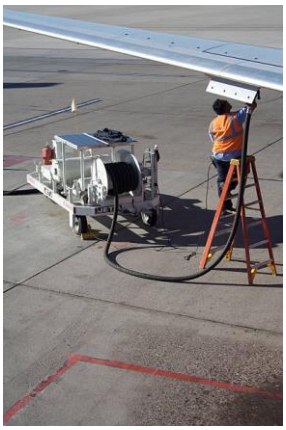
GC analysis of Fame Contamination in Aviation Turbine Fuel (AVTUR)



- Analyze FAME contamination in Jet Fuel at concentration levels <5 mg/kg
- IP 599 compliance
- GC using Heart-cut & refocusing technology
- Measuring range: 2 – 150 mg/kg
- Reliable and rugged method

Keywords: Jet fuel, Biodiesel contamination, FAME, Heart-cut GC analysis, IP 599

Introduction:

Commercial jet fuel is a high-quality fuel, but if it fails to meet this 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 over $50 Billion spent on Aviation fuel per year, lab and process chemists are faced with a variety of challenges in their quality control process.

The introduction of biodiesel into many countries has created a threat to jet fuel quality. It is common for national governments to mandate the use of renewable components in automotive fuels. One of the most common options is to blend Fatty Acid Methyl Ester (FAME) into diesel to produce what is often called 'biodiesel'. Biodiesel is designated like B7 when it contains 7% FAME. Pure FAME is often designated B100.

The introduction of FAME into diesel fuel created some issues with an impact on jet fuel:

- FAME is surface active and tends to stick to metal or glass surfaces. Where supply chains handle both jet fuel and biodiesel this trait creates a risk of cross contamination
- FAME is a non-hydrocarbon fuel component. The jet fuel specification states explicitly that only hydrocarbon components or approved additives are allowed.

This is a serious issue because there have been instances in which jet fuel containing low concentration levels of FAME has inadvertently been supplied to the airport.

Jet Fuel Specification:

The international jet fuel specifications originally had limited the FAME content to less than 5 mg/kg (ppm w/w). In 2018 the specification was raised to 50 mg/kg (ASTM D1655-15 and DEF STAN 91-91 Issue 7 amendment 3).

However, Product Bulletin 106: Guidance on Managing FAME in Jet Fuel (bulletin 75 Update) of the JIG states:

> *Note that despite the relaxation of FAME contamination limits first introduced in ASTM D1655-15 and Def Stan 91-91 Issue 7 Amendment 3,* ***many pipeline owners may still apply the 5 mg/kg limit****. As rapid screening methods can have a lower detection limit of 20 mg/kg, it is not appropriate for use where <5 mg/kg limits exist. The lower detection limit takes into account the known fuel-to-fuel biases unique to this approach that is not reflected in the precision statement. Where FAME testing has been determined to be necessary prior to issuance of either Def Stan 91-91 Issue 7 Amendment 3 or ASTM D1655-15, it will still be required to be conducted by IP585, IP590 or IP599 for supply into systems requiring a less than 5 mg/kg limit, especially when considering incoming fuel may only be released up to the new 50 mg/kg specification limit.*

The most reliable and robust way to measure the FAME content in aviation fuels is the multi-dimensional GC using Deans switching and refocus technology as described in method IP 599. This application, as developed by AC Analytical Controls, can meet the requirements for measuring FAME concentration at the maximum 50 mg / kg specification level, but is also able to measure FAME contamination at a level of 5 mg/kg.

