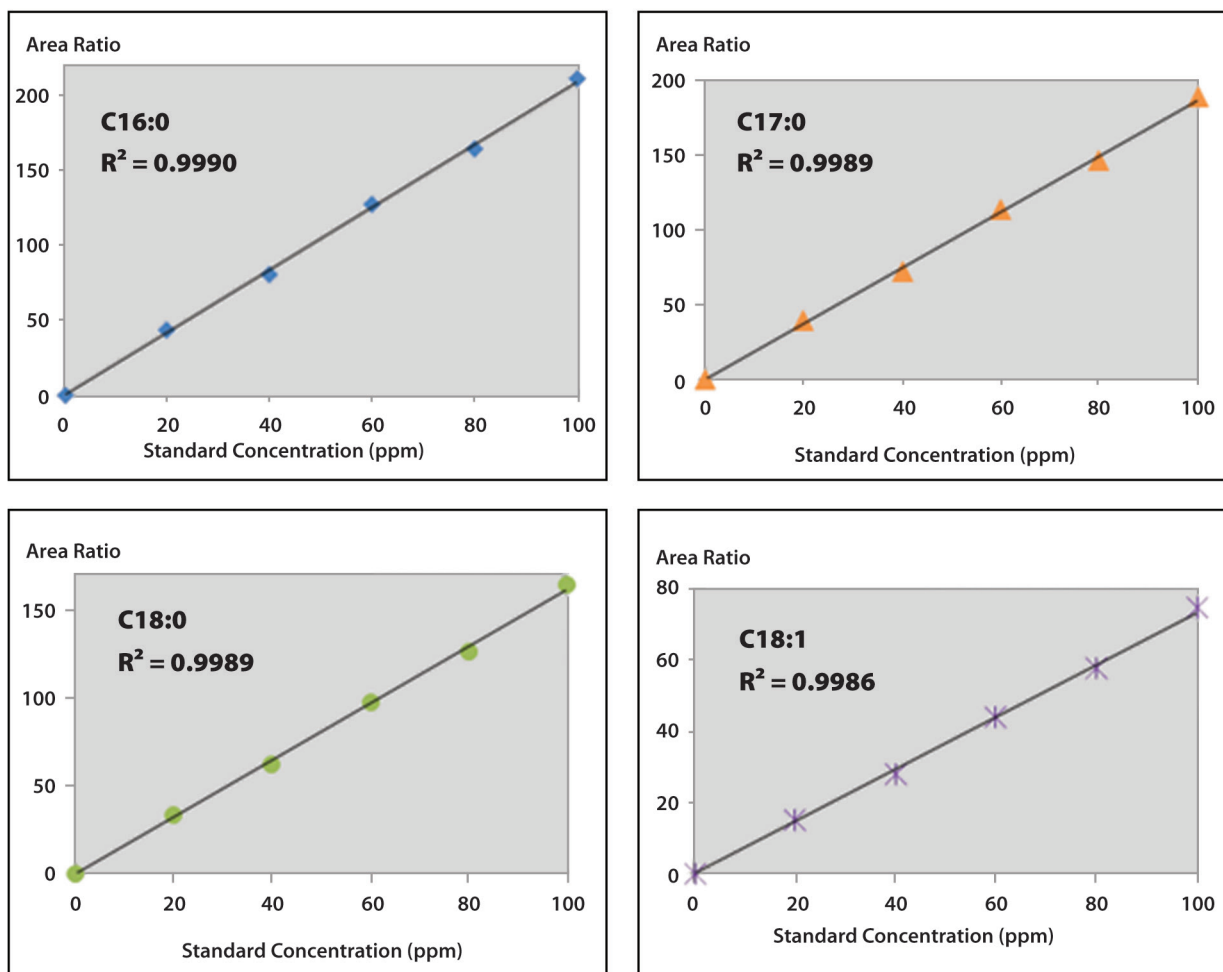
Figure 2: High-Level Calibration Curves (20, 40, 60, 80, and 100 mg/kg of each FAME in *n*-Dodecane; Zero Intercept as per Method IP 585.)
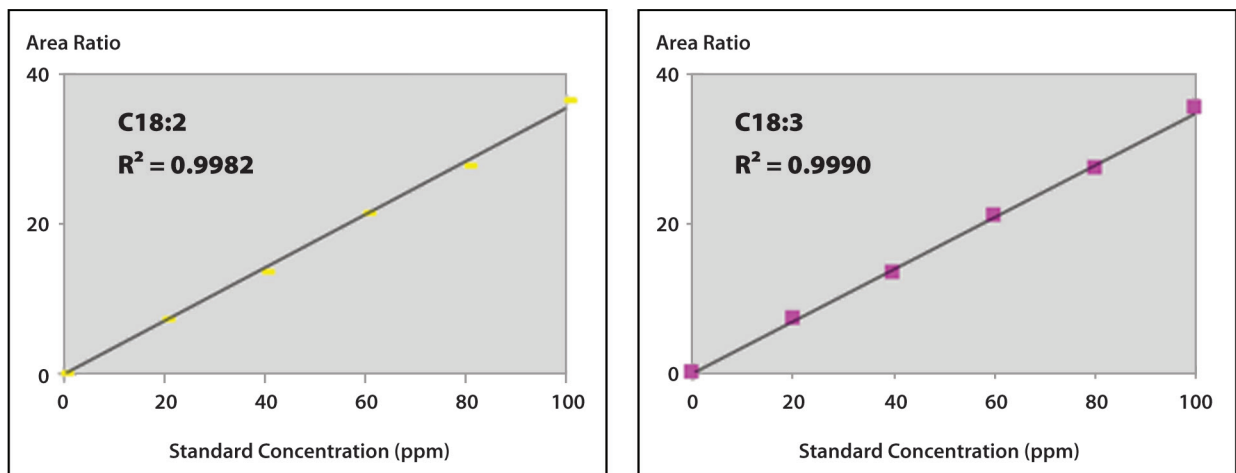
Figure 2 Continued

