Determination of FAMEs in AVTUR with the Agilent 1290 Infinity ELSD

Application Note

Energy & Chemicals

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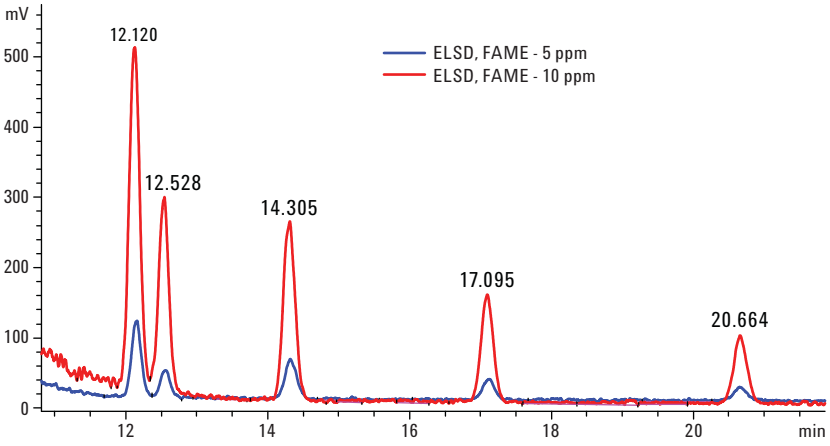
Abstract

This Application Note demonstrates the use of the Agilent 1290 Infinity ESLD for the determination of fatty acid methyl esters (FAMEs) in aviation turbine fuel (AVTUR). The separation of the FAMEs from hydrocarbon compounds in kerosene was done under normal phase conditions. For the detection of FAMEs with the ELSD, it was essential to work at or below ambient temperature enabled by the 1290 Infinity ELSD. A calibration, limits of quantitation (LOQ), limits of detection (LOD), and a statistical evaluation for a standard collection of FAMEs is shown.



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Introduction

Because crude oil is a nonrenewable resource and fossil fuels cause a large portion of the carbon dioxide enrichment in the atmosphere and climatic change, they are partially exchanged with renewable biodiesel compounds. These compounds are typically fatty acid methyl esters (FAMEs) and are added up to 10 % to common automotive fuels. But, they cannot be added to more sophisticated fuels such as aviation turbine fuels (AVTUR). Unfortunately, pipelines are typically used for both kinds of fuels and FAMEs have the ability to stick to the inner surface of pipelines and cause carryover into other types of fuels where they are not tolerable.

There are a large number of country-specific regulations for jet fuels, which can be found in a summary given by Exxon Mobile[1]. The most stringent regulations are given by the ASTM D1655 and Defense Standard 91-91[2,3]. Related to that document, the current maximum tolerable amount of FAMEs in jet fuel is 5 ppm. To guaranty a disruption-free jet fuel supply, a Joint Industry Group (JIP) is examining the influence of a higher concentration of FAMEs on piston- and turbine-driven aircraft engines, showing a possible contamination level of up to 30 ppm[4]. The JIP is also attempting to bring the possible FAMEs limit up to 100 ppm due to the fact that AVTUR batches out of multiproduct systems could be accessible to the supply chain and measurement for quality control causes less effort[5].

For the measurement of FAMEs under the current specifications, a combination of normal phase HPLC and ELSD is possible to achieve the requirements. The boiling point of FAMEs are typically in the same range as the other components in AVTUR, therefore, the ELSD must be able to evaporate the compounds near the ambient temperature. This is shown by using the Agilent 1290 Infinity ESLD for the determination of FAMEs in AVTUR.

Experimental

Equipment

Agilent 1260 Infinity LC System

- Agilent 1260 Infinity Binary Pump (G1312B) equipped with seals for normal phase chromatography (p/n 0905-1420) and with external degasser (G1322A)
- Agilent 1260 Infinity Standard Autosampler (G1329B) with Sample Thermostat (G1330B)
- Agilent 1260 Infinity Thermostatted Column Compartment (G1316B)
- Agilent 1260 Infinity Diode Array Detector (G4212B)
- Agilent 1290 Infinity ESLD (G4261B)

Software

- Agilent OpenLAB CDS ChemStation Edition for LC and LC/MS systems, Rev. C.01.04

Column

- Agilent ZORBAX RxSil, 4.6 × 250 mm, 5 µm (p/n 880975-901)

Chemicals

Chromasolv heptane, ethyl acetate, octyldecane, and kerosene (AVTUR) were purchased from Sigma-Aldrich, Germany.

