

## Gas Chromatography/ Mass Spectrometry

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## Fatty Acid Methyl Ester Contamination of Aviation Fuel by GC/MS

### Introduction

The contamination of aviation fuel with fatty acid methyl esters (FAMES) can arise due to the use of multi-product pipelines for fuel supply and distribution. In some countries, the widespread, mandatory introduction of automotive fuels with a bio-material content means that these pipelines are exposed to both automotive biodiesel with a 5% FAME (BD 5) content as well as to aviation fuel. FAMES can adsorb onto the surface of the pipeline and later desorb, contaminating whatever fuel that follows, including aviation fuel.

FAMES alter the physical properties of the fuel. While presence of FAMES in aviation fuel is of global concern, the United Kingdom is at the forefront of the analysis. The specification of aviation fuel in the UK is defined in the Ministry of Defence (MoD) Defence Standard 91-91. Technical authority for this standard is controlled by the MoD Defence Fuels Group with the agreement of the UK Civil Aviation Authority (CAA). This specification has recently been amended to formalize the acceptance of FAMES in aviation fuel up to a maximum of 5 mg/Kg (ppm) combined total. To measure this specification, the Energy Institute has issued a method entitled IP PM DY: Determination of fatty acid methyl esters (FAME) derived from biodiesel fuel, in aviation turbine fuel – GC/MS with selective ion monitoring/scan detection method. The US specification of aviation fuel is covered by ASTM® D1655; in August of 2009, in a special airworthiness bulletin (NE-09-25R1), the Federal Aviation Administration (FAA) stated its intent to include a similar regulation in its specifications.

Current methods for determining FAME in aviation fuel use a polar 'wax' type GC column with mass spectrometry (MS) for detection. The polar column will be more retentive for FAME compounds relative to the less polar hydrocarbon compounds of the fuel. The MS will identify FAMEs based on unique spectral data, further distinguishing FAMEs from hydrocarbon aviation fuel. The limitation of current methods is that the wax column has a relatively low maximum-temperature limit and high column bleed as it approaches this limit.

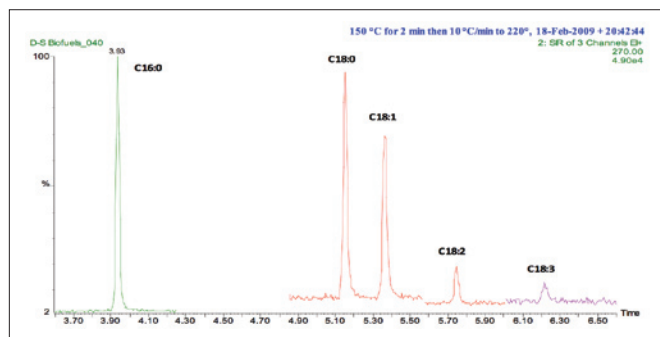


Figure 1. 0.1 ppm (wt/wt) individual FAME compounds in n-dodecane.

In this application note, a different type of polar capillary column is used. This column reduces the temperature necessary to elute all compounds, while also providing a higher maximum temperature. This will reduce both the wear on the column and the amount of signal in the chromatogram associated with column bleed. Additionally, this method will increase sample throughput. The specification of 5 mg/Kg is a total for all FAME compounds present and therefore the limit of detection for individual FAME compounds needs to be significantly lower than 5 mg/Kg. Figure 1 demonstrates that 0.1 mg/Kg is possible using this experimental setup.

## Experimental

This application was performed on a PerkinElmer® Clarus® 680 GC/MS with a capillary split/splitless injector. A 1.0 µL splitless injection was used to introduce the standards and samples into an unpacked, 2 mm i.d., quartz liner. The chromatographic separation was achieved on a 25 m x 0.32 mm i.d. x 0.25 µm BPX70 column (SGE, Australia). The MS was used in single-ion-recording mode (SIR) to provide maximum sensitivity and specificity. Complete instrument parameters are presented in Table 1.

