Application Note: 10216

Determination of Methanol Content in Pure Biodiesel (B100) by Headspace-GC in Compliance with EN 14110

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Key Words

- TRACE GC Ultra
- Biodiesel (B100)
- EN 14110
- Headspace
- Methanol

Introduction

In order for biodiesel to be commercialized as pure biofuel or blending stock for heating and diesel fuels, it must meet a set of requirements defined in ASTM D6751 and EN 14214 standard specifications.[1,2] These standards indicate the maximum allowable concentrations of contaminants in pure (B100) finished product, along with other chemical-physical properties necessary for a safe and satisfactory engine operation.

Gas chromatography (GC) is commonly adopted to characterize pure Biodiesel (B100) according to the following standard methods:

- **EN 14103:** Determination of total FAMEs (Fatty Acid Methyl Esters) and Linolenic Methyl Ester (C18:3)[3,4]
- **EN 14105/ASTM D6584:** Determination of Free and Total Glycerine[5,6,7,8]
- **EN 14110:** Determination of residual methanol content[9]

Comprehensive Thermo Scientific GC solutions have been developed in compliance with each of these methods, based on the Thermo Scientific TRACE GC Ultra™ and the versatile TriPlus™ autosampler (Figure 1). This application note relates to the determination of methanol in biodiesel according to EN 14110.

Figure 1: TRACE GC Ultra with TriPlus HS autosampler

Monitoring residual methanol in B100 is a matter of safety since even small amounts of this material can reduce the flash point of the biodiesel. Moreover, residual methanol can affect fuel pumps, seals and elastomers and can result in poor combustion properties. EN 14110 requires a headspace GC method, based on either polar or non-polar columns, and is applicable for a concentration range from 0.01% m/m to 0.5% m/m of methanol (MeOH). The method is not applicable to mixtures of FAME that contain other low boiling components, although the use of the Thermo Scientific TRACE™ TR-BIODIESEL(M) column allows for good separation of methanol from most of these volatiles, producing reliable results.

EN 14214:2003 standard specifications require the methanol content to be < 0.2% m/m. In this note, the analysis was performed using an external calibration procedure, which is preferred over internal standard calibrations when automatic headspace equipment is used.

Methods

Instrumentation and Reagents

A Thermo Scientific TRACE GC Ultra equipped with a split/splitless (SSL) inlet and a flame ionization detector (FID), automated by a TriPlus Autosampler configured for headspace was used, with instrument control through the Thermo Scientific Chrom-Card data system. The analytical column was a non-polar Thermo Scientific TRACE TR-BIODIESEL(M), 30 m, 0.32 mm ID, 3.0 µm f.t. For calibration, methanol with purity > 99.5% and a reference FAME with methanol content < 0.001% m/m were used.

Sample Preparation

A reference sample of FAME can be prepared by extraction with water to ensure low methanol content, taking 30 mL of biodiesel and extracting four times with 10 mL of water. Then, the extracted biodiesel layer must be dried with $MgSO_4$ for 15 minutes, and analyzed using the parameters reported below. This prepared sample has to provide methanol content less than 0.001% m/m. Such a reference FAME can also be obtained from various commercial sources. In this note, raw sunflower oil has been used, featuring a very low methanol content.

Using the reference FAME, three calibration solutions (A, B and C) were prepared by adding pure methanol to obtain concentrations of 0.5, 0.1 and 0.01% m/m respectively. 2 mL from each calibration solution and unknown biodiesel sample were transferred into headspace vials, which were tightly crimped in order to prevent leaking.

Analytical Parameters

Table 1 includes selected instrument parameters for the TRACE GC Ultra and the TriPlus HS autosampler. These settings were used for all sample analyses.

TRACE GC Ultra	
Injector	Split/Splitless (SSL)
SSL Mode	Split injection mode, split flow of 100 mL/min
SSL Temperature	160 °C
Carrier Gas	Helium, 1.5 mL/min, constant flow mode
FID	250 °C
Oven Program	50 °C (1 min) to 130 °C @ 10°C/min, final hold 0.5 min

TriPlus Headspace Autosampler	
Incubation temperature	80 °C
Incubation time	40 min
Syringe temperature	85 °C
Injected amount	500 µL

Table 1: Selected instrument and method parameters for the TRACE GC Ultra and TriPlus HS

Results and Discussion

Figure 2 shows a typical chromatogram obtained from a biodiesel sample analyzed following the conditions reported above.

External standard calibration was performed by analyzing the three calibration solutions, and plotting the methanol contents vs. the respective peak areas. Figure 3 shows the calibration function calculated using linear regression. The correlation coefficient (R^2) for this calibration was 0.9999, demonstrating excellent linearity for this method.