Standards

F.A.M.E., Mix GLC-10 standard was purchased from Sigma-Aldrich, Germany.

This standard contains 100 mg neat FAME. The following fatty acid methyl esters were included in equal amounts: methyl palmitate (C16:0), methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), and methyl linolenate (C18:3).

Sample preparation

The neat FAME standard was dissolved in 1 mL octyldecane and a 1:100 dilution in octyldecane was used as stock solution. The stock solution was diluted 1:10 in kerosene, the resulting solution contains 20 ppm of each FAME. For the calibration, a dilution series of 20, 10, 5, and 2.5 ppm in kerosene was used. These samples were used directly for injection without further purification.

HPLC method	
Solvent	Heptane + 0.25 % ethyl acetate
Flow rate	1.0 mL/min
Elution conditions	isocratic
Stop time	25 minutes
Injection volume	40 µL
Needle wash	In vial with heptane
Column temperature	20 °C
ELSD method	
Nebulizer temperature	75 °C
Evaporation temperature	25 °C
Gas flow	1.15 SLM
Detector gain	10
Smoothing	2 seconds
Data rate	10 Hz

Results and Discussion

FAMEs typically have their boiling points in the range of 130–190 °C. The hydrocarbon fraction used for AVTUR fuel has a boiling range of 50–300 °C. Therefore, the detection of FAMEs with an ELSD requires an instrument which must be able to evaporate the compounds near the ambient temperature to avoid the loss of the low-boiling FAMEs like methyl palmitate (C16:0), with its boiling point at 135 °C. Due to the overlapping boiling point of FAMEs and the hydrocarbon fraction used for AVTUR, a careful optimization of the ELSD method is required to maximize sensitivity performance. For instance, the nebulization temperature has strong influence on the total amount of material (FAMEs and AVTUR) that will become accessible for the evaporation process with increasing temperature. Conversely, the evaporation temperature has a crucial influence on the detection limits of FAMEs and must be near the ambient temperature to avoid the loss of early boiling FAMEs. Unfortunately, it must be high enough to evaporate AVTUR hydrocarbons as much as possible. Otherwise, they tend to produce huge injection peaks which overlay the early eluting FAMEs. An evaporation temperature of 25 °C was the optimum, because C16:0 starts to lose sensitivity significantly above 26 °C. With the ELSD settings mentioned in the experimental part, it was possible to have a reliable range for quantification starting below 5 ppm with typical LOQs at approximately 2.5 ppm (Figure 1 shows the chromatogram for 5 ppm and 10 ppm).

For the calibration of instruments to measure FAMEs quantitatively, there are a large number of standards available. Typically, those standards contain five FAME compounds in equal amounts. The standard used in this Application Note is one of the more commonly used because, the inherent FAMEs (see experimental part) are more or less ubiquitary. Individual calibration curves from 2.5 ppm to 20 ppm were generated in a FAME-free AVTUR for the five FAME compounds inherent in the standard (Figure 2). Typically, the LOQ was approximately 2 ppm with a signal-to-noise (S/N) ratio of 8–25. Therefore, 2.5 ppm was chosen as the lowest calibration point.

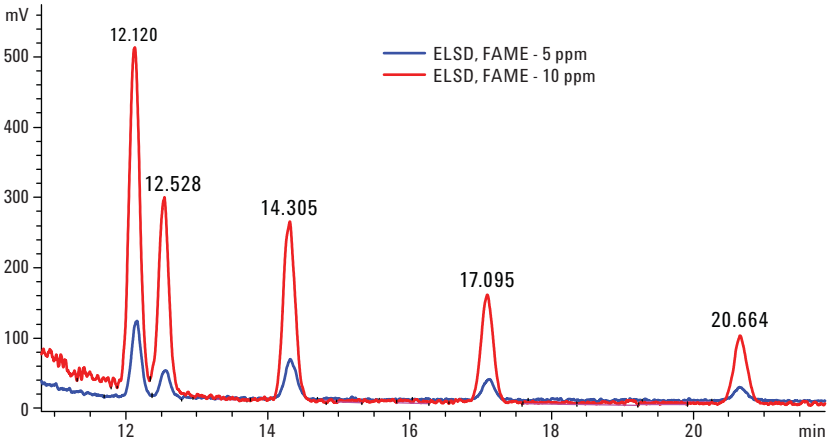

Figure 1. ELSD signals for FAME at a concentrations of 5 and 10 ppm.