**Table 1. Detailed instrument parameters for the GC/MS analysis of FAMEs.**

| GC Conditions   |  |
|-----------------|--|
| Column          | 25 m x 0.32 mm id x 0.25 µm BPX70                                    |
| Injector        | Split/splitless @ 280 °C with glass wool packed liner                |
| Carrier Gas     | Helium @ 15 psig at injector and 3 psig at Swafer                    |
| Injection       | 1.0 µL splitless for 0.75 minutes then 50 mL/min                     |
| Oven            | 150 °C for 2 minutes then 10 °C/min to 220 °C and hold for 6 minutes |
| MS Conditions   |  |
| Mode            | Electron Ionization (70 eV)  |
| Source          | 180 °C   |
| Transfer Line   | 300 °C   |
| Photomultiplier | 550 V  |

**Table 2. Calibration summary for FAMEs with GC/MS.**

| FAME  | Concentration Range | Coefficient of Determination ( $r^2$ ) |
|-------|---------------------|--|
| C16:0 | 0.5 to 10.0 ppm     | 0.999929                               |
| C18:0 | 0.5 to 10.0 ppm     | 0.999872                               |
| C18:1 | 0.5 to 10.0 ppm     | 0.999744                               |
| C18:2 | 0.5 to 10.0 ppm     | 0.999577                               |
| C18:3 | 0.5 to 10.0 ppm     | 0.999092                               |

## Calibration

A commercially available standard (Supelco®) containing equal masses of pure C16:0, C18:0, C18:1, C18:2 and C18:3 was diluted by weight to 2000 mg/Kg with n-dodecane solvent, as recommended in Institute of Petroleum method PM-DY/09. Calibration standards were prepared at 0.5, 1.0, 2.5, 5.0 and 10.0 mg/Kg and spiked with 2.0 µL of C21:0 in n-dodecane solution used as an internal standard.

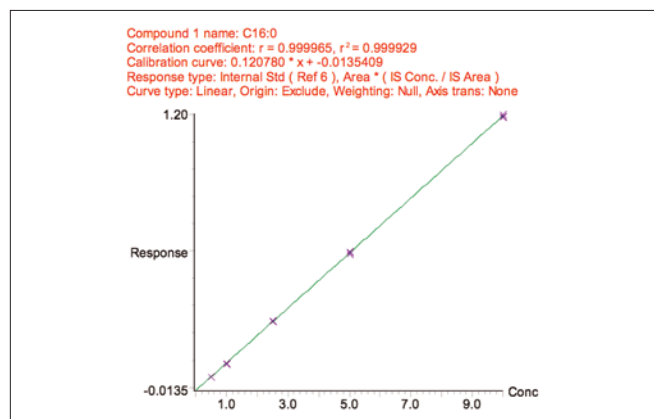


Figure 2. The calibration result from TurboMass™ GC/MS software demonstrating the linear response of FAME C16:0 across a range of 0.5-10.0 mg/Kg.

The calibration standards were analyzed in triplicate. All data points were used without exception. The response across the calibration range was very linear ( $r^2 > 0.9991$ ) for all FAME compounds; complete calibration data is presented in Table 2. Additionally, Figure 3 demonstrates the calibration output from the PerkinElmer TurboMass software.

Immediately following the instrument calibration, a 5 mg/Kg standard was analyzed to provide additional precision data. The results of this precision study are reported in Table 3.

**Table 3. System precision evaluation, replicate injections (n=15) of the 5.0 mg/Kg calibration mixture.**

| FAME  | Concentration | RSD% Absolute Peak Area | RSD% IS Resp. Ratio |
|-------|---------------|-------------------------|---------------------|
| C16:0 | 5.0 ppm       | 1.34                    | 0.78                |
| C18:0 | 5.0 ppm       | 1.34                    | 0.50                |
| C18:1 | 5.0 ppm       | 1.40                    | 0.62                |
| C18:2 | 5.0 ppm       | 1.22                    | 0.86                |
| C18:3 | 5.0 ppm       | 1.55                    | 0.86                |

The ability of the method to determine a wide range of FAMES at various concentrations was verified by analyzing a commercially available rapeseed oil standard (Supelco®). The standard was diluted 100 fold (100 mg to 10 g) by weight in n-dodecane, with a further 200:1 dilution resulting in a mixture with the composition in Table 4.

