Application News

GC-MS GCMS-QP™2020 NX

Determination of Fatty Acids Methyl Esters (FAMEs) in aviation turbine fuel by GCMS Scan/SIM mode as per IP585

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User Benefits

- A GC-MS method for the determination of 6 FAMEs in aviation jet fuel as per the proposed IP 585.
- The IP method criteria were met easily with better sensitivity (S/N ratio) for individual FAMEs.

Introduction

Jet Fuels or Aviation Turbine fuels (AVTUR) are petroleum products used to power gas turbine engines in aircrafts. It is a mixture of variety of hydrocarbons and the individual ratios of these hydrocarbons varies based on petroleum sources.

Recently there is an increasing trend of blending AVTUR with biodiesel to overcome the excess dependence of petroleum sources. Biodiesels are fuels which are normally produced from plant oils or vegetable fats. Biodiesel consists of shorter or longer chain Fatty Acid Methyl Esters (FAMEs) which are inherited from the feedstock.

The presence of these FAMEs in biodiesel affects the fuel properties of jet fuels. Biodiesel in jet fuel can cause thermal breakdown under storage conditions or during use in aircraft fuel systems leaving deposits which compromise performance and safety. Furthermore, biodiesel freezes at very lower temperatures which is typical at high altitudes. Because of these concerns, IP has regulated the concentration of FAMEs in jet fuels. The maximum permitted level for FAMEs in jet fuel is limited to 50 mg/kg.

The method described here is followed based on the directions laid down by IP 585 method. The analysis is performed on Shimadzu GCMS-QP2020 NX (Fig. 1) using Shimadzu Stabilwax™ capillary column. The system configuration and instrument parameters are given in Table 1 & 2 respectively. The ions used for the quantification of the various analytes are given in Table 3.

Fig. 1 GCMS-QP™2020 NX system

Experimental

Individual FAME standard was purchased from Accustandard. These individual FAME was then dissolved using dodecane to a concentration of 10000 ppm. Similarly, 1000 mg/kg of methyl heptadeconate d33 in dodecane was also purchased from Accustandard. It was used as internal standard as required by IP 585. Cyclohexane was used as rinsing solution for autosampler syringe.

Preparation of standard stock : 500 µL of each FAME solution was pipetted into a 5 mL container, vortexed and finally made up to 5 mL with dodecane. This was then labelled as Standard Stock solution with concentration of 1000 ppm.

Calibration standards and sample preparations : Two different sets of calibration standards were prepared as per IP 585 method.

Set 1: Low level standards with concentrations 0.0, 2.0, 4.0, 6.0, 8.0 and 10.0 ppm.

Set 2: High level standards with concentrations 0.0, 20.0, 40.0, 60.0, 80.0 and 100 ppm.

All standards were prepared by diluting 1000 ppm stock solution. To 1000 µL of these standards, 10 µL of heptadecanoate methyl ester d33 (C17:0 d33) was added as internal standard before analysis. LOD standard with concentration 0.5 ppm was included in the batch to evaluate S/N ratio of the analysis.

Sample analysis and spiked samples preparations : Similar to standards, 1000 µL of jet fuel sample was taken to which 10 µL of Internal standard was added.
Likewise, 1000 µL of spike standards with FAME concentrations, 0.5, 25.0 and 50.0 ppm were also prepared in jet fuel sample to study the recovery of the method.

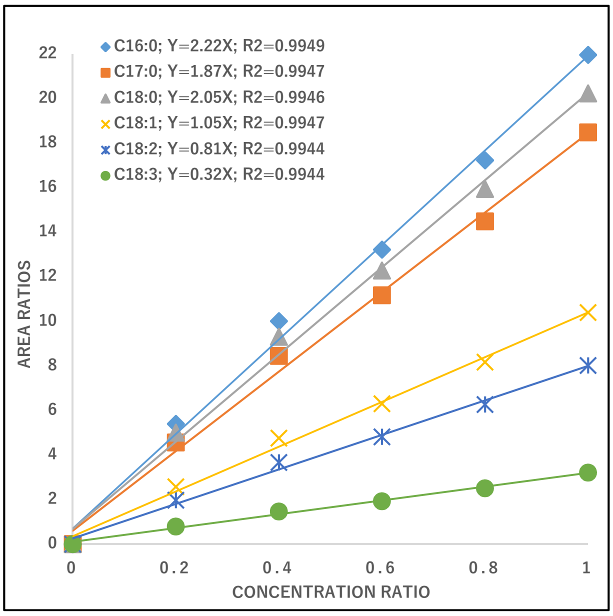
System Configuration

Shimadzu GCMS-QP2020 NX system was used for this analysis. The FASST (Fast Automated Scan/SIM Type) feature of Shimadzu GCMS was utilized during this experiment. With FASST feature, it is possible to carry out both Scan and SIM analysis simultaneously. Scan mode is used for identifying the FAMEs whereas SIM mode is used for quantifying. The IP guidelines were followed for the analysis.