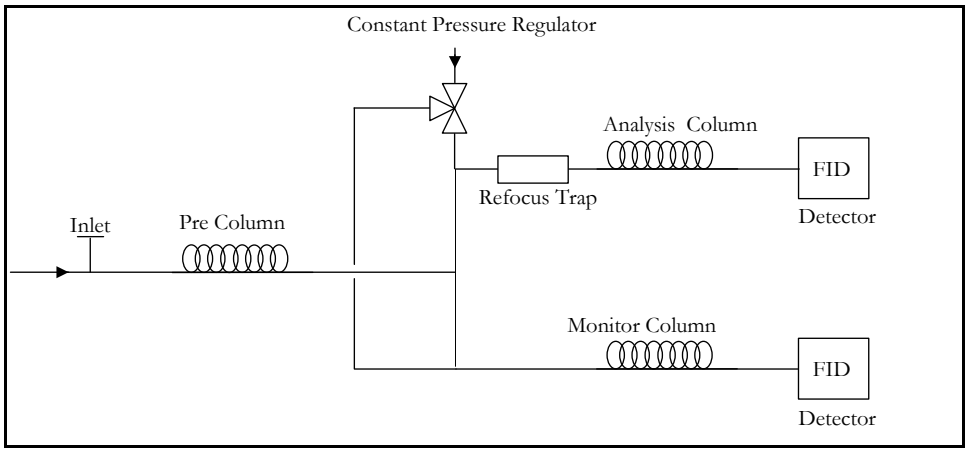
The FAME components determined using this multi-dimensional GC heart-cut method are listed in table below. These components have been specifically chosen as they typically make up greater than 95% of the composition of the major biofuel vegetable oil feeds currently used in biodiesel blends with conventional mineral diesel.

FAME	Molecular formula	Symbol used
methyl hexadecanoate (methyl palmitate)	C17H34O2	C16:0
methyl octadecanoate (methyl stearate)	C19H38O2	C18:0
methyl octadecenoate (methyl oleate)	C19H36O2	C18:1
methyl octadecadienoate (linoleate)	C19H34O2	C18:2
methyl octadecatrienoate (linolenate)	C19H32O2	C18:3

ANALYSIS DESCRIPTION

A test portion of AVTUR is run neat on a multi-dimensional gas-chromatographic system that accommodates both Deans-switching and refocusing technology. A pre-separation of the sample takes place on a non-polar 1st dimension column. After 1st dimension separation the FAME species of interest are transferred towards a highly polar 2nd dimension column by performing a heart-cut using Deans-switching.

Before final separation the FAME species are refocused on the first part of the 2nd dimension column by using temperature-based trapping. When the last specified FAME component (C18:0) has eluted from the pre-column the GC is set towards optimum flow and temperature conditions for the 2nd dimension column. When these conditions have been established the trapping of the FAME species is stopped, introducing/injecting them onto the 2nd dimension column where they can be separated from each other and the remaining matrix. A flame-ionization detector (FID) is used for identification and 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. Table 1 shows the Retention Time stability, with a maximum variation of 0.02% in Retention time, identification of FAME components is clearly unambiguous.

Table 1: retention time stability of a "real life sample"

