By examining the shortcomings of some analysis techniques it is possible to determine the best solution for testing FAME levels in jet fuels

A new approach

Fatty Acid Methyl Esters (FAMEs) are used as blending stock for diesel fuel in refinery applications. Major jet engine manufacturers agree that jet fuel must contain less than 5ppm of FAME because there is concern that FAME products, using the same production, storage, and transport systems as jet fuel, can become cross-contaminated into jet fuel and exceed the 5 ppm (mg/kg) limit.

Currently, only jet fuel containing less than 5 mg/kg of FAME is acceptable for use. This limit is described in the reference standards DEF STAN 91-91 and ASTM D1655.

Jet fuel is the most highly specified transportation fuel, but the airline industry has long recognised that a small amount of cross-contamination is unavoidable in a shared fuel system. Biodiesel is already moved through pipelines in Europe, and the EU currently allows up to 5 ppm in its spec for jet fuel. But there has been concern over the potential for cross-contamination.

FAME contamination of jet fuel could create problems with jet engine performance, including fuel gelling, coking (deposits), and even possible engine failure in-flight. Deposit formation leads to increased maintenance and downtime and can be very destructive to engine components.

The thermal stability of FAMEs and blends of FAMEs with conventional jet fuel is an area of concern. The higher carbon number and viscosity of FAMEs compared to jet fuel could affect atomisation and vaporisation in the combustion chamber. FAMEs are more viscous than conventional jet and have higher molecular weight affecting atomisation and vaporisation in the combustor, resulting in incomplete combustion and particulate emissions, especially at low engine power settings.

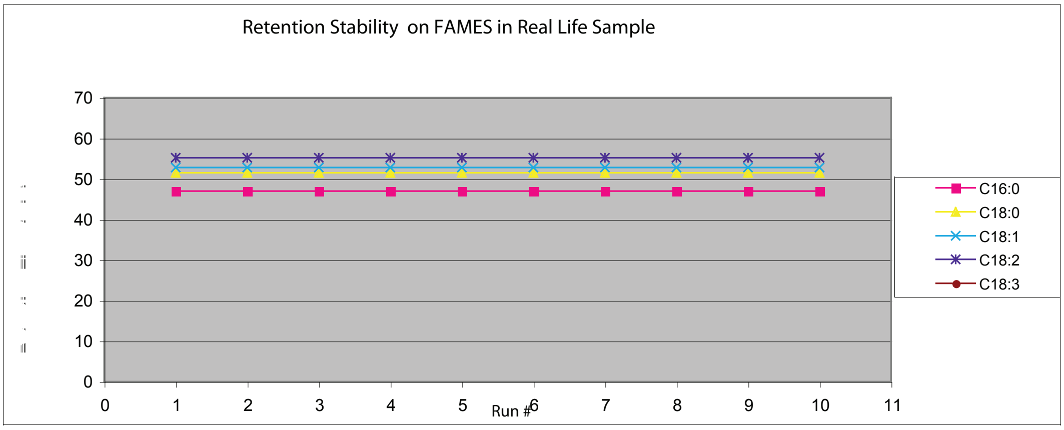
The introduction of FAME into diesel fuel created some

Typical FAME components in biodiesel

FAME	Molecular formula	Symbol used
Hexadecanoate (methyl palmitate)	$C_{17}H_{34}O_2$	C16:0
Methyl octadecanoate (methyl stearate)	$C_{19}H_{38}O_2$	C18:0
Methyl octadecenoate (methyl oleate)	$C_{19}H_{36}O_2$	C18:1
Methyl octadecadienoate (linoleate)	$C_{19}H_{34}O_2$	C18:2
Methyl octadecatrienoate (linolenate)	$C_{19}H_{32}O_2$	C18:3