Table 1 System Configuration

Model	: GCMS-QP2020 NX / AOC™-20i Plus + AOC-20s Plus
Glass Insert	: Splitless Insert with deactivated glass wool (P/N:227-35008-01)
Analytical Column	: SH-Stabilwax (60 m x 0.25 mm I.D., df= 0.5 µm) (P/N:227-36248-02)

Low Level Standards



High Level Standards

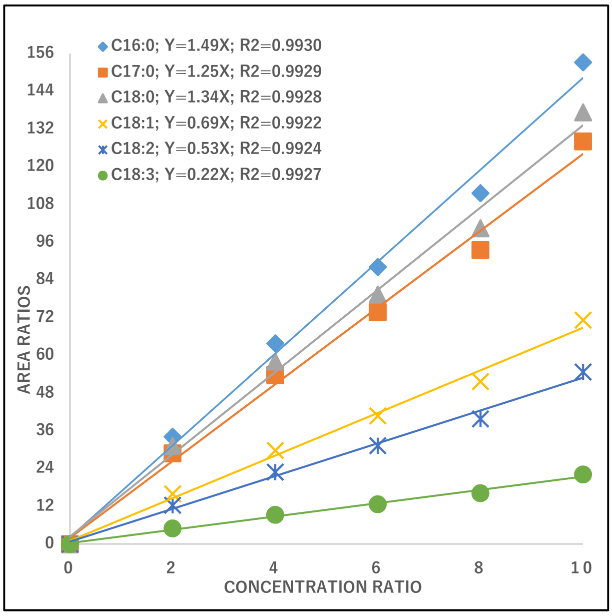


Fig. 2 Calibration Curves of FAMEs Low and High Levels

Table 2 Instrument Parameters

GC Parameters

Injector Temperature	: 260℃
Flow mode	: Constant flow
Column Flow	: 0.8 mL/min
Purge Flow	: 3 mL/min
Injection volume	: 1 µL
Oven Program	: 150℃ (5min) - 12℃/min - 200℃ (17min) - 3℃/min - 252℃ (6.5min)

MS Parameters

Ion Source Temperature	: 230℃
Interface Temperature	: 260℃
Solvent Cut Time	: 20.00 min
Detector Voltage	: 1.27 kV
Event Time	: Scan 0.1 sec / SIM 0.3 sec
Scan Range(*m/z*)	: 32-332

Table 3 Mass Table

Analyte	Type	Ions *m/z*
C16:0	Target	227, 239, 270, 271
C17:0 d33	ISTD	317
C17:0	Target	241, 253, 284
C18:0	Target	255, 267, 298
C18:1	Target	264, 265, 296
C18:2	Target	262, 263, 264, 294, 295
C18:3	Target	236, 263, 292, 293

The linearity graphs for both low-level and high-level standards were drawn by plotting area ratios of analyte and internal standard peak against the concentration of analyte. The linearity curves are shown in Fig. 2 and the results are shown in Table 4. The linearity curve was forced through the origin as directed in the IP method. For all the analytes the linearity exceeds the minimum criteria of $R^2 > 0.985$.

The analysis result of 0.5 ppm of all the specified FAMEs in dodecane resulted a signal to noise ratio greater than 10:1 as per the IP 585 guidelines. The observed S/N value at 0.5 ppm concentration of various FAMEs are provided in Table 5. Analyzed 3 available marketed samples, #201,#202 & #203 and checked for the FAME content. No FAMEs were detected in any of the samples. #202 was used for spike recovery study. The recovery of all the FAMEs were also found to be within the standard criteria of 80-120%. The recovery results were shown in Table 6. The scan TIC for 40 ppm of FAMEs in dodecane and an overlay of SIM TICs for the un-spiked jet fuel, 0.5, 25 and 50 ppm FAMEs spiked in jet fuels are shown in Fig. 3 & 4 respectively.

