APPLICATION NOTE

Gas Chromatography

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HS-GC: Accurate Analysis of Methanol Content in B100 Biodiesel According to EN14110

Introduction

Biofuels continue to be of key importance to the energy sector as more renewable fuel solutions are developed to contribute to global climate goals and resolve energy shortages. Fatty Acid Methyl Ester (FAME) Biodiesel (B100) is a key component for blending with fossil-fuel diesel in portions of up to 30% depending on the region and engine type. Standards specifications for B100 biodiesel exist in the form of ASTM D6751 – Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels and EN14214 – fatty acid methyl esters (FAME) for use in diesel engines and heating applications – requirements and test methods. For both standards the specifications state that methanol content in B100 should not exceed 0.2 % m/m. Methanol is an important requirement in the transesterification reaction used to produce the FAME. The methanol is separated after the completion of the reaction and precise analysis is required to ensure that any residual methanol content within the FAME is within specification to ensure it is fit for purpose. The standard test method to determine methanol content in B100 is EN14110 which specifies the use of manual or automatic headspace gas chromatography. This application note covers the analysis of methanol in B100 utilizing the PerkinElmer GC 2400™ System and PerkinElmer HS 2400™ Headspace Sampler.

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Instrumentation

A GC 2400 System along with a HS 2400 Headspace Sampler was used to test B100 samples for methanol content by EN method 14110. PerkinElmer SimplicityChrom™ CDS Software was used for all instrument control, data acquisition and data processing. EN14110 offers several suggestions for the column used to perform the analysis.[3] For the analysis presented in this application note a PerkinElmer Elite 1 column (30 m x 0.32 mm x 1.8 µm) was used. The instrument method parameters are listed in Table 1.

Figure 1. PerkinElmer GC 2400 System configured with HS 2400 Headspace Sampler.

Experimental

It is necessary for standards to be made up in a B100 matrix that contains less than 0.001 % Methanol. To determine if the matrix is methanol-free, a blank B100 sample should be measured to see if any methanol peak is observed. If methanol is observed in the matrix, it is required to remove any traces using a procedure such as the one described below.

For 100 mL of methanol-free B100 matrix:

1. Wash with three 50 mL aliquots of water with agitation.
2. Separate the water from the B100 matrix.
3. Heat the washed B100 matrix on a hot plate at 90 °C for two hours whilst stirring.

Materials

A B100 reference blank (<0.001 % Methanol), Methanol (>99.5%) and 2-Propanol (>99.5 %) were purchased from LGC standards (United Kingdom). All instrument consumables and tools are listed in Table 2.

Table 1: HSGC Instrument Parameters.

GC Parameters	
Instrument	GC 2400 System
Column	Elite 1: 30 m x 0.32 mm x 3.0 µm
GC Oven Parameters	Isothermal @ 50 °C
Headspace Parameters	
Instrument	HS 2400 Headspace Sampler
Oven Temperature	80 °C
Needle Temperature	90 °C
Transfer Line Temperature	110 °C
High Pressure Injection	Off
Carrier/mode	Hydrogen, constant pressure, 12 psi
GC Cycle Time (min)	10
Pressurization Time (min)	3
Thermostat Time (min)	45 min
Withdrawal Time (min)	0.5
Vent Time (s)	5
Injection Time (min)	0.04 (80 µL)
Injector Parameters	
Carrier/mode	Hydrogen, constant pressure
Temperature	150 °C
Septum Flow	3 mL/min
Detector Parameters	
Type	FID
Temperature	240 °C
Hydrogen	35 mL/min
Air	400 mL/min
Make up Gas (Nitrogen)	25 mL/min
Data Rate	10

Table 2: Application consumables and tools.