Different unknown biodiesel samples from several sources were then analyzed, delivering results within the standard specification stated in EN 14214 (methanol < 0.2% m/m), as shown in Table 2.

After a long sequence of unknown biodiesel samples, "blank" headspace samples, prepared by filling the vials with nitrogen, were analyzed, demonstrating total absence of any carryover of MeOH, as well as of any interference compounds from vials or septa.

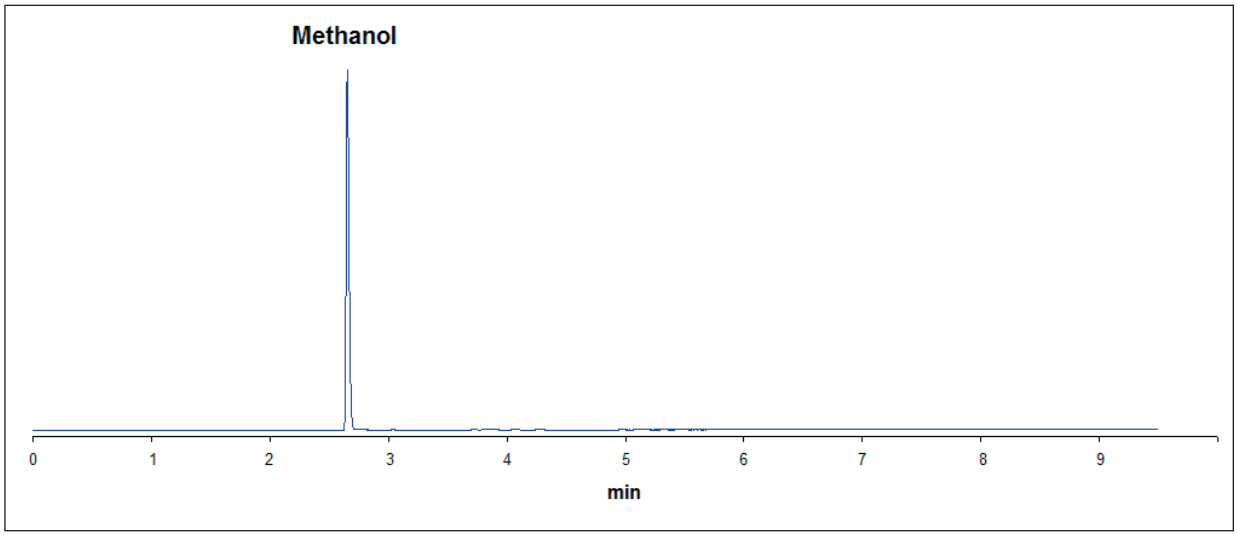

Figure 2: Biodiesel chromatogram showing methanol (headspace injection)

Finally, repeatability of the assay was tested by performing five consecutive injections for each biodiesel sample, resulting in excellent performance.

	Sample	% (m/m) MeOH	% RSD
1	Rapeseed biodiesel	0.18	1.4
2	Soybean biodiesel	0.05	1.9
3	Sunflower biodiesel	< 0.01	-
4	Mix 1-3 biodiesel	0.09	1.8
5	Mix 1-2 biodiesel	0.13	1.5

Table 2: Results for 5 biodiesel samples (5 runs each)

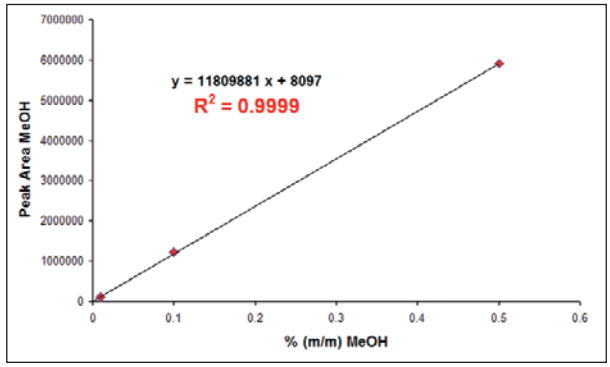

Figure 3: Methanol calibration curve, with levels at 0.01, 0.1, and 0.5% mass/mass (m/m)

Conclusion

The determination of residual methanol in pure biodiesel (B100) can be successfully achieved using the Thermo Scientific TRACE GC Ultra equipped with SSL injector and FID, and the TriPlus Headspace Autosampler, in full compliance with method EN 14110.

Although the procedure described here was based on external calibration and is preferred when a headspace autosampler is available or when a long sequence of samples needs to be analyzed, equivalent results can be obtained by applying the internal standard calibration procedure, either with the TriPlus autosampler or even manually.

As a further possibility, methanol content can be successfully determined by liquid injection of biodiesel diluted in *n*-Butanol, using a PTV Backflush system to vent out the heavier fraction without letting it enter the capillary column.

References

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

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