Detection of FAME in aviation turbine fuel: Challenges and new approaches

Introduction

In efforts to reduce greenhouse emissions, biofuels have seen increased use in most parts of the world. In particular biodiesel, i.e. fatty acid methyl esters (FAME), is extensively used as a blending component in diesel, typically in the range from 5-20 vol%. The use of biodiesel has increased the risk for cross-contamination of other fuel types present in the same fuel distribution system, most notably aviation turbine fuel. In pipeline systems, the risk of cross contamination of the jet fuel is reduced by running gasoline fractions between diesel and jet fuel or resorting to all aviation fuel pipelines. For fuel which is transported via truck, barge, or railcars, either dedicated equipment or cumbersome cleaning procedures are used to reduce the risk of contamination of aviation turbine fuel.

The presence of FAME in aviation turbine fuel increases the ability of the fuel to absorb water and leads to degraded low temperature properties and is suspected to increase the probability of clogging of fuel filters.

Because of these severe effects of FAME contamination on the aviation fuel's quality, the concentration of FAME in aviation turbine fuel is limited to 50 mg/kg by international specifications like ASTM D1655.

GC/MS (IP585) and HPLC (IP590)

The detection of trace levels of FAME in aviation turbine fuel represents a challenge to most analytical techniques due to the complicated matrix of the fuel itself, potential interference of jet fuel additives and the variations of ester chain length distribution from different sources. To meet this challenge, the industry has developed various standards based on techniques like GC/MS (IP585) and HPLC (IP590). While these techniques provide excellent detection limits and low interference due to their high degree of molecular selectivity, they are time consuming, lab intensive techniques requiring skilled operators and well-equipped laboratories. These methods are typically used for fuel certification by refinery laboratories, but due to their complexity are not well suited for screening jet fuel along the fuel distribution system.

Infrared (IR) spectroscopy

In contrast to these complex methods, Infrared (IR) spectroscopy offers a fast, easy to use and portable solution to screen fuels for additives and contaminations, anywhere along the fuel distribution system. IR spectroscopy makes use of the vibrational fingerprints of molecules as different molecules absorb in different regions of the infrared spectrum. While IR spectroscopy is extensively used for higher concentrations (i.e. FAME measurement in diesel fuel in % range in ASTM D7806), the use for trace level detection is typically limited by matrix effects and interferences from molecules with similar structural motifs as the target compound.

ASTM D7797

One way to mitigate the effect of the sample matrix is to employ a sample preparation step including solid phase extraction (SPE) to isolate the compounds of interest or to remove interferences. In the case of FAME in a jet fuel, the simplest approach is to measure the difference between the unperturbed fuel and a portion where all polar compounds (including FAME) have been removed by an SPE procedure. In ASTM D7797 (or IP583), an FTIR is used to measure in IR absorption of the FAME's carbonyl group before and after the SPE step and the signal is used to quantify the FAME concentration.

This simple approach rests on the assumption that all polar components reflect the target contaminant. The fact that even ASTM D1655 *Standard Specification for Aviation Turbine Fuels* defines a limit on acid number clearly demonstrates the presence of acidic compounds (various oxidation products and their pre-cursors) in jet fuels. Typically, the acidic compounds tend to increase as the fuel is exposed to air during storage and transportation but also depends on the refinery process used to produce the fuel.

Besides the complicated matrix, a number of (usually proprietary) additives are added to the fuel to reach the desired performance. These additives include antioxidants, anti-static additives, anti-corrosion, fuel icing inhibitors etc. If these additional components are not removed by the sample SPE clean up, both the additives as well as the oxidation products may produce interference in the spectral range used to detect FAME.

eralytics dual SPE method with era**jet FAME**

Based on multiple requests by international customers for a solution to this problem, in 2023 eralytics developed an innovative dual SPE measurement procedure as well as the state-of-the-art non-dispersive IR spectrometer era**jet FAME** for a more accurate detection of traces of FAME in aviation turbine fuel. eralytics dual SPE is a method for a more accurate, faster, and cheaper detection of FAME in aviation turbine fuel.

Dual SPE procedure

In this procedure, the sample is first passed through one sorbent selected to retain polar compounds with a higher polarity than FAME. Then the IR absorbance of the transmitted sample is measured in the carbonyl region. The second part of the procedure involves passing the jet fuel sample though a sorbent retaining polar compounds with a polarity less than that of FAME, followed by the IR measurement. The fully automated dual SPE procedure defines a polarity window, thus only allowing signals from compounds of the desired polarity. The IR measurement in addition provides spectral selectivity to distinguish compounds of similar polarity but with different IR signatures.

The use of two different sorbents allows to define a polarity window, here indicted in red, removing potential interferences from various compounds present in the neat jet fuel or in the form of additives. A measurement with ASTM D7797 would in addition measure the contaminants indicated by the back box.

