wilks
simple analytical solutions

Comparison of EN 14078 and ASTM D7371 Infrared Biodiesel Methods

Infrared (IR) analysis is the most widely used measurement technology for measuring biodiesel in diesel. Both EN 14078 and ASTM D7371 methods use infrared as the analytical method and more specifically FTIR (Fourier Transform Infrared) spectroscopy. Infrared is a common spectroscopic technique used for quantitative and qualitative analysis. In the biodiesel measurement, the fatty acid methyl ester (FAME) has a characteristic absorption at 1745 cm^{-1} (5.4 micrometers) due to the carbonyl group. Both the EN and ASTM methods specify this wavelength for the biodiesel measurement.

EN 14078 uses a transmission sampling cell with typically a 0.5 mm pathlength cell. The cell 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 (see Figure 1 below). The absorbance increases and decreases with the biodiesel concentration so the IR absorbance can be correlated with a concentration in percent (see Figure 2 biodiesel spectra).

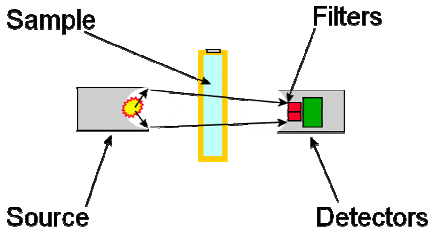


Figure 1: Schematic of a transmission sample system

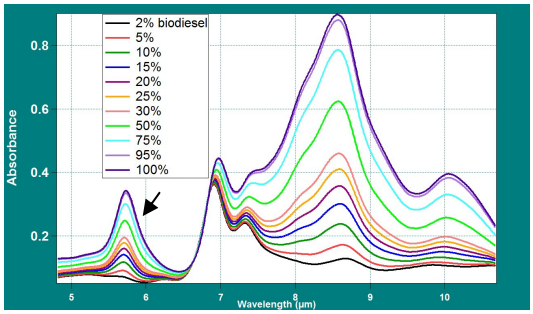


Figure 2: Schematic of a transmission sample system

One disadvantage with this method is that with a 0.5 mm pathlength cell biodiesel is completely absorbing. In order to be below the saturation point, the samples need to be diluted with cyclohexane prior to analysis. For concentrations up to 11.4%, it is a 1:10 dilution. From 11.4 to 22.7%, it is a 1:20 dilution. Above 22.7%, the EN method states “adequate dilution ratios should be used in order to bring the absorption in the specified absorbance range of the calibration”. This adds an awkward step to the analysis along with an added chance for operator error in the dilution process. If the operator does not know which range the sample falls into, it may take more than one attempt to get the correct dilution. For operators at a fuel loading dock that are not trained technicians, determining the “adequate dilution” for the “specified absorbance range of the calibration” would not be a straightforward task. The short pathlengh cell is also difficult to clean which adds the risk of leaving residual fuel in the cell that could lead to errors in subsequent analyses.

Wilks Enterprise, Inc.
25 Van Zant Street, Suite 8F
East Norwalk, CT 06855 USA
www.WilksIR.com
info@wilksir.com · Tel 203-855-9136 · Fax 203-838-9868

The calibration procedure for EN 14078 is a relatively simple one that uses five standards of biodiesel blended in cyclohexane for a linear regression calibration. One concern with this calibration method is some diesel fuels could potentially cause a baseline shift that would not be accounted for in the calibration. ASTM D 7371 uses an attenuated total reflection (ATR) sample system to overcome the limited measurement range of a transmission sample system. With ATR, infrared light is focused onto one end of a crystal (such as zinc selenide or diamond) and the light bounces through the crystal penetrating about 1 micrometer into the sample which is placed on the ATR crystal. The light reflects back into the crystal and is focused back onto a detector (see Figure 3). The short effective pathlength of the ATR crystal allows for a sampling range as low as 0.2% up to 100% biodiesel. The exposed ATR crystal is easy to clean, reducing the possibility of contamination in future samples.

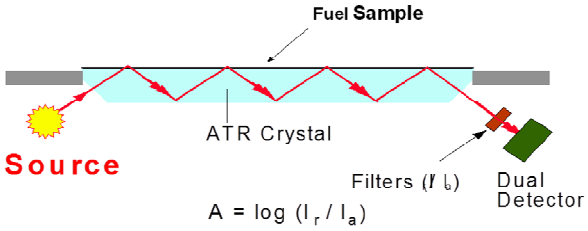
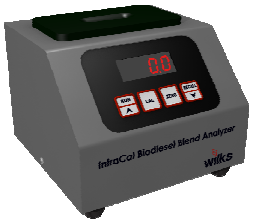


Figure 3: Schematic of an ATR sample stage

D 7371 utilizes a chemometric calibration to account for the baseline offset that could come from different diesel fuels. The calibration requires 70 calibration standards and uses three base diesel fuels (low cetane index, high cetane index and ultra high cetane index). While a chemometric calibration will help with reducing the effect of diesel, chemometric calibrations perform better if samples in the calibration data set contain as much variety as could be seen in the field. This would require an unwieldy number of samples so the reasonable decision uses three diesels to span the potential variation. As with the linear regression calibration in EN 14078, ASTM D 7371 will also experience some outliers due to the diesel fuel.

The Wilks InfraCal Biodiesel Blend Analyzer (pictured to the right) incorporates the most trouble-free portions of each method providing an infrared analyzer that is less expensive, simple to operate and more rugged than an FTIR. The filter based analyzer uses the carbonyl band for measuring biodiesel that is called out in EN 14078 and ASTM D 7371. Since the filter is mounted directly onto the detector, the analyzer has no moving parts which add to its durability and portability. It is rugged enough to be located at the loading rack at a fuel terminal or for operation out of a truck for testing at a fuel pump.



The InfraCal Biodiesel Blend Analyzer uses a linear calibration similar to the EN 14078 method which simplifies the calibration procedure. The exposed ATR crystal allows for easy introduction and cleaning of the sample, as well as the extended measurement range from 0.2-100% without the need for sample dilution. For the operator, all it takes to make a measurement is to place the sample on the sample plate, select the “run” button and the result is displayed within a minute. The plate is cleaned and the analyzer is ready for the next sample.

While FTIR spectrometers have the capability to do much more than a simple biodiesel blend analysis, the InfraCal Biodiesel Blend Analyzer is an ideal workhorse to provide on-site biodiesel measurements for those individuals who only need to do a routine blend check.

Wilks Enterprise, Inc.
25 Van Zant Street, Suite 8F
East Norwalk, CT 06855 USA
www.WilksIR.com
info@wilksir.com · Tel 203-855-9136 · Fax 203-838-9868