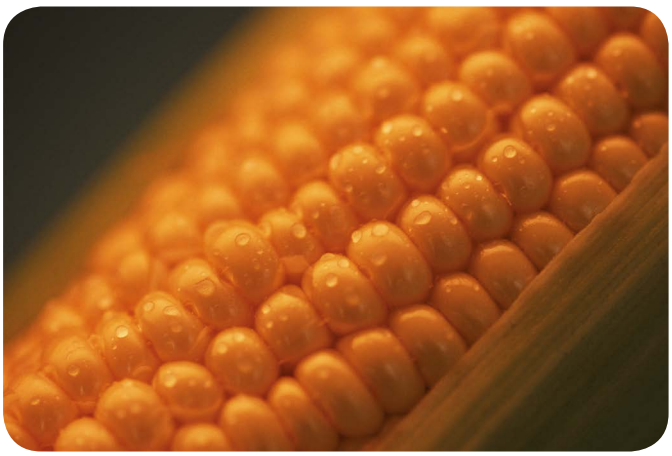

Application Note AN M60

Determination of FAME in Biodiesel blends using FTIR

Introduction

Biodiesel is a renewable alternative to petrodiesel and consists of fatty acid methyl esters (FAME). The synthesis of biodiesel uses mainly vegetable oils that are subjected to a base catalyzed transesterification reaction with methanol. The final product is a clear yellow liquid with a viscosity similar to standard diesel fuel. Biodiesel has excellent lubricating properties thereby reducing the wear of both fuel injection pumps and engines. Due to its high oxygen content, the emissions of carbon black particles are clearly reduced when compared to petrodiesel. Other benefits of biodiesel are the low sulfur content, its low toxicity and its high biodegradability.

In suitable engines biodiesel can be used undiluted (B100), but it is normally blended with petrodiesel up to a maximum concentration of about 30 % v/v (B30). Regulations in Europe and the US specify that blends with a biodiesel content of up to 5 % may be sold as normal diesel fuel without a special labeling. At different locations during the production process of diesel the FAME content has to be controlled. The actual concentration of biodiesel can be easily determined by FTIR spectroscopy since fatty acid methyl esters have a pronounced infrared absorption at around 1745 cm^{-1}.

This absorption band is characteristic for organic esters and does not occur in petrodiesel that consists mainly of alkanes and aromatic hydrocarbons. In order to gain precise results down to concentrations of about 0.02 % the measurement is best performed in transmission utilizing a liquid cell.

Figure 1: ALPHA II with multireflection ATR (top) and with transmission module and touch PC (right) for FAME in diesel analysis.

The Bruker FAME in diesel analysis kit allows quantifying the FAME content in diesel according to DIN EN 14078. The measurement is performed by using a liquid flow through cell in combination with a FTIR spectrometer like the ALPHA II. The kit contains a dedicated software-wizard that guides the user through the analysis procedure including measurement, data evaluation and reporting. Its simple and intuitive user interface allows operation even by spectroscopically inexperienced personnel.

Instrumentation

The IR-spectra for the calibration were measured with an ALPHA II spectrometer by using a liquid flow through cell with spacers of 100 µm and 500 µm respectively. The ALPHA II is a very robust, compact spectrometer with the footprint of a lab notebook and a weight of only 7 kg. It is equipped with wear free components such as Bruker´s patented RockSolid™ interferometer, a durable diode laser and a sturdy aluminum case. Figure 1 shows the ALPHA II spectrometer with different setups.

Of course, the FAME in diesel analysis kit can also be used in combination with an INVENIO or VERTEX spectrometer.

Methods

The FAME content of a diesel blend is accessible via the carbonyl band around 1745 cm^{-1}. Because there are no overlapping bands of the diesel fuel, the analysis can be done via a univariate linear function derived from the Lambert- Beer law.

