# Stay ahead in developing green energy solutions: fatty acid methyl ester (FAME) analysis for jet fuel using GCMS

James Pachlhofer<sup>1</sup>, Adam Ladak<sup>2</sup>, Nicholas Warner<sup>3</sup> and Daniel Kutscher<sup>3</sup> <sup>1</sup>Thermo Fisher Scientific, Austin, TX, USA, <sup>2</sup>Thermo Fisher Scientific, Hemel Hempstead, UK, <sup>3</sup>Thermo Fisher Scientific, Bremen, DE

## Abstract

Using the Thermo Scientific<sup>™</sup> ISQ<sup>™</sup> 7610 GCMS with an extend linear dynamic range to analyze FAMEs in jet fuels in accordance with Method IP585. A dedicated GC column was used to enable a reduction of analysis time by 20 minutes per run. Recoveries of 5 and 50 mg kg-1 from spiked kerosene ranged from 87 to 94% with accurate quantification were demonstrated. A long-term study was performed showing stable results over 1 week of continuous operation.

# Introduction

As the world's energy demands continue to increase, new sources of energy are needed to replace dwindling fossil fuel resources. Biofuels, such as biodiesel, offer an attractive alternative to solve the ever-growing energy crisis. Consisting of fatty acid methyl esters (FAMEs) chemically derived from vegetable oils and animal fats, biodiesel provides a renewable energy resource. As carbon sources to produce biodiesel originate from the surrounding environment, combustion of biodiesel helps close the carbon cycle, helping move towards a carbon neutral society.<sup>1</sup> In addition, life cycle analysis show a significant reduction in harmful environmental impacts (i.e., emissions, waste products) in production of new generation biodiesels compared to fossil fuels;<sup>2</sup> further increasing its attractiveness as replacement energy resource.

The transportation sector consumes up to 60% of the world's oil reserves,<sup>3</sup> making it an ideal for the implementation of biofuels. Despite similarities between biofuels and it's fossil fuel counterparts, small differences in physical/chemical properties have posed challenges for the implementation of biofuel, particularly in the aviation sector. FAMEs possess a lower freezing point in comparison to fossil fuels and can solidify in fuel lines and filters (also known as fuel gelling) at low temperatures present at high altitudes causing unsafe flying conditions. Resistance and tolerance of engine components is also problematic, particularly in older engines. FAMEs can oxidize/corrode metal components and/or dissolve elastomer-based materials like tubing or sealings, causing potential engine rupture over long exposure.<sup>1</sup>

Research has shown that blending of biodiesel with traditional petroleum-based jet fuels can help mitigate these risks in engine operation. However, to ensure absolute safety in daily aviation operations, the current allowable limit for FAMEs content within jet fuel is 50 mg·kg<sup>-1</sup>. Contamination of jet fuel by FAMES can occur during transport through sharing pipeline infrastructure with biodiesel and its use in other sectors. As FAMEs composition can vary depending on the application and type of plant/animal sources used, the content present in jet fuels can vary, requiring accurate quantification over large concentration ranges. The petroleum hydrocarbon matrix also poses analysis challenges where efficient separation and selective detection between FAMEs and relatively non-polar sample matrix is needed to avoid interferences.

This poster will follow the established method IP 585 for the analysis of FAMEs in jet fuels. As part of method validation, linearity was assessed using two calibration ranges, which resulted in accurate and reliable results.

# **Experimental conditions**

#### Standard and sample preparation

Calibration standards were prepared as described in the IPA 585 method.<sup>4</sup> Briefly, a FAMEs stock solution of 1000 ppm concentration containing Palmitic acid methyl ester (C16:0), Heptadecoaoic acid methyl ester (C17:0) Stearic acid ethyl ester (C18:0), Methyl cis-9-octadecenoate (C18:1), Linoleic acid methyl ester (C18:2), and Linolenic acid methyl ester (C18:3) (Accustandard, USA) was diluted in a 1:10 ratio to produce a secondary FAMEs stock solution of 100 ppm. Serial dilution of the secondary stock solution was preformed to produce calibration standards (2, 4, 6, 8, 10, 20, 40, 60, 80, 100 mg kg<sup>-1</sup>). To each calibration standard, methyl heptadecanoate-d33 (1000 ppm, Accustandard, USA) was added as an internal standard to produce a final concentration of 10 mg·kg<sup>-1</sup> in each calibration standard. To evaluate method performance, kerosene (Fisher Scientific, USA) was used as a surrogate matrix to mimic int fuel and spiked with the FAMES stock solution at 5 and 50 mg kg<sup>-1</sup> concentration levels.

#### Scan QR code for full instrument parameters



### Results

#### Chromatography and sensitivity

Using the Trace TR-FAME capillary column and oven temperature program described here, separation from hydrocarbon matrix within kerosene was achieved showing minimal impact on full scan analysis. All targeted compounds were efficiently separated in under 24 minutes using simultaneous full scan and TSIM acquisition: a 20-minute reduction in analysis time compared to the IP 585 method (Figure 1A). Quantification of FAMEs below 1 mg kg-1 was easily achievable using acquired TSIM data (Figure 1B) providing trace level sensitivity well below regulatory requirements (i.e., 50 mg kg-1).



TSIM acquisition of FAMEs of 0.7 mg kg-1 FAMEs in kerosene.

#### Linearity

Results from the calibration analysis carried out using the criteria defined in the IP 585 method (forced origin) are shown in Figure 2 and Table 3. Implementation of two calibration ranges (low and high) within the IP 585 method is attributed to differences in response factors between these concentration ranges with higher response (i.e., slope) occurring at the higher concentration range (Table 1.). However, excellent linearity at the low (2-10 mg·kg-1), high (20-100 mg·kg-1) and over the entire calibration range (2 – 100 mg·kg-1) was observed for all FAME components investigated with correlation coefficients surpassing the IPA 585 method criteria (r2 > 0.985).