**Table 4. Composition of fame mixture used to verify the method identification of a mixture of FAMES.**

| FAME  | Initial Concentration | Final Concentration |
|-------|-----------------------|---------------------|
| C14:0 | 1.0 %                 | 0.5 ppm             |
| C16:0 | 4.0%                  | 0.8 ppm             |
| C18:0 | 3.0%                  | 0.6 ppm             |
| C18:1 | 60.0%                 | 30.0 ppm            |
| C18:2 | 12.0%                 | 6.0 ppm             |
| C18:3 | 5.0%                  | 2.5 ppm             |
| C20:0 | 3.0%                  | 1.5 ppm             |
| C20:1 | 1.0%                  | 0.5 ppm             |
| C22:0 | 3.0%                  | 1.5 ppm             |
| C22:1 | 5.0%                  | 2.5 ppm             |
| C24:0 | 3.0%                  | 1.5 ppm             |

The rapeseed oil was analyzed in ten replicates to verify the precision of the method when the FAME materials span a wide concentration range (Table 5). An example chromatogram from this analysis is shown in Figure 3.

**Table 5. The precision results from the analysis of a rapeseed oil mixture (n=10).**

| FAME  | Conc. (%) in original mix | Conc. (ppm) final | RSD% Absolute Area | RSD% Int'l Std. Response Ratio |
|-------|---------------------------|-------------------|--------------------|--------------------------------|
| C14:0 | 1.0                       | 0.50              | 2.02               | 0.86                           |
| C16:0 | 4.0                       | 2.00              | 1.66               | 1.18                           |
| C18:0 | 3.0                       | 1.50              | 2.08               | 0.63                           |
| C18:1 | 60.0                      | 30.00             | 1.52               | 0.54                           |
| C18:2 | 12.0                      | 6.00              | 1.84               | 0.19                           |
| C18:3 | 5.0                       | 2.50              | 2.34               | 0.89                           |
| C20:0 | 3.0                       | 1.50              | 2.08               | 0.33                           |
| C20:1 | 1.0                       | 0.50              | 3.41               | 1.71                           |
| C22:0 | 3.0                       | 1.50              | 2.83               | 1.10                           |
| C22:1 | 5.0                       | 2.50              | 3.04               | 1.53                           |
| C24:0 | 3.0                       | 1.50              | 3.66               | 1.86                           |

**Internal Standard = C21:0**

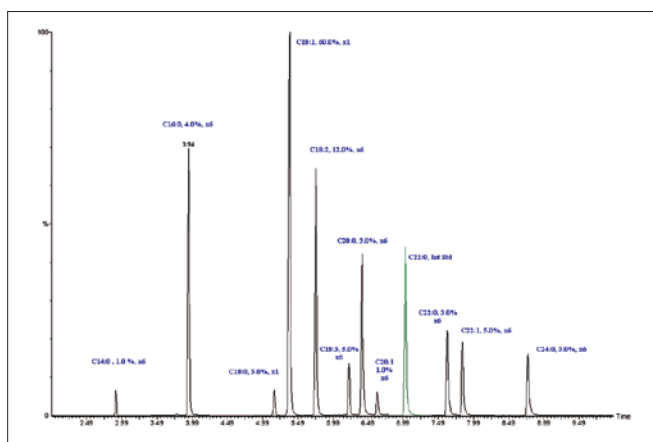


Figure 3. Chromatography of the rapeseed oil reference mixture using SIR.

The final verification of this method was to analyze an aviation-fuel sample spiked with a known amount of FAME. Figure 4 presents the resultant chromatogram from the analysis of an aviation-fuel sample spiked with between 0.5 and 30 ppm FAME.

