Determination of Methanol Content in Biodiesel using Gas Chromatography with Headspace Sampling According to EN-14110

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Introduction

The popularity and interest in biodiesel is significantly growing 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 via transesterification using methanol to yield Fatty Acid Methyl Esters (FAME) and glycerine. The yield, pure FAME (once the glycerine and the residual methanol has been recovered/removed) is called B-100. 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 GC methods in use today to 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 % (m/m) to 0.5 % (m/m) methanol*.

Instrumentation

Varian 430-GC

- Injector: Split / splitless 1177, full EFC control
- Detector: FID, full EFC control

Headspace sampler

- QUMA, QHSS-40, sample loop mode

GC control and data handling software

- Varian Galaxie™ Chromatography Data System

Materials and Reagents

Column

- Varian Select™ Biodiesel for Methanol, 30 m x 0.32 mm x 3.0 µm, CP-9083
- Fatty Acid Methyl Ester mixture (FAME) with a methanol content of <0.001 %

Sample Preparation

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, and transferred into a 20 mL vial and then immediately capped.

Sample

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

Conditions

GC conditions

- Injector: 250 °C,
- Split rate: 50:1
- Detector: 275 °C, FID
- Oven: 80 °C (0.5 min. isothermal) @ 20 °C/min to 160 °C (2 min)
- Carrier gas: 2.0 mL/min const. flow, Helium

QHSS-40

- Sample loop: 1 mL
- Vial/heating: 80 °C
- Equilibrium time: 45 min

Results and Discussion

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

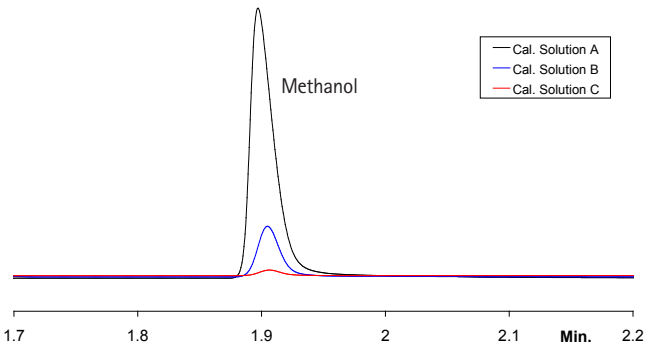

Figure 1. Overlay traces of calibration solutions.

*The method is not applicable to mixtures of FAME which contain other low boiling components.

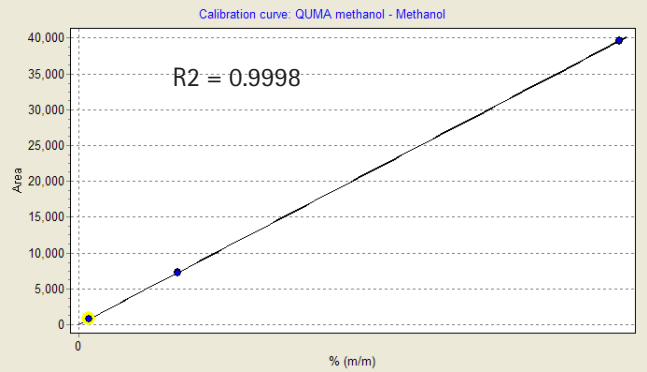

Figure 2. Calibration curve.

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

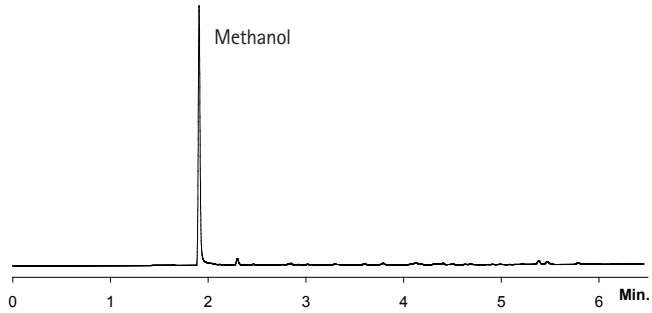

Figure 3. Typical headspace chromatogram of biodiesel.

Since biodiesel generally does not contain volatile components, other than methanol, identification and quantification is quite straightforward.

	Methanol (mass %)
N	15
Average	0.038
St. dev.	0.0007
RSD (%)	1.96

Figure 4. Repeatability figures.

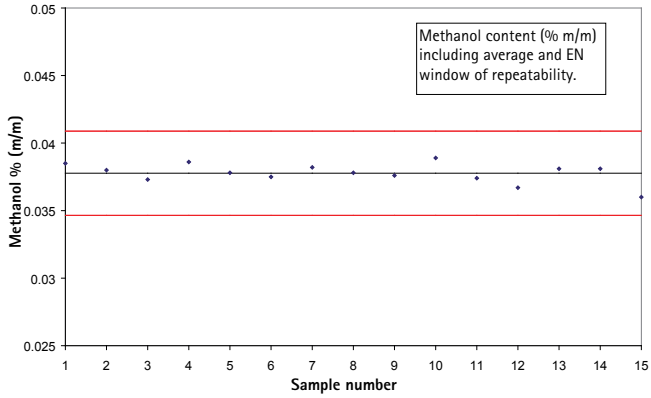

Figure 5. Repeatability values are within the specification boundaries established in EN-14214 as indicated by the red lines in the chart.

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 5, where the analyses trend line is well within the repeatability "window" set forth in the EN-14110 method. In Figure 5 this is visualized by adding the average line and the window of repeatability set in the EN-14110 method.

Conclusion

The GC Headspace system (Varian 430 Gas Chromatograph and a QUMA Headspace Sampler) was shown to be well suited for the determination of methanol content in biodiesel according to specifications outlined in EN-14110, and the biodiesel tested in this application note meets the specifications on methanol content set forth in EN-14214.

References

EN-14110 Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of methanol content.

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

These data represent typical results.
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