

# Detection and Quantification of Fatty Acid Methyl Esters (FAMES) in Jet Fuel by GCxGC-TOFMS

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## 1. Introduction

Jet fuel is frequently shipped in multi-use pipelines and distribution containers. There is high risk of cross-contamination by fatty acid methyl esters (FAMES) from biodiesel residue adherence to pipeline and container walls. FAME contamination of jet fuel in high enough concentrations can impact and compromise jet fuel properties which may lead to engine operational problems and possible engine flameout. The international jet fuel specifications (DEF STAN 91-91) limit the total FAME content to less than 5 mg/kg (ppm w/w). Levels above 5 mg/kg render the fuel off specification.



This analysis of FAMES in jet fuel was conducted using a LECO Pegasus® 4D system to identify and quantify FAMES in jet fuel by GCxGC-TOFMS analysis in the quantitative range from 1 to 150 mg/kg. This application note evaluates the efficacy of comprehensive two-dimensional gas chromatography (GCxGC) coupled to a time-of-flight mass spectrometer for the identification and quantification of FAMES in jet fuel.

## 2. Results

Jet fuel (JP-8) was analyzed by the GCxGC-TOFMS methods developed. Method blanks demonstrated no residual carryover of FAMES or jet fuel. A 1 mL sample of JP-8 was spiked with 10 ppm of the FAME standard and analyzed by the splitless GCxGC-TOFMS method. The raw data collected was processed using the 0–10 ppm calibration curve developed in ChromaTOF software. The results are illustrated in Figure 1 and Table 1. Figure 2 shows 2D chromatogram for an injection of the 40 ppm FAMES standard.

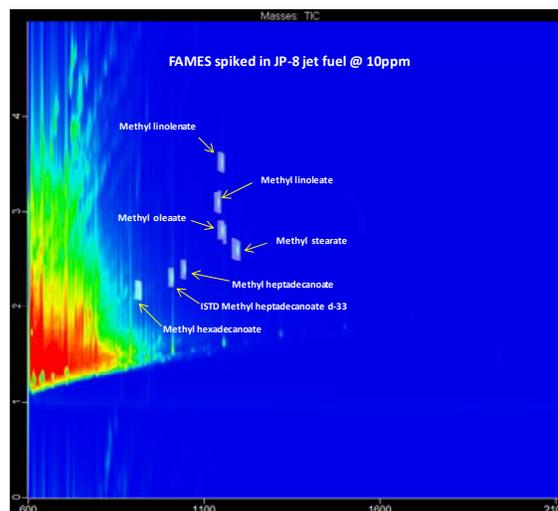


Figure 1. The GCxGC-TOFMS analysis above shows the 10 ppm spike of six FAMES into JP-8 jet fuel.

Table 1. The peak table for the GCxGC-TOFMS analysis in Figure 3 is shown below. The quantitative results are listed for the FAMES processed with the 0-10 ppm calibration.

Name	R.T. (s)	Concentration mg/kg	Similarity	Quant Masses	Area	Library
Methyl hexadecanoate	915, 2.185	10.540	765	74	25121176	Wiley9
Methyl heptadecanoate d33	1010, 2.305	1.000	715	77	35618748	Wiley9
Methyl heptadecanoate	1045, 2.395	10.090	901	74	21616952	Wiley9
Methyl linoleate	1140, 3.100	10.090	900	67	7197283	Wiley9
Methyl oleate	1150, 2.805	10.460	934	74	4315507	replib
Methyl linolenate	1150, 3.515	9.900	918	79	7488155	replib
Methyl stearate	1195, 2.595	9.960	905	74	18700297	replib

