Determination of Methanol Content in Biodiesel Using Agilent Select Biodiesel for Methanol with Headspace Sampling to EN-14110

Application Note

Energy and Fuels

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Introduction

The popularity and interest in biodiesel is growing significantly in many areas of the world and has become a commonly sought after alternative fuel source for use with diesel engines. Biodiesel is produced from vegetable oils or animal fats through transesterification using methanol to yield fatty acid methyl esters (FAMEs) and glycerine. The yield, pure FAME (once the glycerine and the residual methanol have been recovered/removed), is called B-100.

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). GC methods determine whether biodiesel conforms to the standard specifications. One of these methods, EN-14110, is used to determine the methanol content. EN-14110 is applicable for a concentration range from 0.01 to 0.5% (m/m) methanol[a].

a The method is not applicable to mixtures of FAME that contain other low boiling components.

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Materials and Methods

Calibration solutions

Solution A	0.5 % (m/m) methanol in FAME
Solution B	0.1 % (m/m) methanol in FAME
Solution C	0.01 % (m/m) methanol in FAME

A 1 mL aliquot was accurately weighed, transferred into a 20 mL vial and then immediately capped.

Conditions

Sample	FAME mix with methanol content <0.001%
Column	Agilent Select Biodiesel for Methanol, 0.32 mm × 30 m, 3.0 µm (p/n CP9083)
Instrument	Agilent GC
Software	Agilent Chromatography Data Station
Headspace sampler	QHSS-40, sample loop mode (QUMA Elektronik & Analytik GmbH)
Sample loop	1 mL
Vial/heating	80 °C
Equilibrium time	45 min
Injection volume	1 µL
Injector	Split/splitless 1177, full EFC control, 250 °C, split 100 mL/min
Split rate	50:1
Detector	275 °C, FID
Oven	80 °C (0.5 min isothermal) at 20 °C/min to 160 °C (2 min)
Carrier gas	2.0 mL/min constant flow, helium

Results and Discussion

All three calibration solutions were analyzed twice and a calibration curve was obtained. Figure 1 is an overlay of the methanol peaks of the different calibration solutions. The calibration curve (Figure 2) shows excellent correlation with the method.

The correlation coefficient should be >0.95. In this case, the correlation coefficient was determined as 0.9998. A typical chromatogram of a biodiesel sample is shown in Figure 3.

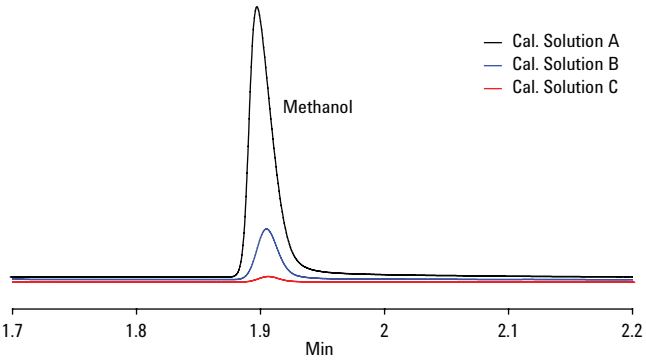

Figure 1. Overlay traces of calibration solutions obtained by gas chromatography using an Agilent Select Biodiesel for Methanol column.

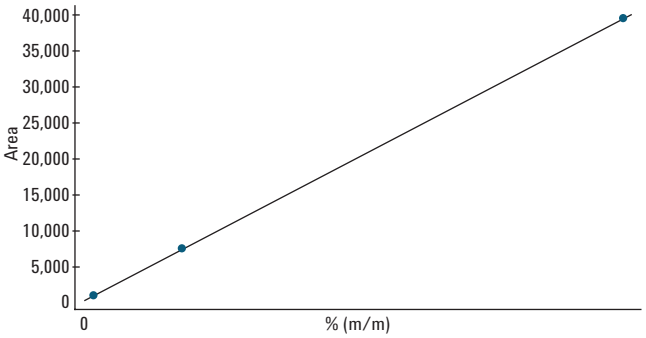

Figure 2 Calibration curve produced by an Agilent Select Biodiesel for Methanol column.

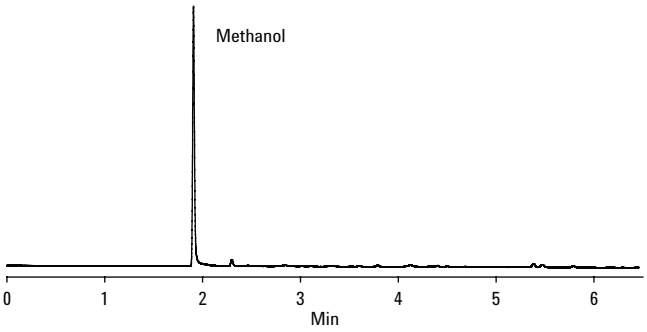

Figure 3. Typical headspace chromatogram for biodiesel produced by an Agilent Select Biodiesel for Methanol column.

Since biodiesel does not generally contain volatile components, other than methanol, identification and quantification is quite straightforward. Repeatability data are shown in Table 1 and Figure 4.

The methanol content of the biodiesel was 0.038% (m/m), thus meeting the specifications set in EN-14214, (methanol content <0.2 %). Furthermore, the repeatability figures indicated that the system was properly optimized for the analysis, as seen in Figure 4, where the analyses trend line is well within the repeatability window according to the EN-14110 method. In Figure 4, this is visualized by adding the average line and the window of repeatability set by the EN-14110 method.

Table 1. Repeatability Results

Parameter	Methanol (mass %)
N	15
Average	0.038
Standard deviation	0.0007
RSD (%)	1.96

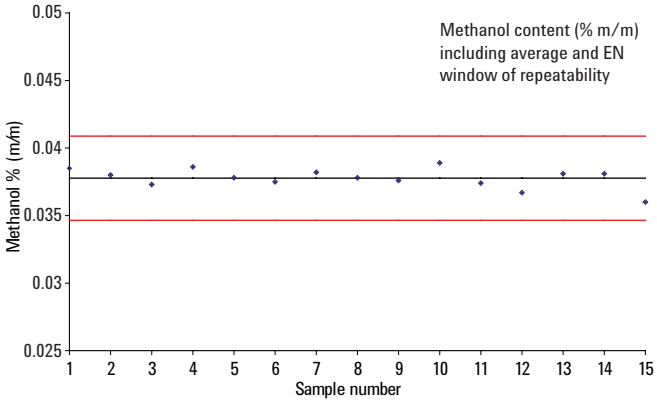

Figure 4. Repeatability values are within the specification boundaries established in EN-14214, as indicated by the red lines in the chart.

Conclusion

The GC headspace system (Agilent GC, QUMA Headspace Sampler and Agilent Select Biodiesel for Methanol column) was well suited for the determination of methanol content in biodiesel according to EN-14110, and the biodiesel tested met the specifications on methanol content according to EN-14214.

References

1. EN-14110 Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – determination of methanol content.
2. EN-14214 Automotive fuels – Fatty Acids Methyl Esters (FAME) for diesel engines – requirements and test methods

For More Information

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