

Analysis of Fatty Acid Methyl Esters (FAMEs) in Jet Fuel by GC-TOFMS

LECO Corporation; Saint Joseph, Michigan USA

Key Words: Pegasus HT, GC-TOFMS, FAMEs, Jet Fuel, Calibration



1. Introduction

Fuels are generally not processed and transported with dedicated equipment and pipelines for each type of fuel. Instead, different fuels can pass through the same containers, which may introduce potential contamination between fuel types. One specific concern is biofuel contamination of jet fuel. Biofuels contain fatty acid methyl esters (FAMEs) that can impact the thermal stability of jet fuel and lead to engine problems if present at elevated levels in the jet fuel. An upper threshold of 5 mg/kg (ppm, w/w) has been specified to ensure proper functionality and safety. Additionally, Method IP 585¹ has been developed to screen jet fuels for potential FAME contaminants through gas chromatography (GC) coupled to a quadrupole mass spectrometer (MS). The quadrupole is operated in scan mode for identification and in SIM mode for quantification. These data may be acquired simultaneously with some MS instruments, otherwise two injections for the same sample are required.



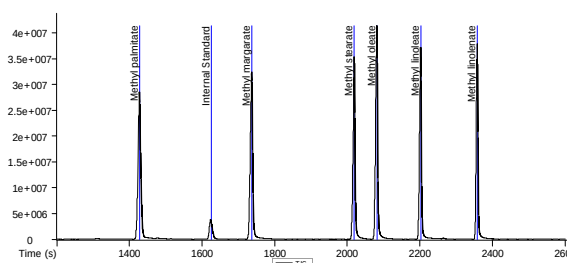
In this application note, a GC time-of-flight mass spectrometry (TOFMS) method based on IP 585 is demonstrated. TOFMS detection acquires full mass range data, thus can offer both quantification with selected ions and identification with the full mass range data collected from a single GC separation.

2. Results and Discussion

Calibration Standards

The calibration standards were identified and quantified with ChromaTOF® software's Automated Peak Find and library search functions. ChromaTOF software will automatically select a unique mass for quantification or the user can specify desired masses to be used for quantification, as in this application. The calibration standards ranged from 0 to 100 ppm and the instrument successfully measured the target FAME standards over the

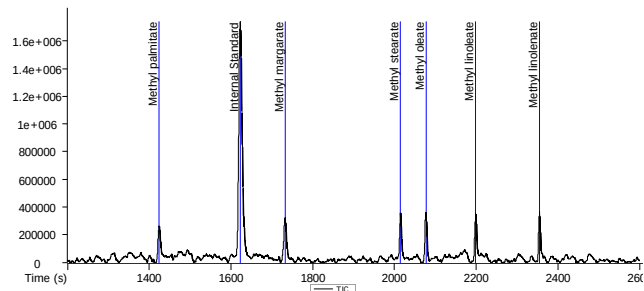
required range. Representative data, the TIC chromatogram, and corresponding Peak Table for the highest concentration calibration standard, 100 ppm, are shown in Figure 1. The same data for the lowest level calibration standard, 2 ppm, are shown in Figure 2.



Name	R.T. (s)	Match	Quant S/N
Methyl palmitate	1427.94	919	14888
Methyl heptadecanoate, d33	1625.32		2168.9
Methyl margarate	1737.34	905	21091
Methyl stearate	2019.79	919	23733
Methyl oleate	2081.99	934	15594
Methyl linoleate	2202.49	918	6985.5
Methyl linolenate	2358.54	915	3838.4

Figure 1. The TIC chromatogram and corresponding Peak Table for the 100 ppm (w/w) calibration standard. No Match Value is reported for the internal standard, spiked at 10 ppm, because its spectrum was not present in the library database.