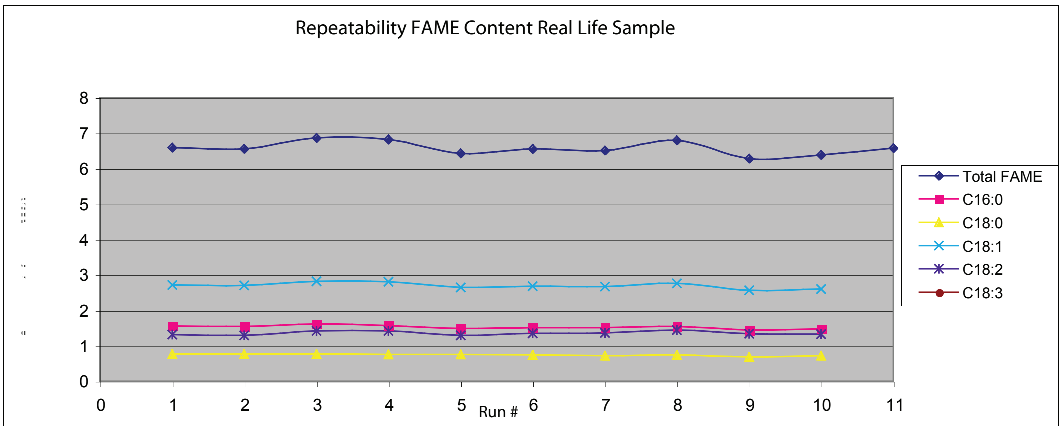
These components have been specifically chosen as they typically make up greater than 95% of the composition of the major biofuel vegetable oil feeds currently used in biodiesel blends with conventional mineral diesel

Retention time stability for individual FAME components



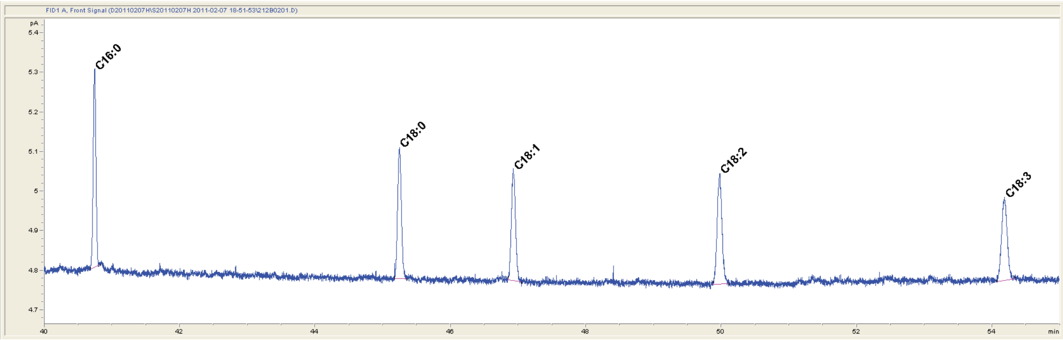
With a maximum variation of 0.02% in retention time, identification of FAME components is clearly unambiguous

Result repeatability for individual and single component FAME



Data for a representative jet fuel sample. Even at the very low level of 6.6 ppm w/w FAME for this particular sample, the repeatability for the method is only 2.8% (n=10). Even C18.0, found at a concentration of 0.75 ppm w/w has a more than acceptable repeatability at 3.4% RSD

Sensitivity of the method: 1 ppm of individual FAME components



The method developed has sensitivity of better than 0.5ppm w/w per FAME component or 2 mg/kg total FAME. The Linear Dynamic Range for the method was tested for C16:0 in two concentration ranges.

issues with an impact on Aviation Turbine Fuel, or AVTUR. First, FAME components are surface active and tend to stick to metal or glass surfaces. Where supply chains handle both jet fuel and biodiesel this property brings the risk of cross contamination.

Secondly, FAME is not derived from conventional sources. As defined in DEF STAN 91-91, conventional sources include crude oil, natural gas liquid condensates, heavy oil, shale oil and oil sands. . The jet fuel specification states explicitly that jet fuel shall consist predominantly of refined hydrocarbons. The international jet fuel specifications (e.g. DEF STAN 91-91) limit FAME content to less than 5mg/kg (ppm w/w). Levels above 5 mg/kg render the fuel off-specification. This is a serious issue because there have been instances in which jet fuel containing more than 5 ppm FAME has inadvertently been supplied to airports.