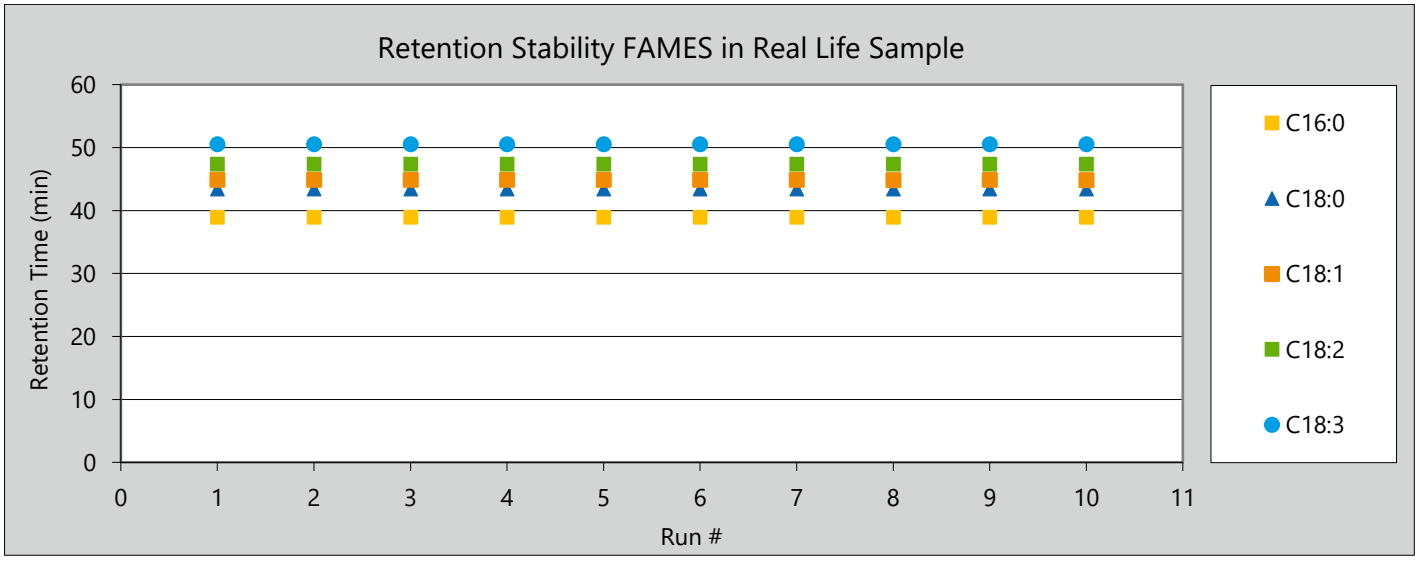
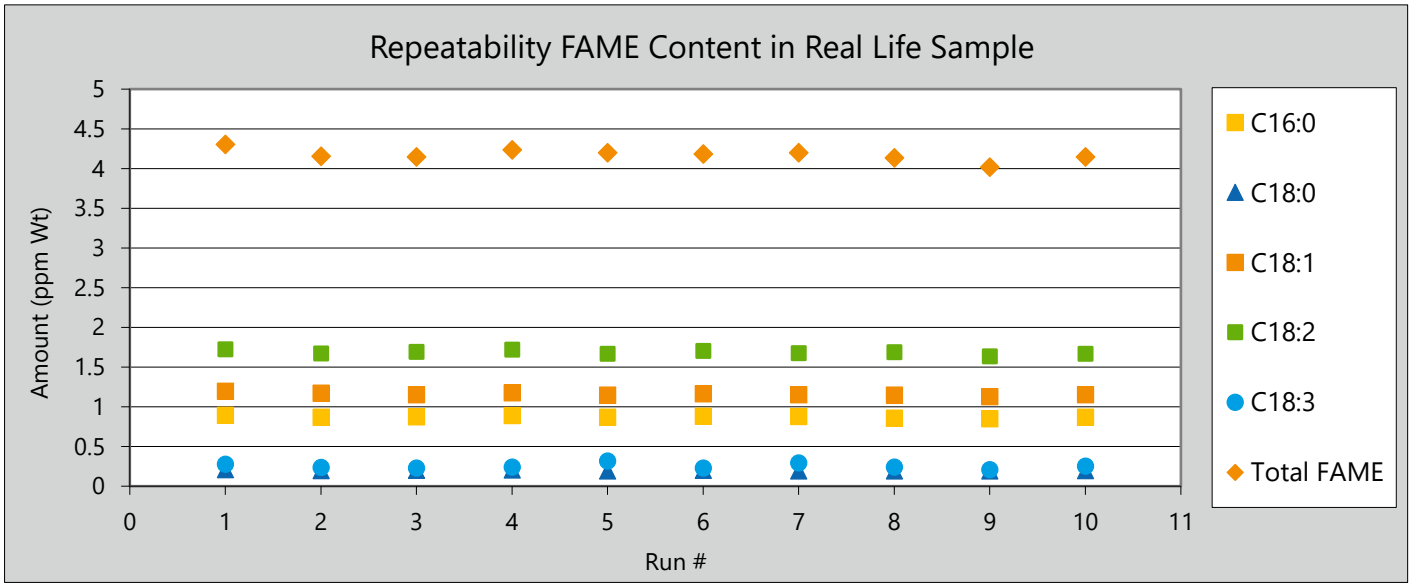


Table 2 shows data for a representative Jet fuel sample. Even at the very low level of 6.6 ppm w/w FAME for this particular sample, the repeatability for the method is only 2.8% (n=10). Even C18.0, found at a concentration of 0.75 ppm w/w has a more than acceptable repeatability at 3.4% RSD.