¹IP 585:2010 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



Name	R.T. (s)	Match	Quant S/N
Methyl palmitate	1424.03	904	119.17
Methyl heptadecanoate, d33	1622.61		1020.1
Methyl margarate	1732.63	803	170.23
Methyl stearate	2015.28	879	198.18
Methyl oleate	2077.48	935	108.71
Methyl linoleate	2198.88	889	59.740
Methyl linolenate	2355.33	916	35.020

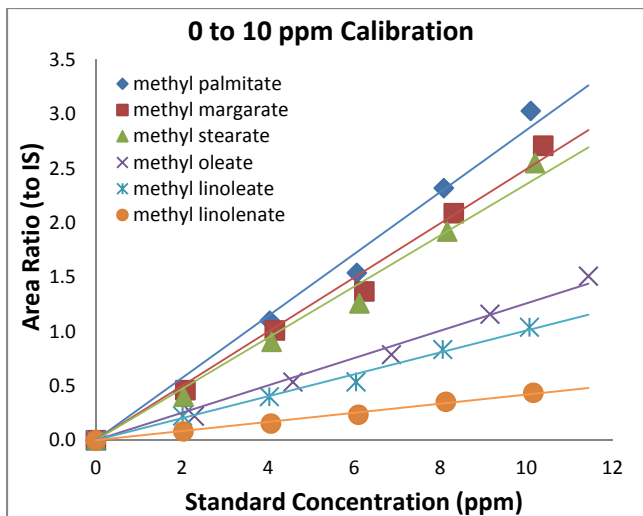
Figure 2. The TIC chromatograms and corresponding peak table for the 2 ppm calibration standard. The internal standard is spiked at 10 ppm.

Calibration Results

Method IP 585 specified that two calibration equations be generated from these standards. The first calibration equation covers FAME contamination at low levels between 0-10 ppm (utilizing the 0, 2, 4, 6, 8, and 10 ppm standards) and the second calibration equation covers high-level FAME contamination up to 100 ppm (utilizing the 0, 20, 40, 60, 80, and 100 ppm standards.)

The ChromaTOF software includes a Calibration Feature that determines calibration equations and applies the equations to unknown samples through Automated Data Processing. The user selects the chromatograms associated with the appropriate standards and specifies the actual concentration of the standard. User input adjustments can be made to dictate whether or not an internal standard is applied and what masses should be used for quantification, in addition to other adjustable processing parameters. Through automated data processing, the peak areas for each analyte in each standard are calculated and calibration equations are generated.

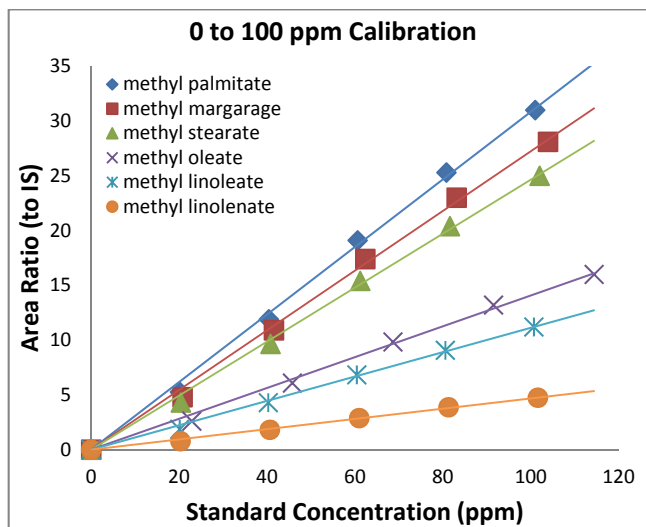
The calibration data for the low-level standards are shown in Figure 3. The corresponding calibration equations and R^2 values are also listed in the included table. The method specifications require that R^2 values for calibration equations must be greater than or equal to 0.985. The calibration equations for these standards have R^2 values between 0.9858 and 0.9927, all of which exceed the method requirement.



FAME standard	R^2	Calibration Equation
methyl palmitate	0.9880	$0.2853x$
methyl margarate	0.9897	$0.2494x$
methyl stearate	0.9858	$0.2355x$
methyl oleate	0.9897	$0.1259x$
methyl linoleate	0.9909	$0.1009x$
methyl linolenate	0.9927	$0.0420x$

Figure 3. Low level calibration data, equations, and R^2 values.

The high-level calibration standards are compiled in Figure 4 with the corresponding calibration equations and R^2 values also listed in the included table. The calibration equations for the high level standards have R^2 values between 0.9966 and 0.9980, all of which also exceed the method requirement.