Consumable/Tool	Part #
PerkinElmer Elite 1 Capillary Column, 30 m x 0.32 mm x 3 µm	N9316025
1 mm ID straight liner	N6502037
20 mL Crimp Top Headspace Convenience Kit	N9303992
20 mm Hand Crimper	N9302785
Green Injection Port Septa	N9306218
Graphite Capillary Column Ferrules 0.5 mm ID	09200785
O-ring for Injector Liner	09200714
Triple Filter (Hydrogen and Nitrogen)	N9306110
Moisture/Hydrocarbon Trap (Air)	N9306117

Calibration

The vials must be prepared in an environment free of methanol vapour which is common in FAME B100 production facilities. Alternatively, the vial can be purged with an appropriate gas (clean air, nitrogen, etc.) to ensure no traces of methanol from the ambient environment is present.

EN14110 specifies a three-point linear calibration be used using either internal standard (with 2-propanol as internal standard), or external calibration. Internal standard calibration is a requirement for manual analysis but optional for automatic headspace analysis. The internal standard is also useful to determine the quality of the headspace injection. For example, an inconsistent internal standard peak could identify a vial that was not prepared or crimped correctly. The calibration range specified by EN14110 is displayed in Table 2.

Table 3: EN14110 Calibration Levels

	Concentration %(m/m)
Standard Level A	0.01
Standard Level B	0.1
Standard Level C	0.5

5 (+- 0.01 g) of the standard is accurately weighed into a 22 mL headspace vial. 5 µL of 2-propanol is added to the liquid phase with a syringe. The vials are then immediately crimped and shaken to ensure sufficient mixing.

Sample Preparation

5 (+- 0.01) g of B100 sample is accurately weighed into a 22 mL headspace vial. If internal standard calibration is used, 5 µL of 2-propanol is added to the liquid phase using a syringe before capping the headspace vial securely and shaking to allow sufficient mixing.

Results and Discussion

As the vast majority of the B100 matrix is non-volatile, the methanol peak is simple to resolve without substantial optimization. Only two analyte peaks are of interest for this method, the methanol peak itself and the 2-propanol peak if used as an internal standard. EN14110 states that a baseline resolution between the methanol and 2 – propanol peaks should have a value of at least 1.5 according to the following resolution equation:

$$Rs = 1.18 \frac{tB - tA}{wA + wB}$$

Where:

tA is the retention time of methanol.

tB is the retention time of 2-propanol.

wA is the peak width at half-height of methanol.

wB is the peak width at half-height of 2-propanol.

Figure 2 shows a chromatogram of the 0.5% methanol standard and it is clear that baseline resolution has been achieved with the methanol peak eluting at 1.850 minutes and the 2-propanol peak eluting at 2.837 minutes. When calculating the resolution for this chromatogram using the resolution equation the result is calculated to be approximately 15, indicating the method and configuration exceeds the requirements to performing this separation.

Figures 3 and 4 display chromatograms of samples where the methanol has not been completely removed from the sample but does not exceed the limit of 0.2 %. Both samples contain less than 0.01 % methanol and are a good indication of the sensitivity of the method.

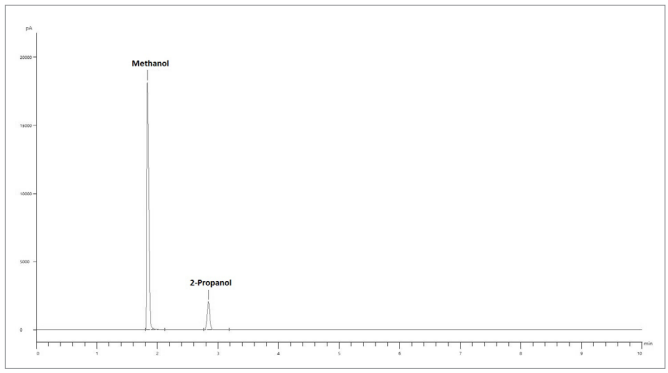

Figure 2: 0.5 % Methanol standard.

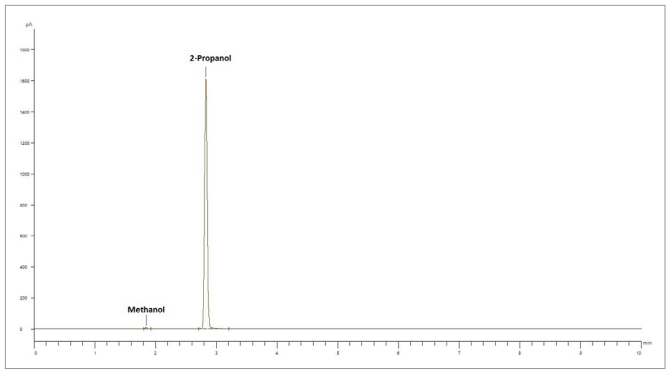

Figure 3: B100 sample with less than 0.01 % methanol.