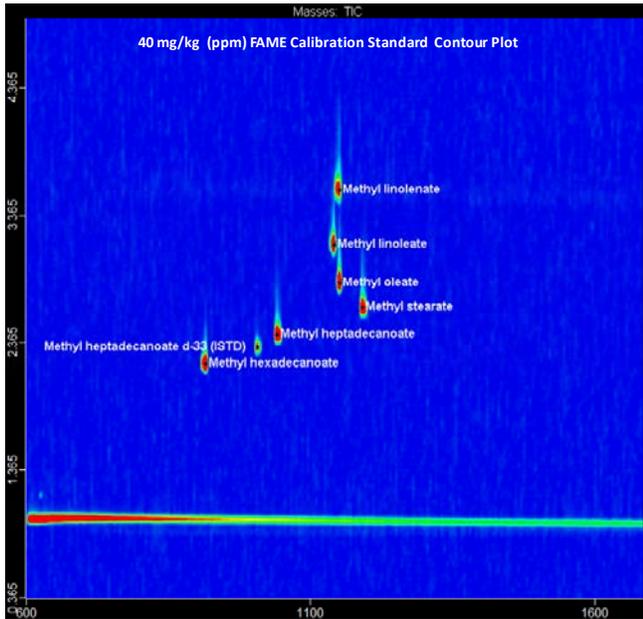


Figure 2. The two-dimensional contour plot above shows the 40 mg/kg FAME calibration standard GCxGC-TOFMS analysis with peak markers and labels for each FAME.

### Calibration Curve Development

A low-level calibration was developed from 0–10 ppm using the 0, 2, 4, 6, 8 and 10 mg/kg FAME standards by the splitless GCxGC method. A broad range calibration was developed from 0–100 ppm using the 0, 20, 40, 60, 80, and 100 mg/kg FAME standards by the 20:1 split GCxGC method. The results of both calibration standard curves are illustrated in Figure 3, Figure 4, Table 2, and Table 3.

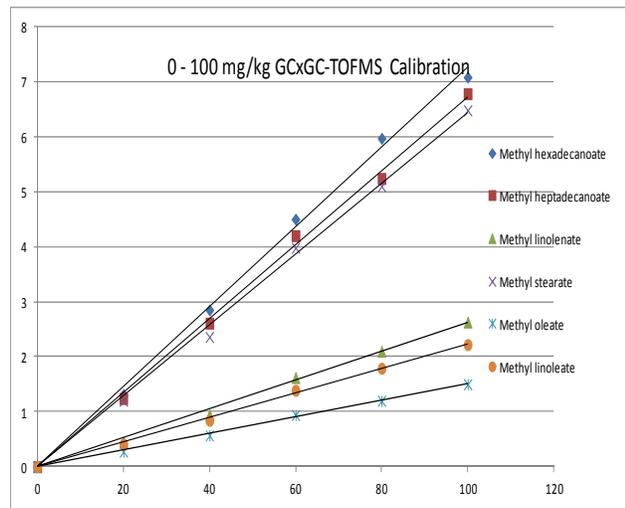


Figure 3. The calibration curves above show the 6 FAMES standards with a linear fit from 0 – 100 mg/kg (ppm).

**Table 2. The table below shows the 1<sup>st</sup> order equation and R<sup>2</sup> correlation coefficient values for the FAMES standards from 0–100 ppm. All R<sup>2</sup> correlation coefficient values achieved linearity of greater than 0.990.**

Standard	Methyl hexadecanoate	Methyl heptadecanoate	Methyl linolenate	Methyl Stearate	Methyl oleate	Methyl linoleate
Equation	$y = 0.0725x$	$y = 0.0672x$	$y = 0.0642x$	$y = 0.015x$	$y = 0.0223x$	$y = 0.0261x$
Correlation Coefficient	$R^2 = 0.9973$	$R^2 = 0.9979$	$R^2 = 0.9976$	$R^2 = 0.9981$	$R^2 = 0.9982$	$R^2 = 0.9981$

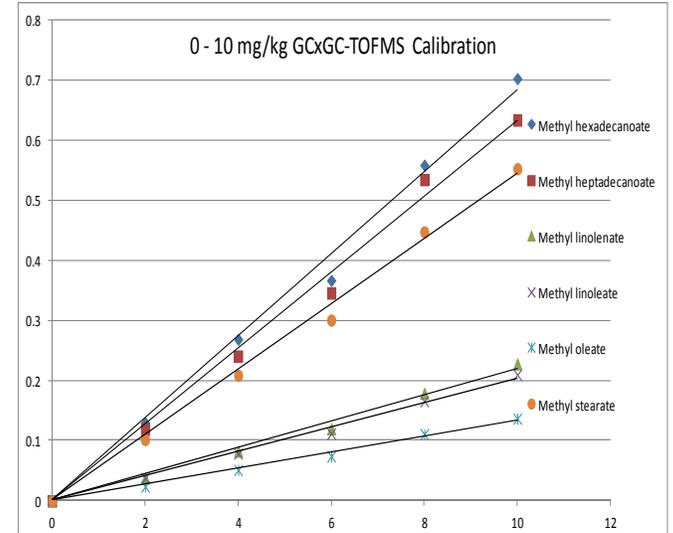


Figure 4. The calibration curves above show the 6 FAMES standards with a linear fit from 0–10 mg/kg (ppm).