FAME standard	R^2	Calibration Equation
methyl palmitate	0.9977	$0.3083x$
methyl margarate	0.9978	$0.2724x$
methyl stearate	0.9980	$0.2463x$
methyl oleate	0.9966	$0.1407x$
methyl linoleate	0.9978	$0.1112x$
methyl linolenate	0.9972	$0.0467x$

Figure 4. High level calibration data, equations, and R^2 values.

Jet Fuel Analysis

With this chromatographic method and analytical column, the bulk of the jet fuel elutes ahead of the FAME contaminants. Some naphtha compounds do elute in the region of the chromatogram that contains the FAMEs. The high masses that are used for quantification were selected as they are representative of the FAMEs, but not generally present in the coeluting hydrocarbons from the jet fuel. Quantification with these masses, listed in Table 1, helps minimize interferences and reduce errors in quantification.

JP8 jet fuel standard was used as a representative sample for this demonstration and was prepared for analysis according to Section 9 of IP 585 with the addition of internal standard. JP8 standard does not contain any FAME contaminants, as shown in Figure 5.

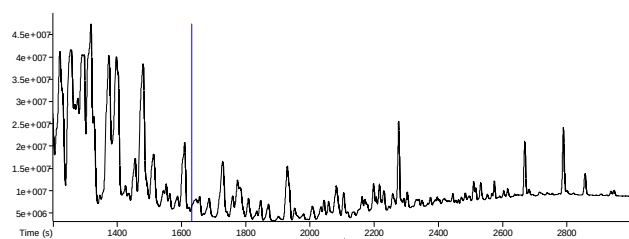


Figure 5. TIC chromatogram of JP8 jet fuel sample with internal standard added. The vertical blue line indicates the retention time of the internal standard. No other FAMEs are detected.

In the TIC chromatogram, it can be difficult to see the internal standard peak due to the coeluting interferences from the jet fuel. Because all m/z were collected by TOFMS, individual m/z can be displayed to better highlight various analytes. The ChromaTOF software also provides deconvolution to mathematically separate analytes that are overlapped with each other and with background noise in order to further isolate individual analyte signal. None of the targeted FAME analytes were measured in the JP8 sample.

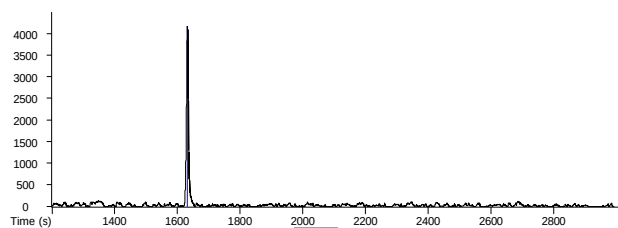


Figure 6. m/z 317. This mass trace chromatogram of JP8 jet fuel highlights the peak corresponding to the internal standard.

The JP8 standard was also spiked with the FAME calibration standards at roughly 10 ppm. All 6 FAMEs were measured and quantified with the calibration equations. The TIC chromatogram is shown in Figure 7 and the individual m/z chromatograms for each FAME standard are shown overlaid in Figure 8. By displaying the individual mass traces, the peak shapes of the FAME standards are better visualized.

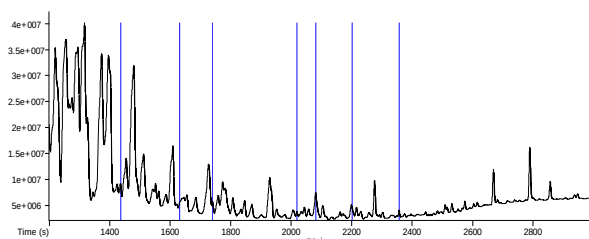


Figure 7. TIC chromatogram of JP8 jet fuel sample with FAME standards added. The vertical blue lines indicate the retention times of the standards.