Figure 2 shows the spectra of samples with different FAME concentrations. The measurements were performed with a 100 µm flow through cuvette and show clearly the linear trend of the absorbance. The calibration curve is depicted in the picture inset. Within the calibration range of 0 to 5 % m/m it shows a good linearity with a correlation coefficient of 0.9999 and a standard deviation of 0.017 % m/m. Higher sample concentrations can of course be measured after sample dilution.

An even higher sensitivity can be reached with a path length of 500 µm where concentrations between 0.02 and 1 % m/m can be measured. Figure 3 shows some sample spectra with FAME contents in the range of 0 to 0.5 %. It is evident that concentrations as low as 0.02 % can be measured since the corresponding spectrum (green in fig. 3) is clearly differentiated from that of pure diesel (blue in fig. 3).

The inset of figure 3 shows the calibration curve with an upper limit of 1 %. Again the correlation coefficient has an excellent value of 1.0000 and the standard deviation is significantly better with a value of 0.003 % m/m.

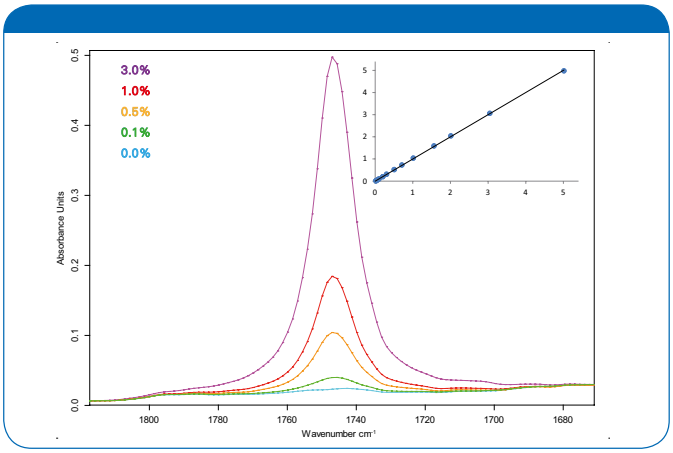

Figure 2: Spectra and calibration curve (Fit vs. True, % m/m) of diesel-FAME blends measured with a 100 µm flow through cuvette.

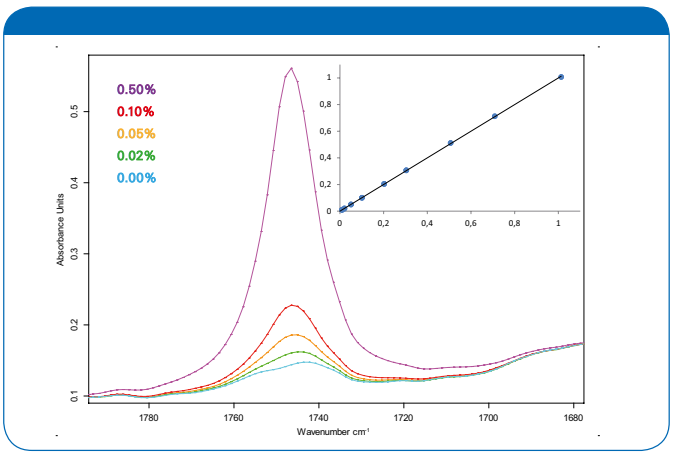

Figure 3: Spectra and calibration curve (Fit vs. True, % m/m) of diesel-FAME blends measured with a 500 µm flow through cuvette.

Example application

The Bruker FAME in diesel analysis kit comes with a dedicated software-assistant, the "FAME-wizard". This wizard is assisting the user in many different ways:

- It guides the user through the measurement and evaluation process
- It helps calculating the result of the measurement when the sample was diluted.
- The path length of the flow through cell can be detected automatically and the appropriate calibration is selected accordingly.
- It helps to transfer the calibration to another measurement setup.
- The Wizard also allows to configure and to control an autosampler.

In order to demonstrate the use of the wizard we will show an example application where the FAME content of a diesel blend is controlled.