Table IV: R and R^2 Values for Low-Level Calibration Curves (2, 4, 6, 8, and 10 mg/kg of each FAME in *n*-Dodecane)

Compound	Low Level		High Level	
	R^2	R	R^2	R
C16:0	0.9982	0.9991	0.9990	0.9995
C17:0	0.9978	0.9989	0.9989	0.9994
C18:0	0.9978	0.9989	0.9989	0.9994
C18:1	0.9975	0.9987	0.9986	0.9993
C18:2	0.9985	0.9992	0.9982	0.9991
C18:3	0.9972	0.9986	0.9990	0.9995

Jet Fuel Analysis

Suitability of the Stabilwax column for the analysis of biodiesel FAME in jet fuel under method IP 585 conditions was evaluated using jet fuel samples that were fortified either with FAME standard or with soy biodiesel B100. As discussed in the method, methyl oleate (C18:1) sometimes elutes as two peaks falling within half a minute of each other that correspond to the *cis* and *trans* isomers of methyl oleate. This was observed in the soy biodiesel B100 analysis (Figure 3), so results for the individual isomers were combined for reporting as directed in Method IP 585.

The unfortified jet fuel itself was found to contain 1.5 mg/kg of methyl oleate. This small amount of contamination was background subtracted from the calculated results for the fortified samples. Reported results were also adjusted for solvent/sample density differences as per the method. As shown in Table V, the final results deviated only minimally from the expected values, demonstrating that the Stabilwax column performed very well under method conditions.

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Figure 3: Biodiesel Sample in Isooctane with *cis/trans* C18:1 Isomers

Peaks
1. Methyl hexadecanoate (C16:0, methyl palmitate)
2. Methyl heptadecanoate-d33 (IS, methyl margarate-d33)
3. Methyl octadecanoate (C18:0, methyl stearate)
4. *cis*-Methyl octadecenoate (C18:1, methyl oleate)
5. *trans*-Methyl octadecenoate (C18:1, methyl oleate)
6. Methyl octadecadienoate (C18:2, methyl linoleate)
7. Methyl octadecatrienoate (C18:3, methyl linolenate)