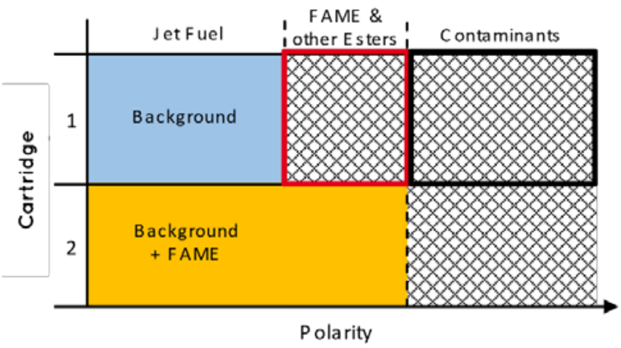

Figure 1a: Principle of the dual SPE procedure and its effect on various molecular types.

era**jet FAME:** FAME in jet-fuel tester

To minimize measurement time, instrument cost, sample volume and complexity, eralytics developed the portable era**jet FAME**, a state-of-the-art non-dispersive IR spectrometer. The entire measurement, including the dual SPE procedure and the IR measurement takes only 5 minutes and requires less than 25 ml of fuel, still offering mg/kg sensitivity.

The two different SPE cartridges are attached to a common inlet tube of the era**jet FAME**, which is immersed into the sample to be tested. The instrument then passes defined volumes of sample through each cartridge before delivering it to the IR measurement cell.

Evaluation

To evaluate the performance of era**jet FAME**, a set of certified reference materials (CRM) for ASTM D7797 as well as commercial fuels were investigated. The CRMs and the commercial jet fuel were measured as received. In addition, the commercial jet fuel was spiked with FAME to obtain concentrations above and below the limit defined by international aviation specifications. The results are summarized in table 1 and the results for the CRMs are additionally presented in Figure 2.

Type	Density @15°C g/cm^3	Reference value (mg/kg)	ERAJET FAME (mg/kg)	Deviation (mg/kg)	ASTM D7797 Reproducibility (mg/kg)
D7797 CRM	0.8169	30	29.3	-0.7	6.5
D7797 CRM	0.8169	75	71.9	-3.1	8.7
D7797 CRM	0.8169	100	97.4	-2.6	9.9
D7797 CRM	0.8169	100	98.2	-1.8	9.9
D7797 CRM	0.8169	125	121.9	-3.1	11.2
D7797 CRM	0.8169	150	145.1	-4.9	12.4
A1	0.7980	0	2.7	2.7	5.0
A1	0.7980	32	34.1	2.1	6.6
A1	0.7980	94	97.4	3.4	9.7

Table 1: FAME in mg/kg for the investigated samples. The sample density was determined with eralytics ERADENS X density meter according to ASTM D4052. The commercial jet fuel was obtained directly at a local refinery. The sample was spiked with FAME to different concentrations.

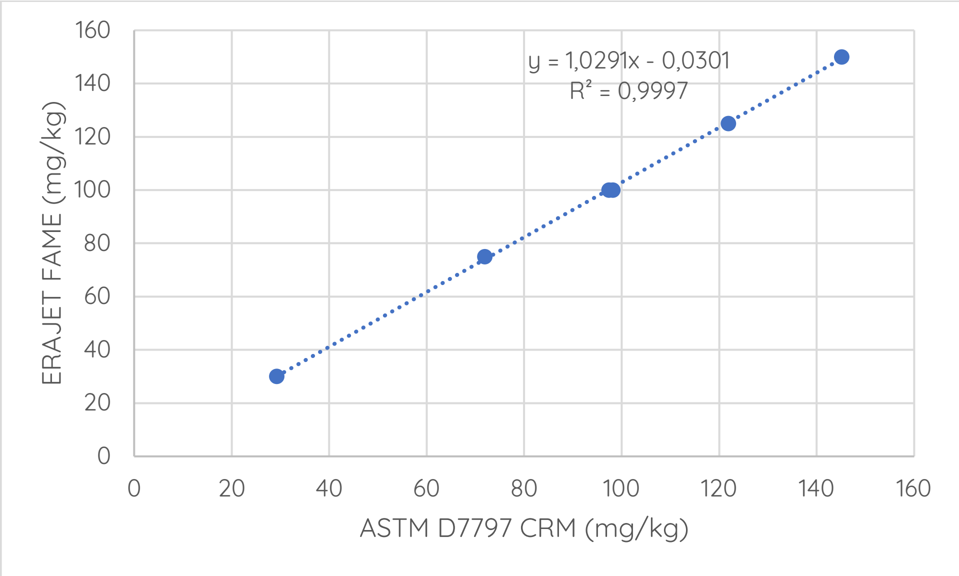

Figure 2. Plot of the era**jet FAME** results vs. ASTM D7797 CRM concentrations. The linear fit to the results shows an excellent correlation and linearity of the investigated method.

Conclusion

Due to the fact that the presence of FAME in aviation turbine fuel increases the probability of clogging of fuel filters, the concentration of FAME in aviation turbine fuel is limited to 50 mg/kg by international specifications like ASTM D1655.

In addition to sophisticated laboratory test methods, there is a strong demand for the fast, but still highly accurate testing of such traces of FAME anywhere along the fuel distribution system. The method of choice is Infrared (IR) spectroscopy, as it is fast, easy to use and sufficiently rugged to be used directly in the field. With the innovative, automated dual SPE sample cleanup, era**jet FAME** is able to deliver highly accurate results of complicated samples, even in the field.

A direct comparison testing of this dual SPE method with ASTM D7797 shows that all samples were measured well within the reproducibility of ASTM D7797. Next to this outstanding method accuracy, eralytics portable era**jet FAME** needs less than 5 minutes for this test and requires only 25 mL of sample.