Figure 2. Calibration curves obtained for FAMEs in the (A) low calibration range  $(2 - 10 \text{ mg} \cdot \text{kg} \cdot 1)$  and (B) entire calibration range  $(2 - 100 \text{ mg} \cdot \text{kg} \cdot 1)$ 

Learn more at thermofisher.com/ISQ7610

Table 1. Retention time, acquisition ions and correlation coefficients for low, high, and entire calibration range for FAMEs

Compound	Retention time (min)	SIM ions <sup>a</sup>	Low calibration (2 – 10 mg·kg <sup>-1</sup> )		High calibration (20 – 100 mg·kg <sup>-1</sup> )		Overall calibratio (2 – 100 mg·kg <sup>-1</sup> )	
			r²	slope	r²	slope	r²	slope
C16:0	15.52	<b>227</b> , 270, 239	0.9995	0.51	0.9992	0.62	0.9989	0.62
C17:0-d33 (IS)	16.82	<b>286</b> , 317, 267	N/A	N/A	N/A	N/A	N/A	N/A
C17:0	17.61	<b>241</b> , 284, 253	0.9995	0.46	0.9994	0.57	0.9991	0.57
C18:0	19.73	<b>255</b> , 298, 267	0.9997	0.49	0.9995	0.59	0.9993	0.59
C18:1	20.57	<b>264</b> , 265, 296	0.9991	0.21	0.9993	0.27	0.9987	0.27
C18:2	21.97	<b>262</b> , 263, 294	0.9995	0.08	0.9992	0.10	0.9988	0.10
C18:3	23.60	<b>236</b> , 263, 292	0.9990	0.04	0.9986	0.06	0.9979	0.06

<sup>a</sup>Bold SIM ion represents quantification ion

IS – internal standard

 $r^2$  – linear regression correlation coefficient

N/A- not applicable

#### Method Accuracy

Method accuracy and precision was evaluated through analysis of spiked matrix. The most common used jet fuels (i.e., Jet-A and Jet-1A) are kerosene based. Therefore, spiked concentrations at previous (5 mg kg-1) and current (50 mg kg-1) regulatory limits for FAMEs were prepared in kerosene as a surrogate matrix. Results from spike recoveries shown in Figure 3.



#### Figure 3. Spike recovery of 5 and 50 mg kg-1 FAMES in kerosene (n = 8) Robustness

Stable response was observed with more than 90 injections of kerosene spiked with 5 mg kg<sup>-1</sup> FAMEs with percent relative standard deviation (%RSD) ranging between 1.5 - 3.0 %. In addition, no degradation of separation efficiency was observed after 96 injections of matrix with retention times and absolute response (i.e., peak area) remaining stable at regulatory limits for FAMEs in jet fuel (i.e., 50 mg kg-1, Figure 4). To assess performance stability, a 60 mg kg-1 calibration standard was injected after every 10th sample injection to evaluate ion source sensitivity robustness over a 7-day period of continuous analysis (Figure 5). After a total of 230 injections of spiked kerosene matrix the absolute sensitivity decreased by less than 10% from the initial intensity observed for the 60 mg·kg-1 standard.



Figure 4. Comparison of chromatograms of 50 mg·kg-1 FAMES spike in kerosene after 1 and 96 injections



Conclusions

This application demonstrates the ISQ 7610 MS equipped with the new XLXR detector coupled to the Trace 1610 GC provides a highly robust, efficient, and sensitive methodology required by laboratories for the routine of FAMEs in jet fuels

- 585
- response of the new XLXR detector
- of FAMEs at low mg kg<sup>-1</sup> levels

### **References and Acknowledgements**

- https://doi.org/10.1016/j.rser.2019.01.056
- 588 600. <u>10.1016/j.renene.2020.02.022</u> review-2021

#### Trademarks/licensing

© 2024Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries unless otherwise specified. This information is not intended to encourage use of these products in any manner that might infringe the intellectual property rights of others.

# Thermo Fisher SCIENTIFIC

Figure 5. Absolute sensitivity robustness with continuous analysis over 7 days

 Shorter analysis time was achieved using the Trace TR-FAME capillary column, providing efficient separation of targeted FAMEs with a 20-minute reduction in analysis time compared to method IP

• Linear response was observed over low and high calibration ranges as well over the entire calibration range; surpassing criteria defined by method IP 585

• Recoveries of 5 and 50 mg kg<sup>-1</sup> from spiked kerosene ranged from 87 – 94 % with accurate quantification made possible using a single calibration curve with the high linear dynamic

• Stable response of the Exactabrite ion source over days/weeks for multiple injection sequences provides laboratories with increased uptime and productivity while delivering trace level detection

Rochelle, D.; Najafi, H. A review of the effect of biodiesel on gas turbine emissions and performance. Renew. Sust. Energ. Rev. 2019, 105, 129 - 137.

2. Foteinis, S.; Chatzisymeon, E.; Litinas, A.; Tsoutsos, T. Used-cooking-oil biodiesel: Life cycle assessment and comparison with first- and third-generation biofuel. Renew. Energ. 2020, 153,

IEA (2021), Global Energy Review 2021, IEA, Paris https://www.iea.org/reports/global-energy-

Energy Institute, IP 585, Determination of fatty acid methyl esters (FAME), derived from bio-diese fuel in aviation turbine fuel—GC-MS with selective ion monitoring/scan detection method, 2010.