Column	Stabilwax, 60 m, 0.25 mm ID, 0.50 μm (cat.# 10641)
Sample	Soy biodiesel (B100)
Diluent:	Isooctane
Conc.:	85 mg/kg
Injection	
Inj. Vol.:	1 μL splitless (hold 1 min)
Liner:	4 mm single taper w/wool (cat.# 23303.5)
Inj. Temp.:	260 °C
Purge Flow:	100 mL/min
Oven	
Oven Temp.:	150 °C (hold 5 min) to 200 °C at 12 °C/min (hold 17 min) to 252 °C at 3 °C/min (hold 10 min)
Carrier Gas	He, constant flow
Flow Rate:	0.8 mL/min
Detector	MS
Mode:	Scan

Scan Program:	Group	Start Time (min)	Scan Range (amu)	Scan Rate (scans/sec)
	1	20	33-320	4.8

Transfer Line Temp.:	260 °C
Analyzer Type:	Quadrupole
Source Type:	Extractor
Extractor Lens:	9 mm ID
Source Temp.:	300 °C
Quad Temp.:	180 °C
Electron Energy:	70 eV
Solvent Delay Time:	20 min
Ionization Mode:	EI
Instrument	Agilent 7890B GC & 5977A MSD

GC_PC1315

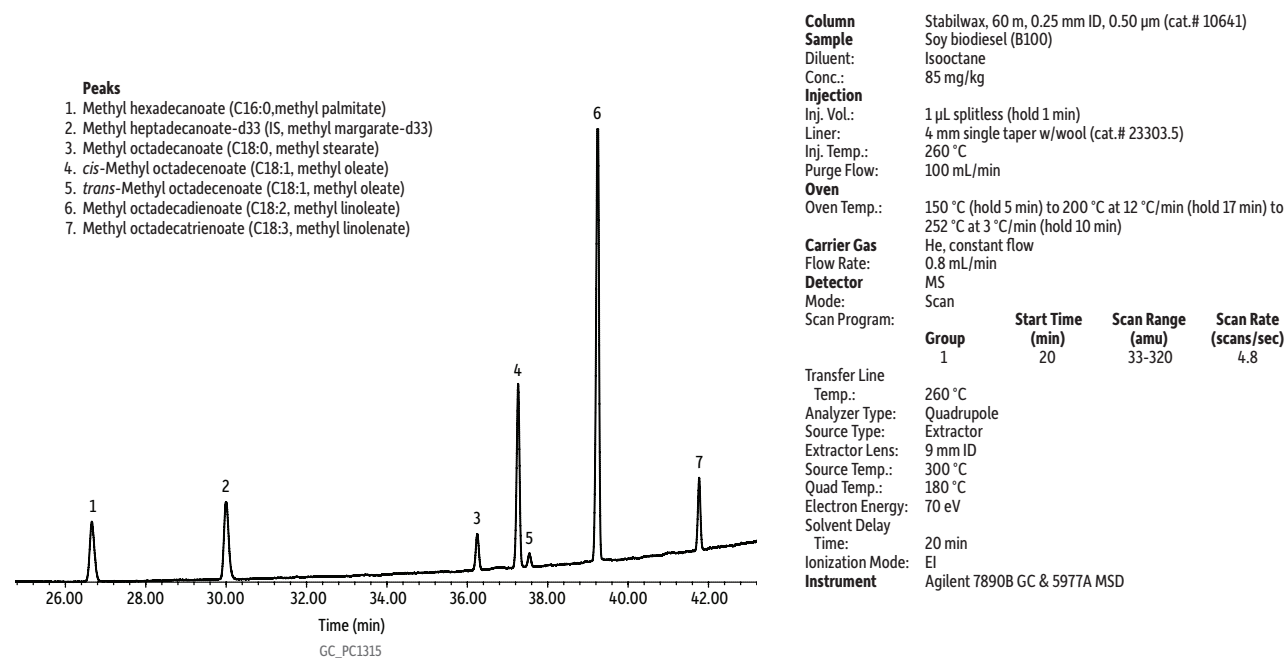**Table V:** Results of FAME Fortified Jet Fuel Analysis (mg/kg)