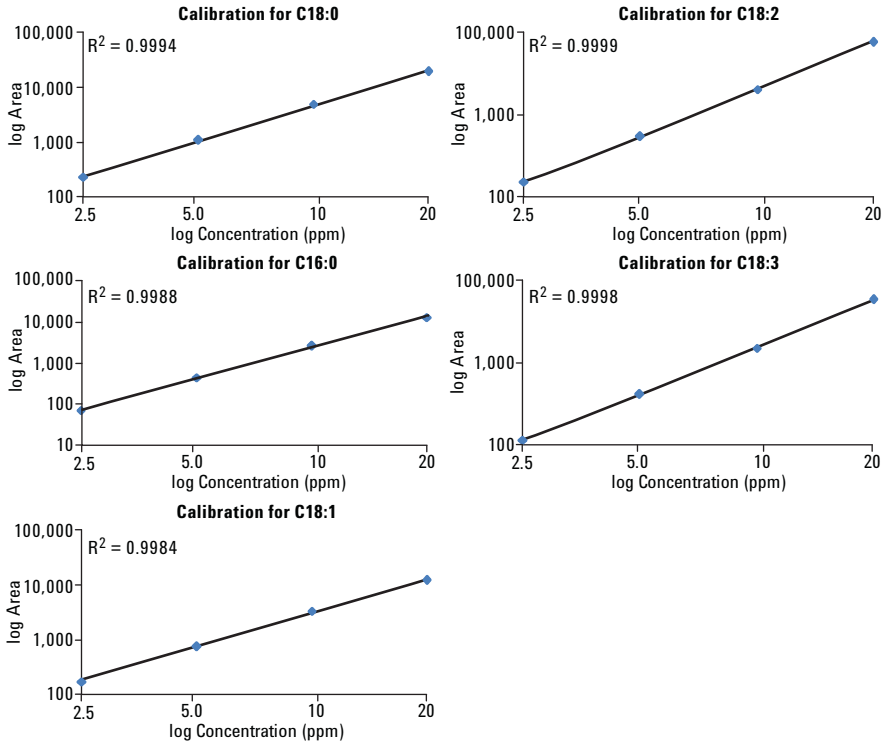

Figure 2. Calibration curves from 2.5 ppm to 20 ppm for the five FAME compounds inherent in the standard mixture (curves are displayed in double logarithmic scale).

The individual LODs were calculated to an S/N ratio of 3, they were approximately 1 ppm or less (Table 1). After injecting the highest calibration level (20 ppm), a blank AVTUR was injected, and no carryover was observed in this blank injection. A statistical evaluation of the retention time and peak area showed RSD values of less than 0.2 %, and typically less than 2 %, respectively.

Table 1. Statistical evaluation of the retention time and peak area (10 ppm, n = 10). The LOQ and R^2 value was taken from the calibration. The LOD was calculated from the individual LOQ to a S/N ratio of 3.

Compound	Average retention time (min)	Retention time RSD (%)	Area RSD (%)	LOD	LOQ	R^2
C18:0	12.075	0.16	2.31	0.50	1.70	0.9994
C16:0	12.482	0.14	3.55	0.75	2.30	0.9988
C18:1	14.244	0.13	1.26	0.55	1.80	0.9984
C18:2	17.029	0.16	1.98	0.65	2.20	0.9999
C18:3	20.593	0.21	1.27	1.01	3.30	0.9998

Conclusion

This Application Note demonstrates the use of an Agilent 1260 Infinity HPLC for the separation of FAMEs under normal phase conditions in combination with the Agilent 1290 Infinity ELSD for their detection. The capability of the 1290 Infinity ELSD to evaporate volatile compounds at, or below, ambient temperature, is essential for the detection of the volatile FAMEs in AVTUR matrix. The achieved LOQs and LODs of the individual FAMEs cope with the currently required detection limits. The obtained calibration curves show excellent linearity, and RSD values of retention time are typically better than 0.2 % and RSD values of peak areas are typically better than 2 %.

References

1. Exxon Mobile Aviation, World Jet Fuel Specifications, Edition **2005**.
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3. Ministry of Defense, Defense Standard 91-91, Issue 6 Publication Date 8 April **2008**, Turbine Fuel, Aviation Kerosine Type, Jet A-1, NATO Code: F-35, Joint Service Designation: AVTUR
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5. JIG – Joint Interest Group – Product Quality, FAME Update, Bulletin No. 61, April **2013**.

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