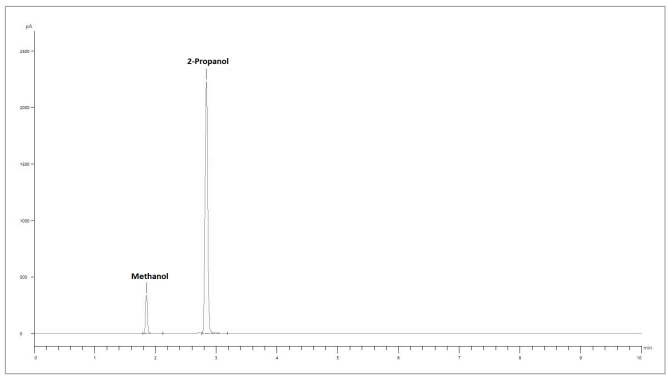

Figure 4: B100 sample with less than 0.01 % methanol.

The three calibration standards were measured using the method and the linear calibration curve shown in Figure 5 was obtained. The coefficient of determination (R^2) is shown to be 0.9999 indicating and excellent degree of data correlation over the specified calibration range.

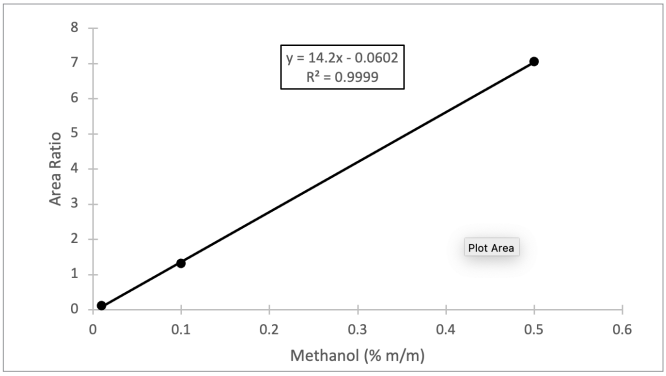

Figure 5: Internal standard calibration curve, EN14110 sampling method.

A 0.15 % control sample was measured five times to determine the repeatability of the method, the results are shown in Table 3. The percentage relative standard deviation (%RSD) was calculated to be 0.963 % for the five repeat measurements of the control sample indicating a high level of robustness of the analytical instrument configuration and method.

	Methanol (% m/m)
Repeat 1	0.159
Repeat 2	0.158
Repeat 3	0.158
Repeat 4	0.157
Repeat 5	0.155
Average	0.157
%RSD	0.963

Conclusion

For the analysis of methanol in B100 according to EN14110, the PerkinElmer GC 2400 System and HS 2400 Headspace Sampler showed accurate results. The linear calibration of the range specified by the standard method was achieved with excellent linearity (R^2 = 0.9999). Should a more sensitive analysis be required the calibration range can be expanded as necessary. The GC 2400 System and HS 2400 Headspace Sampler demonstrated good precision and accuracy for the analysis. Method changes or optimizations were easily accommodated by SimplicityChrom CDS Software.

References

1. ASTM D6751 – 23A, "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels," ASTM International, West Conshohocken, PA, 2023, DOI: 10.1520/D6751-23A, www.astm.org.
2. EN14214:2012+A2:2019, "Liquid Petroleum Products – Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heating Applications – Requirements and Test Methods."
3. EN14110 :2019, "Fat and Oil Derivatives – Fatty Acid Methyl Esters – Determination of Methanol Content".
4. Ruppel. T, Goodman. W, and Huybrighs, T. "Residual Methanol in B100 Biodiesel by Headspace-Gas Chromatography According to EN 14110," PerkinElmer, 2012.

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