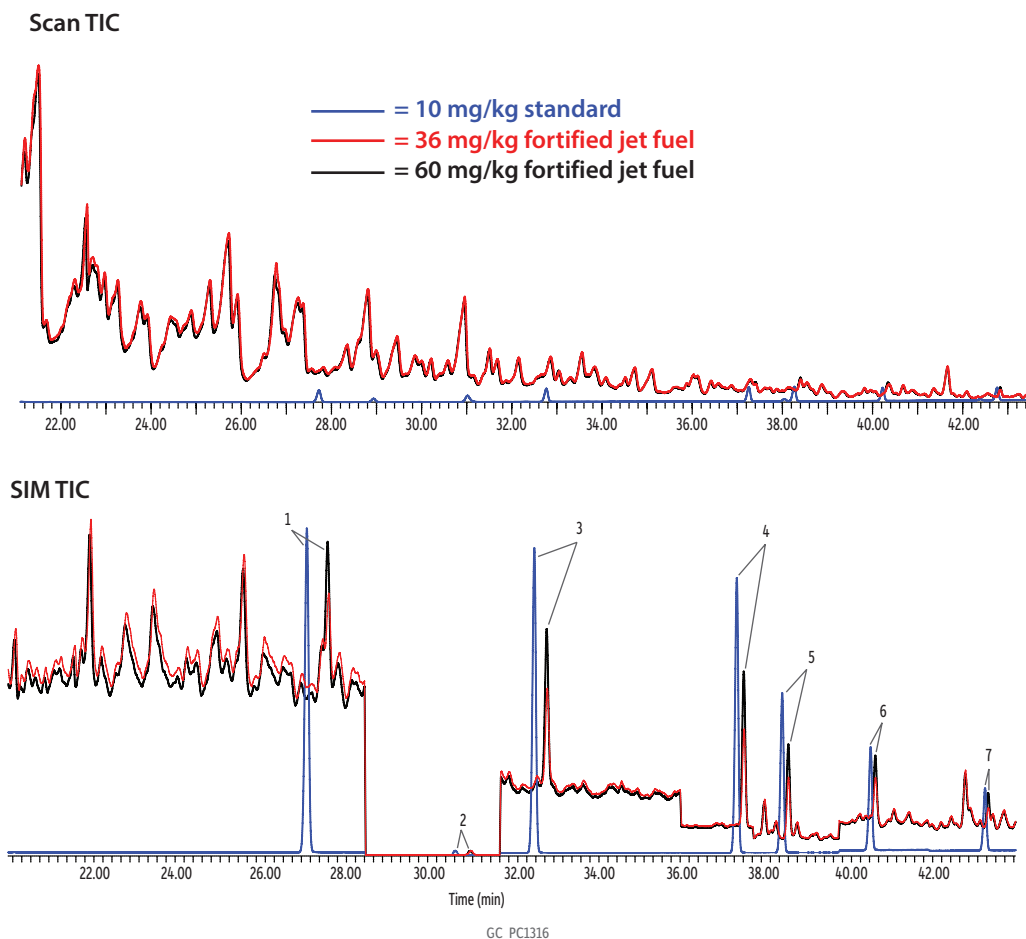| Compound	FAME Compounds and Jet Fuel				Biodiesel and Jet Fuel	
	Neat Jet Fuel	36 mg/kg Total FAME	60 mg/kg Total FAME	120 mg/kg Total FAME	85 mg/kg Biodiesel in Isooctane	85 mg/kg Biodiesel in Jet Fuel
C16:0	0	5.8	9.4	19.2	8.7	8.4
C17:0	0	5.8	9.8	18.8	0	0
C18:0	0	6.1	10.4	18.9	3.4	3.7
C18:1	1.5	7.6	11.8	19.8	17.5	20.7
C18:2	0	7.9	11.4	21.2	45.0	43.5
C18:3	0	5.7	9.5	18.3	6.9	6.5
Total FAME (mg/kg)	1.5	39.0	62.2	116.1	81.5	82.8
Total FAME -Jet Fuel contribution (mg/kg)	–	37.5	60.7	114.6	–	81.3
% Deviation*	–	4.1%	1.2%	4.5%	–	0.4%

*% Deviation is calculated as the deviation between the measured FAME value and the nominal fortified FAME value.

Peak Identification

The high concentration of hydrocarbons in the jet fuel matrix can cause the less abundant FAME peaks to shift to slightly longer retention times compared to where they elute when in solvent (Figure 4). This occurs after injection because large numbers of heavy hydrocarbons are focused at the beginning of the column, effectively creating another layer through which the FAME compounds must partition. This effect is more pronounced with early eluting compounds, but the net effect is relatively minor because the analysis is done in SIM mode and the MS software can generally identify the unique FAME ions and compensate for the retention time shift. Fortifying a jet fuel sample with a relatively high concentration of FAME is a good way to confirm identification of the FAME compounds in the SIM chromatogram. The calibration table can then be updated with corrected retention times and the final quantitative report can be generated.

