Residual Methanol in B100 Biodiesel by Headspace-Gas Chromatography According to EN 14110

Authors

Timothy Ruppel
William Goodman
Timon Huybrighs

PerkinElmer, Inc.
710 Bridgeport Avenue
Shelton, CT 06484

Introduction

Biodiesel quality specifications in B100 biodiesel are covered in EN 14214 and ASTM D6751-07a. The EN 14110 method specifies headspace-gas chromatography for the determination of residual methanol. Automated headspace sample introduction is recommended in EN 14110 but manual headspace sample introduction is allowed if an internal standard is used. The ASTM method specifies that residual methanol can be determined by either flashpoint at 130 ˚C minimum for ASTM D93, or by less than 0.2% methanol by mass for EN 14110. EN 14110 was adopted by ASTM in 2007, resulting from the lack of an ASTM method for the analysis of methanol in biodiesel.

This application note will focus on automated headspace sample introduction without the use of an internal standard. It will follow the EN 14110 method and then show a modification to simplify and speed up the analysis. Compared to the analysis of free and total glycerin in B100 biodiesel, the analysis of residual methanol is very easy.

Experimental

Following EN 14110, 5 mL of B100 biodiesel is added to a 22-mL headspace vial, heated at 80 °C for 45 min and 500 µL of headspace vapor is injected to a split injector of the gas chromatograph. A modification of this method uses only 250 µL of sample, heated to 80 °C for 10 minutes.

Instrumentation: PerkinElmer® TurboMatrix™ HS-40 Headspace (HS) sampler, coupled to a PerkinElmer Clarus® 500 Gas Chromatograph (GC) with capillary injector and FID.

GC Column: Several types of GC columns are listed in the EN 14110 method as possibilities. Any column that delivers resolution and a symmetrical peak for methanol is acceptable. The columns included in this application note are:

- 30 m x 0.32 mm x 1.8 µm BAC-1 (PerkinElmer Part No. N9316579)
- 30 m x 0.28 mm x 3.0 µm Elite-1 (PerkinElmer Part Nos. N9316025 or N9307067)

This application note demonstrates the analysis following both EN 14110 and the modified analysis for greater sample throughput.

Calibration standards should be made in a matrix similar to the analytical samples. To accomplish this, a blank biodiesel matrix free of methanol must be created. Wash 100 mL of B100 biodiesel with 50-mL aliquots of water 3 times with agitation to remove methanol. Heat that 100 mL of B100 biodiesel in a 500-mL beaker on a hot plate to 90 °C for 2 hours while stirring. This will drive off any traces of methanol, leaving a blank biodiesel suitable for creating calibration standards. Test the blank matrix prior to standard preparation to ensure that no methanol is present. Analyzing a blank headspace vial will verify the lab air is also methanol free. Checking the level of methanol in the lab air is important because trace methanol is often in the atmospheric air of biodiesel production facilities, though it is typically 50 times lower than the lowest calibration level C, but still detectable.

EN 14110 specifies a three-point linear calibration curve at 0.01%, 0.1% and 0.5% methanol by mass. Create calibration standards by adding 142 µL of methanol to 25 mL of blank biodiesel matrix. Label this standard dilution as Calibration A at a concentration of 0.5% mass methanol. Add 5 mL of dilution A to 20 mL of blank biodiesel matrix. Label this standard dilution as Calibration B at a concentration of 0.1% mass methanol. Add 1 mL of dilution B to 9 mL of blank biodiesel matrix. Label this standard dilution as Calibration C at a concentration of 0.01% mass methanol.

Table 1. Instrumental Conditions for Both the Standard and Modified EN 14110 Method.

GC Conditions	**EN 14110**	**Modified EN 14110**
Oven:	100 °C Isothermal	50 °C Isothermal
Cap Injector:	110 °C	140 °C
Split:	off	5 mL/min
Carrier Pressure:	off	12 psig
FID Temperature:	240 °C	240 °C
FID Range/Attenuation:	1/-2	1/-2
Headspace Conditions		
Oven:	80 °C	80 °C
Needle:	90 °C	105 °C
Transfer:	110 °C	120 °C
Thermostat:	45 min	10 min
Pressurize:	2.0 min	1.0 min
Inject:	0.02 min	0.04 min
Withdrawal Time:	0.5 min	0.5 min
GC Cycle Time:	7.5 min	5.0 min
Headspace Mode:	constant	constant
Injection Mode:	time	time
Column Pressure:	20 psig	17 psig

Sample preparation: To follow the method presented in EN 14110, measure 5 g of each calibration standard into individual 22-mL headspace vials. Cap vials securely. Measure 5 g of each sample into headspace vials and cap securely. When using automated headspace, internal standard is optional but recommended, as it provides data to verify the quality and precision of the sample pressurization and injection.

