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WHITE PAPER

Guide to Measuring Biofuel Blending

Background



As the global commitment to renewable energy sources grows, the importance of using biodiesel as a blending component with diesel fuel has increased. Biodiesel consists of fatty acid methyl esters (FAME) which are produced by the transesterification of certain feedstock oils, such as soy, rapeseed, canola, and others. The biodiesel is then blended with diesel fuel at amounts required by the regulatory agencies of different countries. It is important for fuel terminals and distributors, as well as regulatory agencies, to check the concentration of biodiesel in the diesel fuel in order to make sure it is within these allowable limits. Diesel fuel with too little biodiesel will not meet renewable fuel standards and fuel with too much biodiesel may cause engine failures.

Measurement Techniques

FIXED FILTER IR ANALYZER



Spectro Scientific InfraCal 2
Biodiesel Blend Analyzer

Fixed Filter IR analyzers provide a very simple and inexpensive analysis of biodiesel in diesel. The analyzer uses a fixed filter at a specific wavelength to determine the quantitative value of the biodiesel up to 100% v/v. This method uses a fixed filter at 5.74 µm and a Horizontal Attenuated Total Reflectance (HATR) crystal to make the measurement. Since the filter is mounted directly onto the detector, the analyzer has no moving parts, which adds to its durability and portability. Also, the use of an HATR crystal makes operation simple enough for non-technical personnel, making it ideal for field use.

To complete a measurement, a sample is placed on the HATR crystal, measured, and a result is displayed in under a minute. The instrument then calculates the absorbance of the sample which is then converted to a concentration reading based on an internal calibration. The calibration uses a point to point calibration that

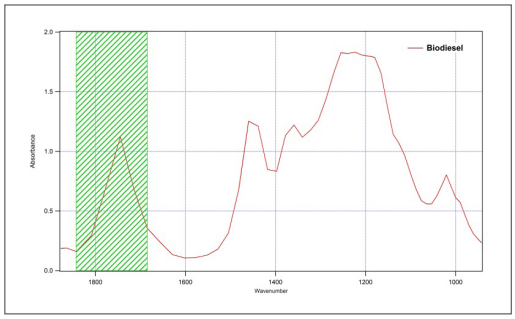
ADVANTAGES
- Provides fast analysis
- Ideal for field use (rugged and simple)
- Inexpensive
- Simple calibration
- Correlates to ASTM D7371 and EN 14078

DISADVANTAGES
- Susceptible to differences in the diesel
- Not ideal for the lab (Does not follow any standards)
- Only measures biodiesel blend amount

makes the calibration process simple, although potentially susceptible to differences in the diesel types (similar to EN 14078). While the method does not conform to any international standards, it has consistently proven to correlate very well with ASTM D7371 and EN 14078. Overall, a fixed filter IR analyzer is the ideal candidate for field operators because of its ease of use, ruggedness, and low cost.

GRATING IR SPECTROMETER

Similar to Fourier-Transform Infrared Spectroscopy (FTIR), grating spectrometers measure the light transmitted by a sample throughout the mid-infrared region. However, they use a diffraction grating to separate the light which allows for a system with no moving parts that is rugged, portable and inexpensive. Since grating spectrometers are measuring the same region of light as an FTIR, they can be used to measure many of the same B99 properties. The grating spectrometer uses a transmission cell with a short path length for measuring samples. The transmission cell is easy to clean and does not require cleaning solvents. The sample is measured by first taking a background of the blank cell. The measurement is then made by placing the sample in the cell and measuring again. The biodiesel concentration is calculated by the instrument software using a multivariate calibration. This multivariate calibration measures the light absorbed by the sample in the region of 1843-1685 cm^{-1}. Since grating spectrometers have the same non-linearities as an FTIR, the calibration needs to be broken up into 5 parts which include 0-1%, 1-5%, 5-20%, 20-80%, and 80-100% v/v. While this initial calibration process can be time consuming, it is possible to transfer the calibration from a master unit to any new units making the process a lot quicker. With a total analysis time of less than three minutes, and no moving parts, grating spectrometers are a great option for measuring biodiesel blend content in the field.