Note that when analyzing jet fuel (especially heavier naphtha-type jet fuels), carryover matrix noise may be observed. However, this will not affect peak identification or interfere with the selected ions, nor will it add to the total mass of the FAME compounds.

Figure 4: Overlay of SIM/SCAN Mode Analyses of a 10 mg/kg FAME Standard, 36 mg/kg FAME Fortified Jet Fuel Sample, and 60 mg/kg FAME Fortified Jet Fuel Sample

Scan TIC

= 10 mg/kg standard
= 36 mg/kg fortified jet fuel
= 60 mg/kg fortified jet fuel

SIM TIC

Time (min)

GC_PC1316

Peaks
1. Methyl hexadecanoate (C16:0, methyl palmitate)
2. Methyl heptadecanoate-d33 (IS, methyl margarate-d33)
3. Methyl heptadecanoate (C17:0, methyl margarate)
4. Methyl octadecanoate (C18:0, methyl stearate)
5. Methyl octadecenoate (C18:1, methyl oleate)
6. Methyl octadecadienoate (C18:2, methyl linoleate)
7. Methyl octadecatrienoate (C18:3, methyl linolenate)

Column	Stabilwax, 60 m, 0.25 mm ID, 0.50 µm (cat.# 10641)
Sample	Methyl palmitate (cat.# 35048)
	Methyl heptadecanoate (cat.# 35050)
	Methyl stearate (cat.# 35051)
	Methyl oleate (cat.# 35052)
	Methyl linoleate (cat.# 35053)
	Methyl linolenate (cat.# 35054)
Diluent:	Isooctane
Conc.:	See notes
Injection	
Inj. Vol.:	1 µL splitless (hold 1 min)
Liner:	4 mm single taper w/wool (cat.# 23303.5)
Inj. Temp.:	260 °C
Purge Flow:	100 mL/min
Oven	
Oven Temp.:	150 °C (hold 5 min) to 200 °C at 12 °C/min (hold 17 min)
	to 252 °C at 3 °C/min (hold 10 min)
Carrier Gas	He, constant flow
Flow Rate:	0.8 mL/min

| **Detector** | MS |
| Mode: | SIM |

SIM Program:

Group	Start Time (min)	Ion(s) (m/z)	Dwell (ms)
1	20	227, 239, 270, 271	50
2	28	317	50
3	29	241, 253, 284	50
4	35	255, 267, 298	50
5	36.6	264, 265, 296	50
6	38.5	262, 263, 264, 294, 295	50
7	40.5	236, 263, 292, 293	50

Transfer Line	
Temp.:	260 °C
Analyzer Type:	Quadrupole
Source Type:	Extractor
Extractor Lens:	9 mm ID
Source Temp.:	300 °C
Quad Temp.:	180 °C
Solvent Delay	
Time:	20 min
Instrument	Agilent 7890B GC & 5977A MSD
Notes	Samples in Overlay
	Blue line: 10 mg/kg standard in solvent
	Red line: 36 mg/kg fortified jet fuel sample
	Black line: 60 mg/kg fortified jet fuel sample

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Conclusion

Using Method IP 585 with a Stabilwax column is a fast, effective way to analyze biodiesel FAME in jet fuel. With the allowable limit for jet fuel A-1 having been increased to 50 ppm, FAME compounds can be easily distinguished from background noise using GC-MS in SIM mode. The Stabilwax column was proven to be a good choice for this analysis, giving FAME compounds enough retention to be positively identified in the jet fuel matrix. Method calibration curve criteria were met and good recoveries of the total FAME content in jet fuel were obtained.

References

[1] Energy Institute, IP 585, 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, January 2010. http://publishing.energyinst.org/topics/renewables/biofuels/ip-585-determination-of-fatty-acid-methyl-esters-fame,-derived-from-bio-diesel-fuel,-in-aviation-turbine-fuel-gc-ms-with-selective-ion-monitoringscan-detection-method

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