To follow the modified method presented here, measure 250 µL of each calibration standard into individual 22-mL headspace vials with a positive displacement pipette. Cap vials securely. Likewise, measure analytical samples adding 250-µL B100 biodiesel into headspace vials and cap securely. Sample weights are not necessary when using a positive displacement pipette. Calibration and sample aliquot can be done by volume with a positive displacement pipette adding to the increased speed and simplicity of the overall method. Biodiesel samples are too viscous to measure with replaceable tipped pipettes.

Results

The analysis of methanol in biodiesel with automated headspace GC-FID is a simple and accurate technique. The chromatographic data is very easy to interpret; resulting in a very simple chromatogram. The simplicity is a result of the non-volatile matrix (97% FAME by definition) with only a few volatile alcohols added during processing. The significant peaks in the chromatogram will be methanol and 2-propanol, if an internal standard is used.

Figure 1 (Page 3) demonstrates the analysis of methanol in biodiesel with 2-propanol as internal standard, a 0.5% weight standard and two sample analyses are also shown. The two samples pictured are a biodiesel: in one sample, the methanol was effectively removed, and in a second sample, the methanol was not removed completely. The large methanol peak is obvious in both the standard and the second sample.

In all three chromatograms in Figure 1, you see a consistent peak for 2-propanol, the internal-standard. In this case, the internal-standard was not used for calibration, rather as a measure of the quality of the headspace injection.

If the vial was improperly crimped or another type of systematic error occurred, the internal-standard area would change, providing the analyst with an indication of the problem. Consistent internal-standard area will improve confidence in the analytical results.

A three-point calibration was run using both analytical methods. The calibration demonstrated a linear response with both curves having r^2 values greater than 0.999 across the calibration range of 0.01% through 0.5%. Additional precision data was generated on each method with the traditional EN 14110 approach, generating approximately 5% RSD over 5 injections and the modified approach, generating less than 2% RSD over 5 injections.

Conclusion

Demonstrated here is the analysis of methanol in B100 biodiesel. Automated headspace sample introduction is a simple, fast and clean technique. The non-volatile matrix is never in contact with the analytical system, eliminating associated maintenance. The automated system provides the laboratory with consistent, high-precision results.

The data shown was generated using both the traditional EN 14110 method and a modified method to improve the speed and precision of the analysis. EN 14110 methodology generated acceptable precision and outstanding linearity, with a 45-minute equilibration time and 7.5-minute injection-to-injection time. The modified methodology with a 250-µL sample volume and 10-minute equilibration time exhibited exceptional linearity and precision with a 5-minute injection-to-injection time.

References

1. ASTM D6751-07a: Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels.
2. EN 14110: Fatty Acid Methyl Ester (FAME) Determination of Methanol.

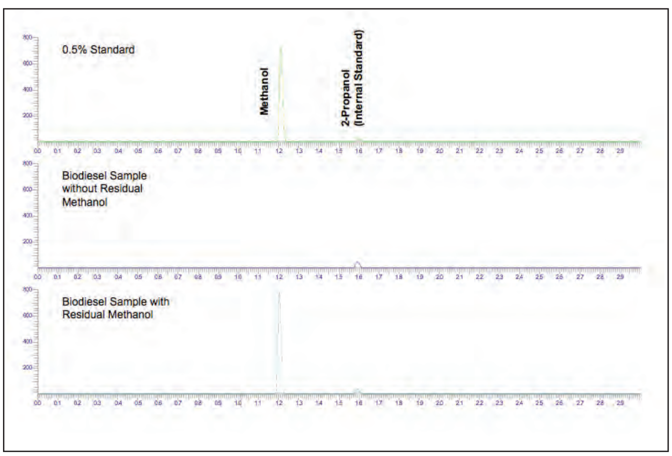

Figure 1. Chromatogram of the analysis of methanol in B100 biodiesel, following EN 14110 methodology.

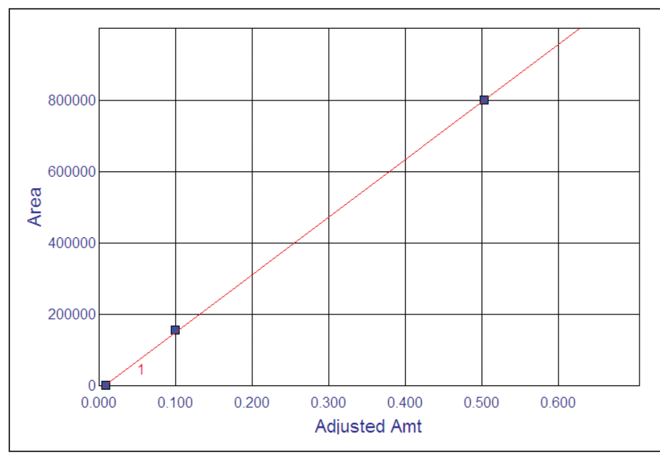

Figure 2. The calibration plot of a curve prepared with 5 g sample volume with linearity of 0.9999.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
Phone: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

008371_01