In the test sample it should be verified that the blend contains at least 30 % m/m of FAME. For the measurement 25 ml of the blend are diluted with petrodiesel in a volumetric flask of 250 ml. The measurement is then performed in three simple steps:

First a background spectrum is measured by clicking the "Measure Background" button (see fig. 4 point 1). Then the liquid cell is filled with the sample using a 5 ml syringe. The cell is placed into the sample compartment and the "Measure Sample" button (point 2) is pressed. Now the sample details and information about the dilution of the sample (250 ml flask, 25 ml sample) are entered. When the checkbox "Diluted" is active the result will be automatically corrected for the dilution of the sample. Finally the measurement is started by clicking "Continue" (see point 3).

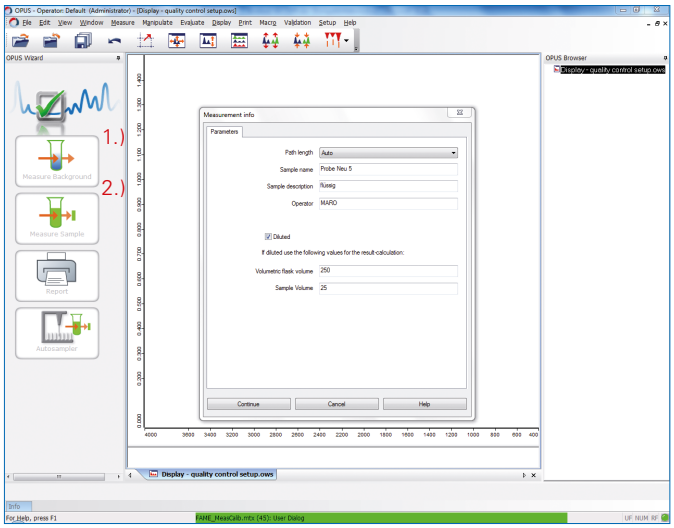

Figure 4: FAME-wizard with measurement dialog.

The measurement including the background can be performed in less than four minutes. During the measurement the spectrum is automatically corrected for device-specific influences, the thickness of the cell is automatically determined and the appropriate calibration is selected. As can be seen in figure 5 the dilution-corrected values as well as the raw values of the measurement are displayed in % (m/m and v/v) and g/L. The result of the measurement evidences a concentration of 30.7 % m/m FAME i.e. the sample is within the specification. As an addition a DIN EN 14078 compliant PDF-Report will be automatically generated and printed if desired.

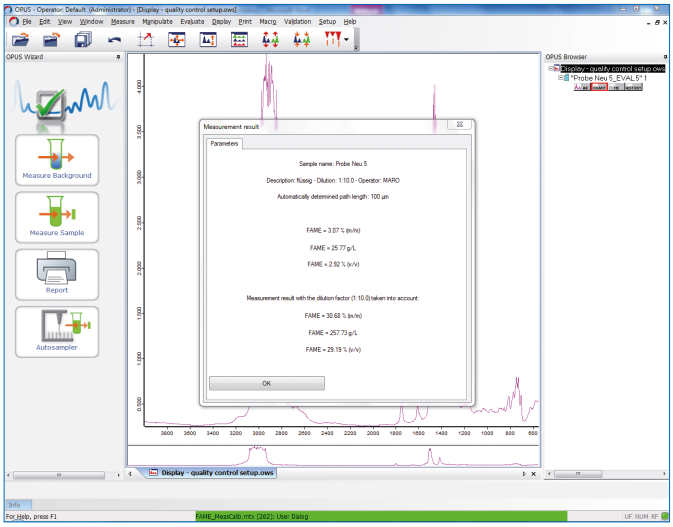

Figure 5: FAME-wizard with measurement result.

Summary

By using a Bruker FTIR spectrometer system with a flow through cell a fast and accurate analysis of the FAME content in diesel according to DIN EN 14078 is possible. Due to a robust instrumental setup, simple sample preparation and a user friendly measurement procedure the analysis can even be performed by untrained users.

Typically the IR-analysis takes less than two minutes per sample. In combination with an autosampler also larger sample numbers can be measured fully automated.

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