**Table 3. The table below shows the 1<sup>st</sup> order equation and R<sup>2</sup> correlation coefficient values for the FAMES standards from 0–10 ppm. All R<sup>2</sup> correlation coefficient values achieved linearity of greater than 0.990.**

Standard	Methyl hexadecanoate	Methyl heptadecanoate	Methyl linolenate	Methyl linoleate	Methyl oleate	Methyl stearate
Equation	$y = 0.0584x$	$y = 0.0632x$	$y = 0.022x$	$y = 0.0204x$	$y = 0.0134x$	$y = 0.0544x$
Correlation Coefficient	$R^2 = 0.9929$	$R^2 = 0.9926$	$R^2 = 0.9924$	$R^2 = 0.9945$	$R^2 = 0.9943$	$R^2 = 0.9954$

### 3. Experimental

Fatty acid methyl ester standards were purchased from Sigma Aldrich, Inc. Methyl heptadecanoate d-33 from Sigma Aldrich, Inc. was used as the internal standard.

Calibration standards were prepared in dodecane at 0, 2, 4, 6, 8, 10, 20, 40, 60, 80, and 100 mg/kg (ppm). Methyl heptadecanoate d-33 was spiked as the internal standard at a concentration of 10 ppm. Two calibration curves were developed from a prepared working calibration standard. A calibration was developed in the 0–10 mg/kg range and a second calibration curve was developed in the 0–100 mg/kg range. Calibrations were developed in ChromaTOF<sup>®</sup> software using the internal standard with a first order linear fit.

A correlation coefficient value of at least 0.985 was required for each analyte. Feasibility of the GCxGC-TOFMS method was demonstrated by analysis of jet fuel (JP-8) spiked with FAMES at 10 ppm.

#### GCxGC-TOFMS Analysis Parameters

An Agilent 7890 gas chromatograph was used equipped with a LECO dual-stage, quad jet thermal modulator and a GERSTEL MPS2 autosampler. The GC primary column used was a 30 m x 0.25 mm id. x 0.25  $\mu$ m film thickness Rxi-5Sil MS (Restek Corp.). The GC secondary column used was a 1.6 m x 0.25 mm id. x 0.25  $\mu$ m film thickness Stabilwax<sup>®</sup> (Restek Corp.). The carrier gas used was Helium set @ 1.0 mL/min. A 1  $\mu$ L injection was made in splitless mode with an inlet temperature of 260°C for the 0–10 mg/kg calibration standards. Splitless injections were made using a single taper gooseneck Sky<sup>™</sup> liner (Restek Corp.) packed with glass wool. A 1  $\mu$ L injection was made in split mode with a split ratio of 20:1 and an inlet temperature of 260°C for the 0–100 mg/kg calibration standards. Split injections were made using a Precision<sup>®</sup> Sky liner (Restek Corp.) packed with glass wool. The GCxGC method temperature program for both split and splitless analysis began at 105°C, held for 2 minutes, and ramped to 190°C at 10°C per minute. The ramp then continued to 230°C at 2°C per minute, and held for 5 minutes. The total analysis time was 35.5 minutes. A LECO Pegasus 4D mass spectrometer was utilized as the detector. The TOFMS method parameters used a mass range of 35–750 m/z. The acquisition rate was set at 200 spectra/s with an ion source temperature of 230°C.

### 4. Conclusions

Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry was utilized to detect and quantify the fatty acid methyl ester (FAME) content found in jet fuel. A fast and robust method was developed using a traditional non-polar/polar GCxGC column configuration that separates, resolves, and quantifies the FAMES listed for determination in Method IP 585:2010. Calibration linearity of greater than 99% was achieved for both the 0–10 ppm and the 0–100 ppm calibration ranges. This application demonstrates that TOFMS can acquire full mass range spectra capable of identification and quantification of FAMES in jet fuel within a single analysis without requiring SIM/Scan detection and quantification. This work presents a reliable and effective GCxGC-TOFMS method for the analysis of FAME contamination in jet fuel.