Determination of Methanol Content in Biodiesel Using Agilent Select Biodiesel for Methanol

Application Note

Energy and Fuels

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Introduction

The purpose of the European Standard EN-14110 is to determine the methanol content of fatty acid methyl esters (FAMEs) intended for use as pure biodiesel, or as a blending component for domestic heating fuels and diesel fuels. The method is applicable for a concentration range from 0.01 % (m/m) to 0.5 % (m/m) methanol. Requirements stated in EN-14214:2003 are <0.2 % (m/m) methanol (MeOH).

The EN-14110 method is not applicable to mixtures of FAME that contain other low boiling components. However, by using the Agilent Select Biodiesel for Methanol column, a good separation from most of these minor compounds can be achieved, resulting in a reliable analysis. In this example, the determination was conducted using the internal standard method, which was appropriate for manual headspace analysis.

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Materials and Methods

Conditions

Sample	Reference FAME with methanol content less than 0.001 % (m/m)
Column	Select Biodiesel for Methanol 0.32 mm × 30 m, 3 µm (p/n CP9083)
Injector	1177, split/splitless
Injector temperature	275 °C, split 150 mL/min, cup liner
Oven	40 °C, isothermal
Carrier gas	Helium, 80 kPa (11.6 psi)
Detector	FID, 300 °C

Reference FAME

A reference sample of FAME with a low methanol content was prepared by extracting with water (taking 30 mL biodiesel and extracted four times with 10 mL water). Next, the extracted biodiesel layer was dried with $MgSO_4$ for 15 minutes. After filtration, the clear biodiesel layer was collected and analyzed. It was found to contain less than 0.001 % (m/m) methanol and no isopropanol[a].

Calibration curve

Using reference FAME, three calibration solutions (A, B, and C) were prepared, yielding concentrations of 0.462, 0.0919, and 0.0092 % (m/m) methanol, respectively.

Samples

Different biodiesel samples were obtained from several sources, including in-house prepared biodiesel. This sample was made from rapeseed oil, but not at optimized conditions, to ensure against a biodiesel sample of suspect quality.

Headspace conditions

From homogenized samples and standards, a 1 mL aliquot was accurately weighed into a 20 mL vial and 5 µL isopropanol (internal standard, IS) was added to each. Each vial was tightly capped to prevent leaking. Next, each vial was shaken and heated at 80 °C for 45 minutes and 100–200 µL headspace was injected into the GC using a syringe preheated to 60 °C.

Results and Discussion

Figure 1 is the chromatogram obtained from the separation of a biodiesel sample. The calibration curve was then recorded and calibration factors were calculated. See Table 1, for detailed results of the calibration, and Figure 2, for the recorded calibration curve. The average response factor was 1.18, with a coefficient of variation of 13.5%. The coefficient of variation was <15%, thus meeting the specifications.

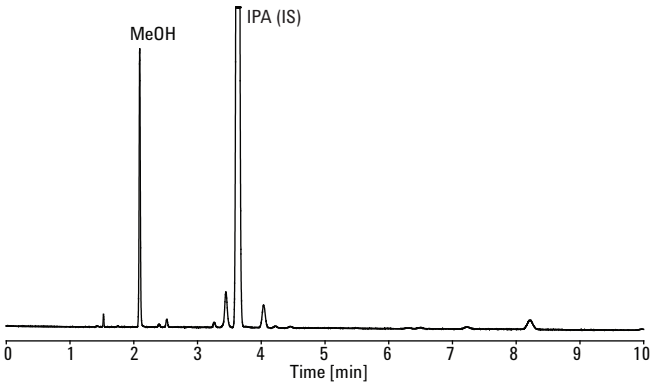

Figure 1. Chromatogram of a summer biodiesel (sample code 1) including some unknown volatiles.

Table 1. Calibration Data with Three Standards Using the Internal Standard Method

Code	Mass % MeOH	Mass % IPA	Mass % MeoH/IPA	µL gas sample	Mrea MeOH	Area IPA	Area MeOH/IPA	RF (F)
Reference FAME	0	0.393	0	200	4815	509865	0.0094	
CAL A	0.462	0.393	1.18	200	1261017	974438	1.2941	1.10
CAL A	0.462	0.393	1.18	100	765768	581293	1.3174	1.12
CAL B	0.0919	0.393	0.23	200	323222	1319992	0.2449	1.05
CAL C	0.00918	0.393	0.023	200	43372	1279566	0.0339	1.45
Average								**1.18**

a Reference FAME can also be obtained from commercial sources.