Table 2: repeatability for 10 runs of a "real life sample"



The method developed has sensitivity of better than 0.5ppm w/w per FAME component or 2 mg/kg total FAME. Figure 1a & 1b show a chromatograms of reference samples with respectively 5.3 and 99.5 mg/kg FAME jet fuel.

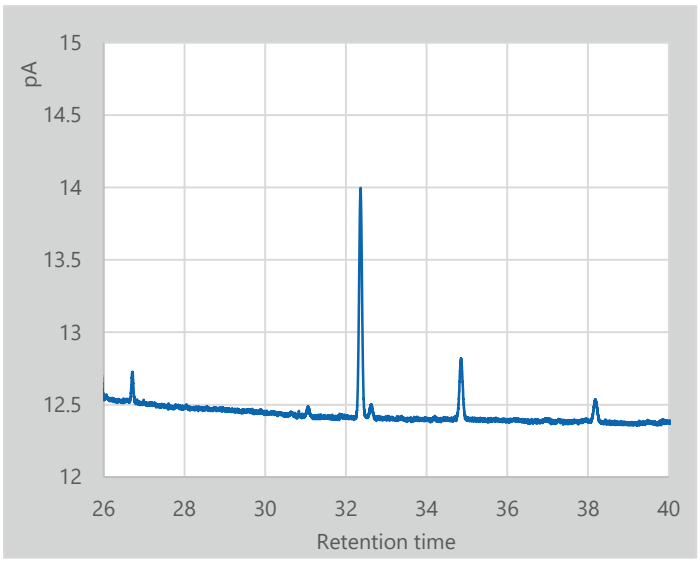


Fig 1a: Reference sample with 5.3 mg/kg FAME

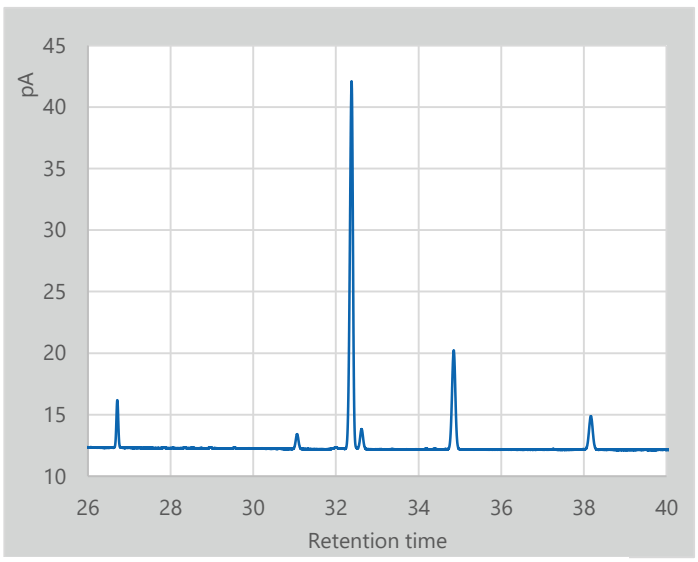


Fig 1b: Reference sample with 99.5 mg/kg FAME

The Linear Dynamic Range for the method was tested for C16:0 in two concentration ranges. The calibration curves for 1 – 50 mg/kg and from 10 - 100 mg/kg ranges show a correlation better than 0.999 over the complete range.

Conclusion

Above results demonstrate that AC Analytical Controls “FAME in AVTUR” analyzer based on the heart-cut technology is a powerful, robust and accurate method for determining trace levels FAME contamination in aviation turbine fuels in accordance to IP 599.

It allows both individual and total FAME to be analyzed. The Quantification Range for total FAME is 2-150 mg/kg (based on two methods), which is sufficient to meet the 50 mg/kg lower quantification limits specified in DEFSTAN 91-91 and ASTM D1655 as well as the 5 mg/kg level that still might be required from time to time.

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