Application Note # CA-270358

Determination of Total FAME and Linolenic Acid Methyl Esters in Biodiesel According to EN-14103

Introduction

In order for biodiesel to be used as a motor fuel or blended with petroleum diesel, it must conform to standard specifications (ASTM D 6751 or EN-14214). There are standard GC methods in use today to determine if biodiesel conforms to the standard specifications, one of which is EN-14103, used to determine the ester and linoleic acid methyl ester content. Other methods include EN-14105 / ASTM D 6584 (free and total glycerine and mono, di and triglyceride content) and EN-14110 (residual methanol). Bruker has designed GC solutions for each of these standard methods. This paper describes work conducted on the Bruker 450 gas chromatograph to analyze biodiesel (B-100) in accordance with EN-14103. EN-14103 is used to verify that the ester content of Fatty Acid Methyl Esters (FAME) is greater than 90 % (m/m) and that the linolenic acid content is between 1 % (m/m) and 15 % (m/m) consistent with the EN-14214 specifications. This method is suitable for FAME which contains methyl esters between C14 and C24.

Instrumentation

Bruker 450-GC

- Injector: Split / splitless 1177, full EFC control
- Detector: FID, full EFC control
- Automatic Liquid Sampler; Model 8410 Software
- GC control and data handling: Bruker Galaxie™ Software

Materials and Reagents

Column

- Bruker Select™ Biodiesel for FAME, 30 m x 0.32 mm x 0.25 µm, part no. CP-9080

Sample Preparation

Accurately weigh approximately 250 mg of sample in a 10 mL vial, then add 5 mL of methyl heptadecanoate solution (10 mg / mL) using a pipette.
Injection volume: 1 µL

Conditions

Injector: 250 °C, split 100 mL / min
Detector: 250 °C, FID
Carrier gas: Helium, 12 psi (83 kPa)
Oven: 210 °C isothermal

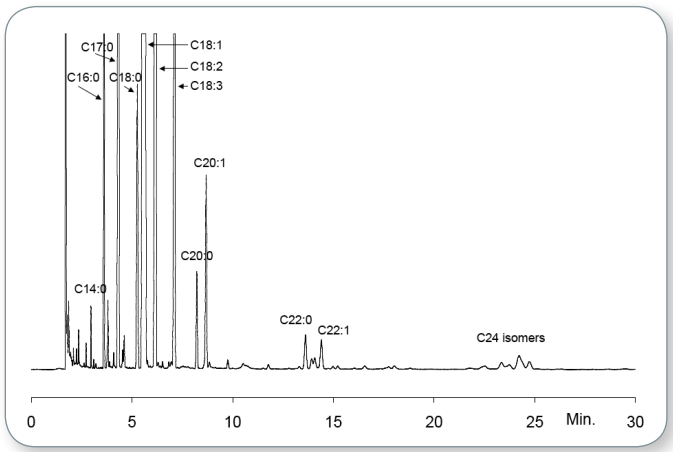

Figure 1: Biodiesel chromatogram.

Peak Identification:

C16:0	Palmitic acid
C16:1	Palmitoleic acid
C17:0	Heptadecanoic acid (int. st.)
C18:0	Stearic acid
C18:1	Oleic acid
C18:2	Linoleic acid
C18:3	Linolenic acid
C20:0	Arachidic acid
C20:1	Gadoleic acid
C22:0	Behenic acid
C22:1	Erucic acid
C24:0	Lignoceric acid
C24:1	Nervonic acid

Results and Discussion

When the conditions outlined above are applied, a chromatogram is obtained, as in Figure 1.

Calculations
The ester content (C), expressed as a mass fraction in percent, is calculated using the following formula:

$$C = \frac{(\Sigma A) - AEI}{AEI} \times \frac{CEI \times VEI}{m} \times 100\ \%$$

ΣA is the total peak area from the FAME C14:0 to C24:1
AEI is the peak area of methylheptadecanoate
CEI is the concentration, in mg / mL, of the methylheptadecanoate solution
VEI is the volume, in mL, of the methylheptadecanoate solution
m is the mass, in mgr, of the sample

The linolenic acid methyl ester content (L), expressed as a mass fraction in percent, is calculated using the following formula:

$$L = \frac{AL}{(\Sigma A) - AEI} \times 100\ \%$$

ΣA is the total peak area from the FAME C14:0 to C24:1
AEI is the peak area of methylheptadecanoate
AL is the peak area of linolenic acid methyl ester

Results

The biodiesel sample tested was shown to be in accordance with the requirements stated in EN-14214 (the method requirements: FAME content > 96.5 % (m/m) and linolenic acid content < 12 % (m/m)). In order to verify the integrity of the system, repeatability was determined. One sample is analyzed 15 times. See Table 2 and Figure 2. A relative standard deviation of 0.21 % was achieved. Figure 2 shows the mass % results of the subsequent injections and the absolute difference obtained compared to specification limits. In the method, the absolute difference between two test results must be:

FAME	> 1.6 % (m/m)
Linolenic acid	> 0.1 % (m/m)

All results obtained are within the limits specified in the method.

Conclusion

The data presented here clearly shows the applicability of the Bruker 450-GC system for the analysis of biodiesel as per the EN-14103 standard method, and does so in a repeatable manner. The biodiesel sample tested in this application note fulfilled the requirements stated in EN-14214.

Table 1: Analysis results of biodiesel.

	Area (µV.Min)	Quantity (mass %)
FAME content	103139	96.6
Linolenic acid	7599.2	7.1

Table 2: Repeatability results.

	FAME (mass %)	Linolenic acid (mass %)
Average	96.4	7.1
Stand. Dev.	0.20	0.015
Rel St.Dev. (%)	0.21	0.21

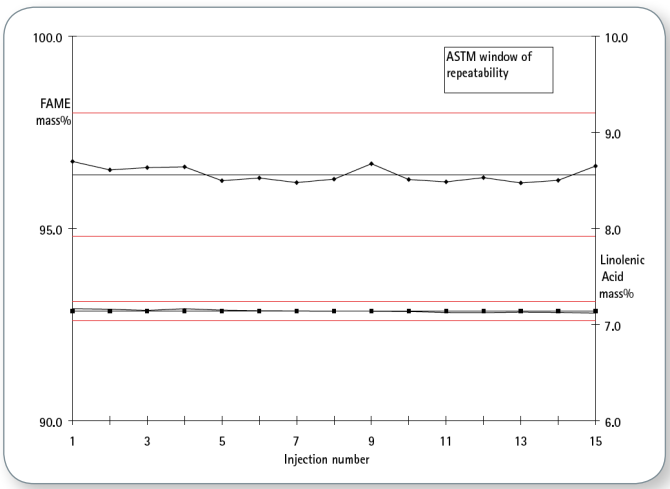

Figure 2: Repeatability figures. Red lines indicate the maximum and minimum allowed variation limits specified in the method.

References

EN-14103. Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of ester and linolenic acid methyl ester contents.

EN-14214:2003. Automotive fuels – Fatty Acid Methyl Esters (FAME) for diesel engines – requirements and test methods.

Keywords
Biodiesel
EN-14103
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Instrumentation & Software
Bruker 450 Gas Chromatograph
Bruker Galaxie™ Software

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