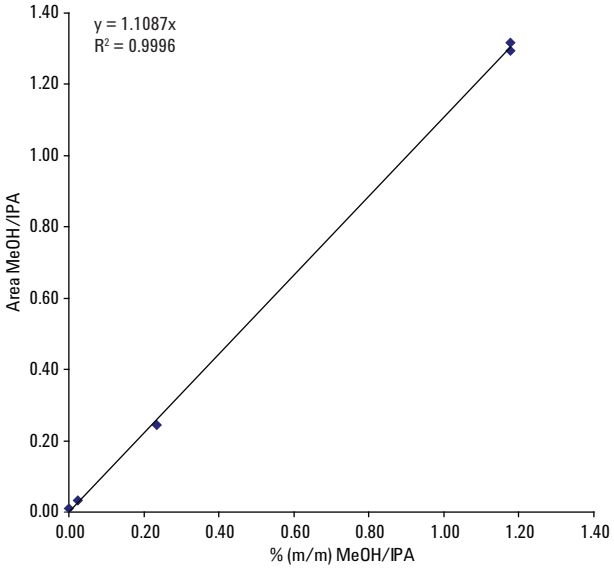

Figure 2. Calibration curve as obtained with the manual headspace method with isopropanol as internal standard.

As some trace level MeOH was present in the reference FAME, the response factor of the lowest calibration standard (C) was slightly higher. This, however, did not have a significant effect on the average response factor. Although use of a regression line was not described in the method, one was calculated and is shown in Figure 2. This resulted in a comparable (and probably better) value.

During this procedure, blank headspace samples were prepared by filling the vials with nitrogen and analyzed as before. These blank samples showed no carryover of MeOH and IPA, as well as no interfering peaks from vials, septa, or from the syringe. Seven different biodiesel (B-100) samples were analyzed (Table 2).

Table 2. Results of the Methanol Headspace Analysis of Different Biodiesel Samples

Code	Description*	Sample mass (g)	µL gas sample	Area MeOH	Area IPA	Area MeOH/IPA	Mass % MeOH
1	Summer biodiesel (2004)	0.910	200	73982	868326	0.0852	0.04
2	Winter biodiesel (3S)	0.884	200	138444	1083819	0.1277	0.06
3	Winter biodiesel (2S)	0.886	200	108693	1252320	0.0868	0.04
4	Winter biodiesel (1N)	0.878	200	146444	1232739	0.1188	0.06
5	FAME mix TOFA	0.890	200	155232	1052582	0.1475	0.07
6	Biodiesel ASTM round robin	0.880	200	206244	1096931	0.1880	0.09
7	In-house biodiesel	0.893	100	76234	107138	0.7115	0.32

**Descriptions of the biodiesel (B-100) samples are based on the original lab code, time period (Germany, summer or winter biodiesel as sold on the pump) or origin of sample; TOFA: Tall Oil fatty acid methyl ester (mainly C18:1 and C18:2 FAMEs).*

The sample weights actually used in the method were slightly modified due to the availability of limited sample. This did not change the principle of analysis and a good result was still achieved, even with a manual headspace method. Optimal sensitivity was obtained by varying the headspace temperature, sampling time, inlet split flow and sample amount injected. All samples analyzed were within standard specifications as stated in EN-14214 (max. 0.2 % (m/m) methanol), except the in-house prepared biodiesel of low quality, which was as expected.

Conclusion

These results clearly demonstrate that the Agilent Select Biodiesel for Methanol column achieved a better resolution than specified in the method (Rs > 1.5). The column provided good separation of other low boiling compounds that may be present and did not interfere with the methanol peak or isopropanol internal standard peak.

References

1. EN-14110 (June 2003) Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – determination of methanol content.
2. EN-14214:2003. Automotive fuels – Fatty Acid Methyl Esters (FAME) for diesel engines – requirements and test methods.

For More Information

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