

# Avoiding engine damage

## Determination of methanol in biodiesel

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Biodiesel production has increased considerably in Europe in recent years. In 1996, production was nearly 0.5 million tonnes. Today, the production capacity is much higher. This development has also been supported by the automobile industry. In fact, several million passenger cars and commercial vehicles have been approved by their manufacturers to run on biodiesel fuel or higher biodiesel blends with mineral diesel. Compliance with the European Biodiesel standard DIN EN 14214 ensures a continuously high quality level.

The production of biodiesel is based on transesterification of plant oils or animal fats to fatty acid methyl esters (FAME, Figure 1). At a temperature of approximately 60 °C, the plant oil, consisting mainly of glycerin esters, is esterified using methanol and a catalyst (alkali hydroxide or alkali alcoholate). In order to quantitatively shift the equilibrium reaction towards the biodiesel or FAME side, methanol is added in excess.

After the reaction is finished, the excess methanol together with the FAME mixture (biodiesel) must be removed.

The DIN EN 14214 standard specifies all legal limits for possible by-products. For safety-related reasons and in order to comply with requirements of the automobile industry, the legal limit for methanol residue has been defined as 0.2 mass percent-ages (% m/m). DIN EN 14110 describes the required method for methanol determination.

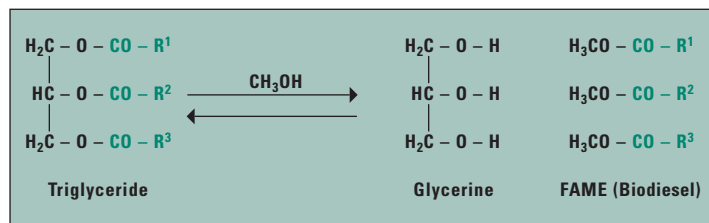


Figure 1: Equilibrium reaction of the transesterification of plant oils (triglycerides) to fatty acid methyl esters (biodiesel)

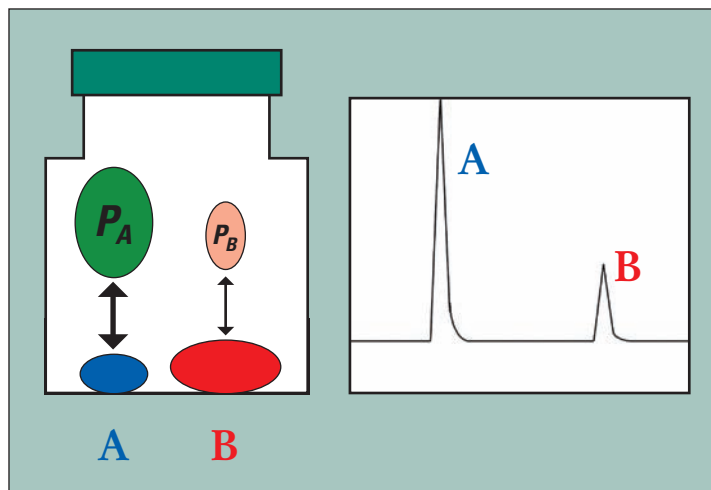


Figure 2: Equilibrium between the liquid- and gas-phase during headspace sample preparation. Although component A is present at a lower concentration in the liquid phase, the concentration ratio in the gas-phase may shift, depending on the vapor pressure of the individual components. Correspondingly, the chromatograms resulting from headspace injection usually produce different signal ratios when compared with those resulting from liquid sample injection.

### GC with headspace injection

Biodiesel can consist of up to 100 different fatty acid methyl esters, depending on the plant oils used during production. For the determination of methanol in such a complex matrix, gas chromatography in combination with headspace injection is the recommended method. This enables separation of low-boiling point methanol from the high-boiling point fatty acid methyl esters

already during the sample preparation step.

The biodiesel samples are heated in a gas-tight 20 mL vial. Methanol is a low-boiling point compound and is enriched in the gas-phase while the high-boiling point compounds remain in the liquid phase (Figure 2). After a specific time, equilibrium is reached and a constant volume can be sampled from the gas-phase (headspace) of the vial and injected into the GC system.



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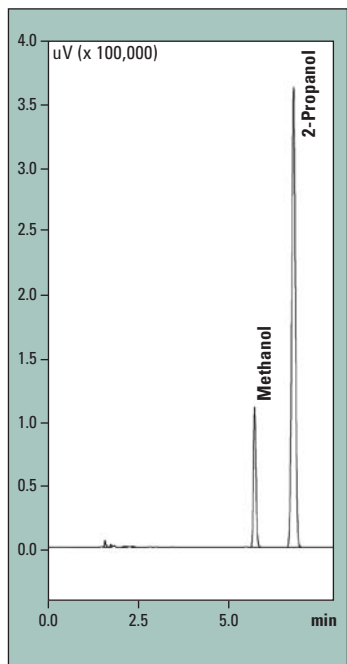


Figure 3: Chromatogram of 0.01 % (m/m) methanol in biodiesel. 2-propanol was added as internal standard.