Table 4 Linearity results

Analyte	RT(min)	Conc. range	R^2
C16:0	26.482	0.0 to 10.0 ppm	0.9949
C17:0	31.531		0.9947
C18:0	36.040		0.9946
C18:1	37.043		0.9947
C18:2	39.011		0.9944
C18:3	41.552		0.9944
C16:0	26.584	0.0 to 100.0 ppm	0.9930
C17:0	31.625		0.9929
C18:0	36.125		0.9928
C18:1	37.127		0.9922
C18:2	39.077		0.9924
C18:3	41.611		0.9927

Table 5 S/N ratios at 0.5 ppm FAMEs in dodecane

Name	S/N at 0.5 ppm
C16:0	4146
C17:0	3742
C18:0	4419
C18:1	2287
C18:2	1752
C18:3	783

Table 6 Spike recovery results

Name	Sample # 202	Conc. Spiked	Conc. found	Recovery
	FAME conc.	ppm (N= 2)	ppm	%
C16:0	ND	0.5	0.43	86.7
		25	26.1	104.4
		50	48.6	97.2
C17:0	ND	0.5	0.48	96.2
		25	27.4	109.7
		50	50.5	100.9
C18:0	ND	0.5	0.50	100.3
		25	27.8	111.4
		50	50.9	101.9
C18:1	ND	0.5	0.49	97.9
		25	27.4	109.7
		50	50.4	100.9
C18:2	ND	0.5	0.45	90.9
		25	27.7	110.9
		50	50.9	101.8
C18:3	ND	0.5	0.55	110.1
		25	28.1	112.4
		50	51.6	103.3

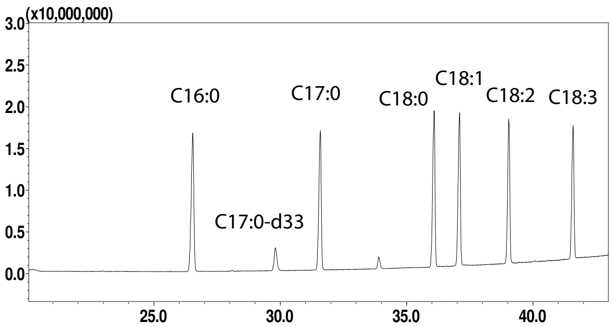


Fig 3. Scan TIC for 40 ppm FAME Mix Standard

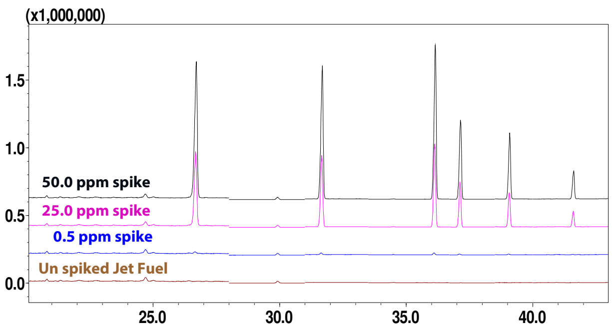


Fig 4. Overlay of SIM TICs for un-spiked and spiked jet fuel sample by FAMEs

■ Conclusion

This application note demonstrates the use of Shimadzu single quadrupole GCMS (GCMS-QP2020 NX) for the estimation of six fatty acid methyl esters (FAMEs) in jet fuel (AVTUR). The FASST feature of Shimadzu GCMS was utilized during this experiment. All the method parameters were set according to IP recommendations.

The results obtained from this experiment satisfies all the necessary criterion laid by IP 585. The calibration curve for all the analytes were found to be linear for both low and high-level standards with regression (R^2) greater than 0.99. The signal to noise ratios for all the analytes at 0.5 ppm was found to be much higher than that specified in IP Method. Additionally, the recovery studies with three spike samples (0.5, 25 and 50 ppm) were found to be with in 80-120%.

This application proves the adaptability of GCMS-QP2020 NX for the use of IP 585 for the determination of FAMEs in jet fuels/AVTUR. Additionally, the superior sensitivity and robustness of Shimadzu GCMS-QP2020NX model resulted in obtaining high quality data for FAME analysis by GCMS.

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