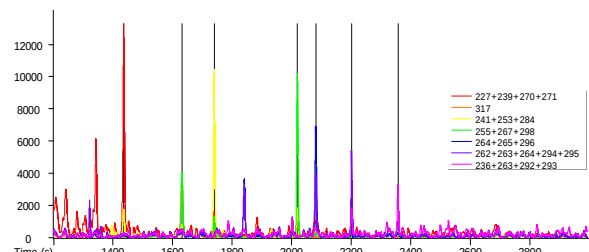


Figure 8. Chromatogram displaying the m/z used for quantification for each FAME standard. A different color mass trace is displayed for each FAME standard.

As part of data processing, the ChromaTOF software can automatically apply the calibration equations and report the quantified amounts of the calibrated analytes in an unknown sample. These equations were applied to the data shown in Figure 7 and 8. Table 2 shows the calculated concentrations for the FAMEs spiked into jet fuel.

Table 1. FAME standards

FAME standard	Symbol	Quant Masses
methyl palmitate	C16:0	227 239 270 271
methyl margarate	C17:0	241 253 284
methyl stearate	C18:0	255 267 298
methyl oleate	C18:1	264 265 296
methyl linoleate	C18:2	262 263 264 294 295
methyl linolenate	C18:3	236 263 292 293
methyl heptadecanoate, d33	C17:0-d33	317

Table 2: Peak Table for spiked JP8 results.

Name	Concentration	S/N
Methyl palmitate	10.4	2312.4
Methyl heptadecanoate, d33	1.00	2613.6
methyl margarate	9.09	608.66
Methyl stearate	8.19	1908.7
Methyl oleate	11.4	1018.4
Methyl linoleate	9.56	1563.0
Methyl linolenate	16.2	1799.1

3. Experimental Conditions

Sample Preparation

Sample preparation followed Section 7 of Method IP 585. C16 through C18 FAME standards (Sigma Aldrich, St. Louis, MO, USA), listed in Table 2, were diluted in dodecane at concentrations ranging from 0 to 100 ppm (w/w). Methyl heptadecanoate-d33 (Sigma Aldrich, St. Louis, MO, USA) was added as an internal standard at 10 ppm to each calibration standard. JP8 jet fuel standard was analyzed as representative jet fuel.

GC-TOFMS Method

The GC method utilized was based on Section 8 of Method IP 585. GC analyses were performed with LECO's Pegasus HT consisting of an Agilent 6890 GC coupled with a GERSTEL MPS2 Auto Sampler and LECO Pegasus TOFMS. Method details are provided in Table 3.

Table 3. GC-TOFMS (Pegasus HT) Method

Injection	1 μ L, splitless in a 260°C inlet
Inlet Purge Time	100 mL/min, 2 min after injection
Carrier Gas:	He @ 1.0 mL/min
Column	Stabilwax, 60 m x 0.25 mm x 0.50 μ m (Restek, Bellefonte, PA, USA)
Temperature Program	5 min at 150°C, ramped 12°C/min to 200 °C and held 17 min, ramped 3°C/min to 252°C and held 6.5 min
Mass Range	33-500 m/z
Acquisition Rate	10 spectra/s
Acquisition Delay	10 min
Source Temp	250°C

Instrument Control and Data Analysis

Data collection and analysis were controlled with LECO's ChromaTOF software (version 4.50). Data analysis was based on Section 10 of Method IP 585 with the following differences. Method IP 585 specifies quantification of each FAME species from the collection of specific high m/z masses, listed in Table 2, in SIM mode. With TOFMS detection, full mass range data were collected for each sample. The complete spectra across the full mass range were used for identification by matching to NIST library spectra and the same ions specified for SIM mode were utilized for quantification. These masses were specified as the quantification masses in the ChromaTOF software during data processing. Calibration data were compiled and calibration curves were generated with LECO's calibration software feature.

4. Conclusions

In this application note, the successful application of a GC-TOFMS based version of Method IP 585 for measuring FAME contaminants in jet fuel samples is demonstrated. LECO's Pegasus HT met the method requirements with TOFMS detection instead of SIM and Scan quadrupole MS detection. For quadrupole systems unable to perform simultaneous SIM/Scan acquisition, this approach offers comparable information with a single GC analysis per sample. The calibration data spanned the required calibration range and met the method specifications.