**Calibration with minimum complexity**

While the biodiesel matrix can influence the equilibrium between the methanol concentrations in the liquid- and gas-phase, calibration standards must be prepared in methanol-free biodiesel. The DIN EN 14110 biodiesel standard recommends preparation of a calibration curve containing 0.01, 0.1 and 0.5 %



Figure 4: GC-2014 and HT200H

(m/m) methanol in FAME. An internal standard should always be used when applying manual headspace injection. When using a headspace autosampler, an internal standard will not be necessary but is, however, recommended to increase the reliability of the results. The additional work is kept within reasonable limits: to each standard and each biodiesel sample, 5 µL of 2-propanol is added (Figure 3).

All measurements are carried out on a Shimadzu GC-2014AFsc system in combination with the HT200H headspace autosampler (Figure 4). Both instruments are easy to operate and designed for daily routine analysis.

For the calibration, 5 g of the respective standard solution as well as 5 µL of 2-propanol are added to a 20 mL headspace crimp vial. Corresponding to 5 g of biodiesel sample, 5 µL of 2-propanol is added as internal standard. The HT200H can handle up to 40 sample vials per tray.

**Automated sample preparation**

Sample preparation is fully automated, whereby each sample is shaken and heated to 60 °C for a given time. The autosampler prepares several samples simultaneously to ensure the highest possible sample throughput and to prevent hold-up at the gas chromatograph. A gas volume of 500 µL is sampled from the headspace of each vial and injected into the GC-2014AFsc system with a split ratio of 1:10.

Additional parameters are recommended according to DIN EN 14110:

- Temperature split injector:** 150 °C
- Column oven (isothermal):** 50 °C
- Flame ionization detector:** 150 °C

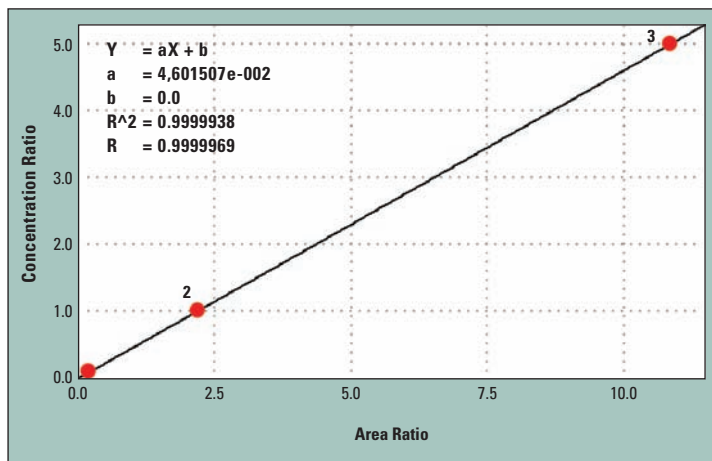


Figure 5: Calibration curve of methanol in biodiesel in accordance with DIN EN 14110 using internal standard calibration

Sample	1	2	3
Average concentration % (m/m)	0.009	0.100	0.500
Reproducibility standard deviation % (m/m)	0.00005	0.00100	0.00485
Reproducibility % RSD	0.54	0.99	0.97

Table 1: Biodiesel sample spiked with three different methanol concentrations.

Table 1 shows the reproducibility over 6 measurements of the same sample using the same method on the same instrument.

**Carrier gas (helium) linear velocity:** 35 cm/s  
**Separation column used for the measurements:** Restek, Stabilwax-DA 30 m, 0.32 mm, df 1.0 µm

At a methanol concentration of 0.01 % (m/m) a signal to noise ratio of higher than 1:2000 was obtained. Thus the technique offers many options for improvements via application of larger split ratios or faster chromatographic separation.

**Results exceeding the standard requirements**

The calibration curve in Figure 5 demonstrates that the combination of the HT200H autosampler and the GC-2014 results in high linearity over the concentration range recommended in DIN EN 14110. Reproducibility of the measurement values for biodiesel samples is higher than the requirements according to DIN

EN 14110 (Table 1). Biodiesel samples with very low methanol content were spiked with variable amounts of methanol.

Samples with the lowest concentrations showed the highest difference of two out of six measurement values 0.00012 % (m/m). DIN EN 14110 allows for 0.00151 % (m/m), a ten-fold higher deviation.

The combination of the HT200H and GC-2014AFsc offers an efficient as well as accurate automation solution for the routine analysis for methanol determination in biodiesel. Smaller scale biodiesel producers will profit from this robust analytical system with its excellent price/performance ratio.