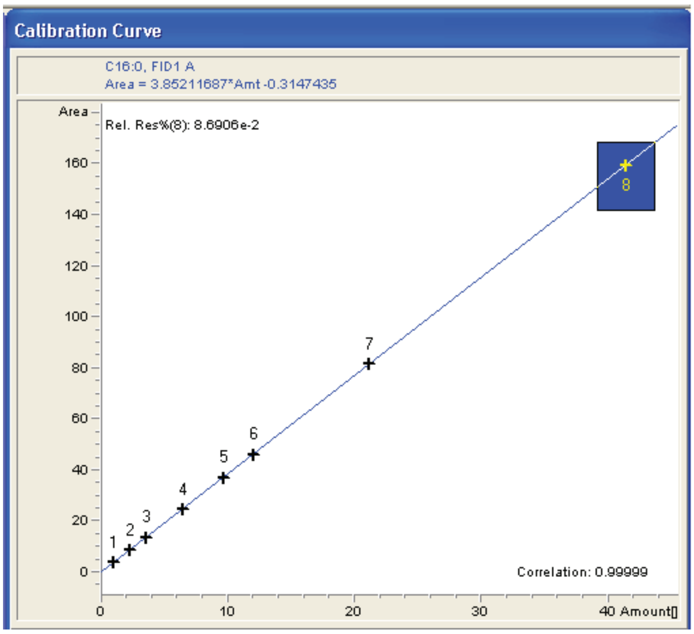
Loss of profit

If commercial jet fuel, a high-quality fuel, fails to meet required purity and other quality tests for use on jet aircraft, it is commonly sold to other ground-based users with less demanding requirements, meaning a loss of profit. With more than \$50 billion (€35 billion) spent on aviation fuel per year, lab and process chemists are faced with a variety of challenges in their quality control process.

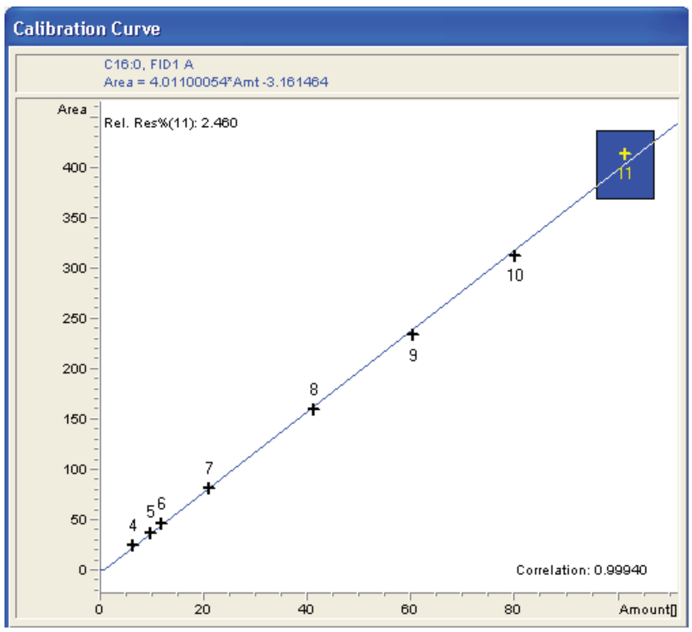
Testing AVTUR to ensure purity and compliance

A reliable and rugged means of measuring FAME content in jet fuels is required to ensure compliance with the 5 mg/kg specification. Multi-dimensional gas chromatography (GC) using Deans switching and refocusing technology supplies such a means, and forms a suitable alternative to existing LC-, GC/GC-, GC/MS- and SPE/GC-techniques for its lower cost, ease of use, robustness and lack of sample pretreatment.

Calibration plot C16:0 1-50 mg/kg



Calibration Plot C16:0 10-100 mg/kg



These figures show calibration plots for 1 – 50 mg/kg and from 10 - 100 mg/kg. Both ranges show correlation better than 0.999 over the complete range

Fuel analysis procedure

A test portion of AVTUR is run neat on a multi-dimensional GC system that accommodates both Deans-switching and refocusing technology. A pre-separation of the sample takes place on a nonpolar first dimension column. After first dimension separation the FAME species of interest are transferred towards a highly polar second dimension column by performing a heart-cut using Deans-switching.

Before final separation, the FAME species are refocused on the first part of the second dimension column by using temperature-based trapping. When the last specified FAME component (C18:0) has eluted from the first dimension column the GC is set towards optimum flow and temperature conditions for the second dimension column. When these conditions have been established, the trapping of the FAME species is stopped, introducing/injecting them onto the second dimension column. There they are separated from each other and the remaining matrix. A flame-ionisation detector (FID) is used for quantification by reference to an external standard of the specified FAME species in a FAME-free AVTUR fuel.

Analysis results

Excellent results were obtained for retention time stability, peak area stability, sensitivity and linear behavior. The standard quantification range of 2-50 mg/kg can be shifted towards a range of 10-150 mg/kg by simply changing injection volume.

Conclusion

These results demonstrate that the newly developed analysis technique based on 2-Dimensional GC is a robust and accurate method for determining trace levels of FAME contamination in aviation turbine fuels, allowing both individual and total FAME to be analysed. The Quantification Range for total FAME is 2-50 mg/kg, complying with DEFSTAN 91-91 specifications for the analysis of FAME in AVTUR, soon to be incorporated into ASTM D1655. ■

For more information:

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