Measurement of biodiesel by FluidScan grating spectrometer



Spectro Scientific FluidScan®

ADVANTAGES

- Provides fast analysis
- Handheld
- Can measure multiple parameters
- Less expensive than FTIR
- No solvent required

DISADVANTAGES

- Initial calibration process can be time consuming
- Multivariate calibration susceptible to differences in diesel fuel
- Not ideal for the lab (Does not follow any standards)

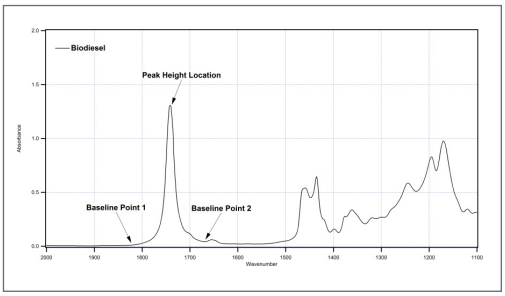
FTIR SPECTROMETER

FTIR (Fourier-Transform Infrared Spectroscopy) is the industry standard for biodiesel blend analysis. FTIR spectrometers measure all the light absorbed by a sample in the mid-infrared region of the light spectrum (4000-400 cm^{-1}). The change in absorbance at specific wavelengths is measured and correlated to the concentration of biodiesel. In addition to biodiesel blend measurements, the wide range of analysis of an FTIR spectrometer can measure important qualities of the biodiesel as well. FTIR spectrometers will measure biodiesel blends by one of the two international standards, ASTM D7371 or EN 14078.



Perkin Elmer FTIR Spectrometer

EN 14078 measures biodiesel using a transmission sampling cell that is filled with the biodiesel/diesel mix. The IR light passes directly through the fluid and the amount of light absorbed by the biodiesel in the sample is measured. After the spectrum is baseline corrected at specific points, the peak height at 1745 cm^{-1} is determined in order to produce a concentration reading. The concentration reading is calculated using a relatively simple calibration that uses only 5 samples and a linear regression. However, the calibration can be susceptible to differences in the base diesel. While the use of a transmission cell allows this method to analyze samples down to very low concentrations of biodiesel (below 1% v/v), it also makes measuring higher concentrations more difficult because a dilution is required. EN 14078 requires a 1:10 dilution for samples up to 11.4% and 1:20 dilution of samples between 11.4% and 22.7%. For levels above 22.7%, the dilution amount must be determined by the user. While EN 14078 is an internationally accepted method for biodiesel analysis, the difficulty in sampling makes it challenging to implement in the field. EN 14078 is well-suited for trained/lab personnel rather than field operators.

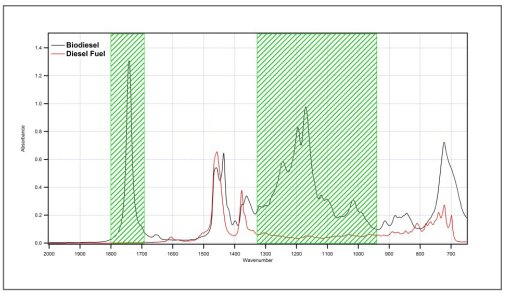


Measurement of biodiesel by EN 14078

ADVANTAGES
- Can measure low levels of biodiesel
- Simple calibration procedure
- Can measure multiple parameters
- Follows EN 14078

DISADVANTAGES
- Best suited for lab analysis
- Sample procedures require dilutions
- Susceptible to diesel differences
- Expensive equipment

ASTM D7371 measures biodiesel using an FTIR system with an ATR crystal in which the biodiesel/diesel mix is placed directly on the crystal. The IR light is reflected to the detector by the crystal and the sample being measured. The use of an ATR crystal allows for a simpler and faster analysis since no dilutions are required. ASTM D7371 uses a chemometric calibration that measures the light absorbed by the sample in the regions of 1800-1692 cm^{-1} and 1327-940 cm^{-1}. Because of the non-linearities caused by peak shifts at different concentrations, the FTIR will require 3 separate calibration ranges of 0-10, 10-30, and 30-100% biodiesel in diesel. While this chemometric analysis will accommodate differences between different types diesels and biodiesels better, it requires a large sample set that can make the calibration process time consuming. Also, any differences not included within the calibration may affect the final reading. Although it requires significant calibration effort, ASTM D7371 is a very fast and simple analysis for determining biodiesel concentration that is suitable for both the lab and the field.



Measurement of biodiesel by ASTM D7371

ADVANTAGES
- Provides fast/easy analysis
- Can be used in the field and lab
- Can measure multiple parameters
- Follows ASTM D7371

DISADVANTAGES
- Calibration process is time consuming
- Expensive equipment
- Susceptible to differences not included in the calibration

Summary

There are several methods available for both laboratory and field analysis of biodiesel in diesel fuel. The choice of method depends on budget, location of testing, time, and other factors. The most important thing is to consistently test the blend level of diesel fuels mixed with biodiesel in order to avoid any regulatory fines and prevent potential damage to the diesel engines that can be caused by too much biodiesel.

Resources

- ASTM International D7371-07: Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FT-IR-ATR-PLS Method).
- European Standard EN 14078: Liquid petroleum products – Determination of fatty acid methyl esters (FAME) in middle distillates.

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Spectro Scientific | One Executive Drive, Suite 101, Chelmsford, MA 01824-2563
978-431-1120 | www.spectrosci.com | sales@spectrosci.com | An ISO 9001:2008 company

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