Test method for low level detection of biodiesel in diesel using the Agilent 5500t FTIR spectrometer

Application Note

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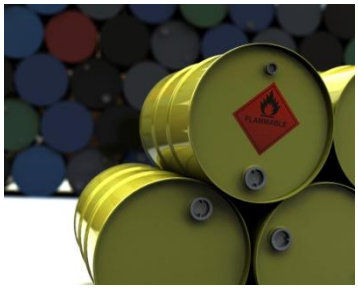

Introduction

Agilent Technologies 4500t and 5500t FTIR spectrometers are gaining rapid acceptance for measuring biodiesel (%FAME) in diesel fuel for applications where low level contamination of diesel fuel by FAME is problematic. Diesel fuel containing up to 5 % biodiesel meets the ASTM D975 standard, which does not require disclosure of the biodiesel level, and this can be a significant issue for certain diesel fuel users. Agilent has now developed an enhanced method for determining contamination levels of FAME in diesel. This method combines the more sensitive transmission IR sampling interface specified in EN 14078 with the universal algorithm and sample set specified in ASTM D7371 to produce the most sensitive and accurate method available. This enables the 5500t FTIR systems to quickly and accurately predict the percentage of biodiesel in diesel fuel in the range from 0.025 % to 20 %. In round robin testing, the accuracy of this method has been found to be superior to the other methods, especially for measuring low levels of biodiesel.

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Instrumentation

The Agilent biodiesel test method was designed around the 5500t FTIR series of portable spectrometers, equipped with the innovative, patented sampling interface. This sampling system has been engineered to provide a highly reproducible 100 micron transmission pathlength, as called for in the EN 14078 method. The sample interface is one area where the ASTM method differs from the EN method. The ASTM method specifies an attenuated total reflectance (ATR) sample interface; the EN method specifies a transmission sample interface. The ASTM ATR method is easy to use, but does not provide the level of detection required for measuring biodiesel contamination; the EN transmission cell method provides the sensitivity required, but traditional IR transmission cells are not easy to use with respect to both filling and cleaning, particularly for viscous liquids like diesel fuel.

Agilent FTIR transmission sampling interface is unique in that it provides the sensitivity and limit of detection as required in EN14078, but at the same time is as easy to use as the ATR cell employed in ASTM D7371. In the sampling system, the upper window of the transmission cell is mounted in a precision rotating assembly. This opens by rotating this window into the upward position. Then, a single drop of fuel is placed on the bottom transmission window, the upper window is then rotated back into the closed position creating a path length of 100 micrometers. Clean-up is equally straightforward, since the sample is simply wiped from the windows when the FTIR instrument is in the open position. This patented sample interface gives the ease of use of the ATR measurement with the path length and sensitivity of a transmission measurement. Furthermore, the design provides a path length reproducibility of better than 0.2 micrometers. Representative spectra measured on the 5500t FTIR spectrometer of biodiesel in diesel are shown in Figure 1.

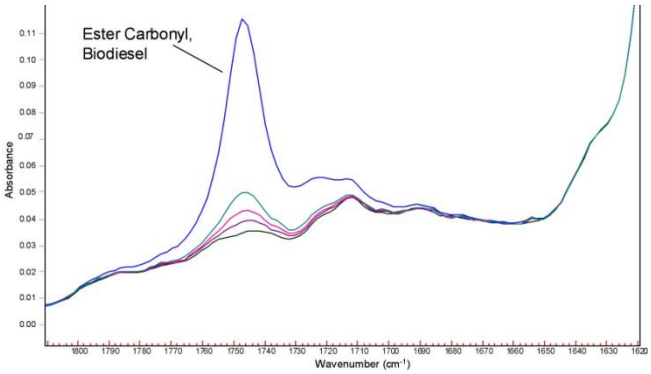

Figure 1. The overlaid IR spectra of diesel fuels with various ultra low concentrations of biodiesel, at 0.50 % (Blue), 0.10 % (Lt. Green), 0.05 % (Red), 0.025 % (Maroon), and 0.00 % (Dk. Green)

Calibration

In order to produce a quantitative measurement, the spectra generated from an infrared spectrometer must be calibrated with quantitative samples. The ASTM and EN methods specify different methods of quantitation. Both methods measure the carbonyl absorbance of the fatty acid methyl ester molecule; the EN method uses a simple linear fit to the band height while the ASTM method uses a multivariate, partial least squared (PLS) method. The univariate method specified in the EN method directly follows a Beers law calibration. As specified in the method, the absorbance of the carbonyl stretching frequency at 1745 cm^{-1} is measured with local baseline points at 1820 cm^{-1} and 1770 cm^{-1}. The absorbance intensity is then plotted against the concentration of 10 standards. A linear fit is used for the calibration curve.

ASTM D7371 specifies a more complicated multivariate PLS method. The method is still based on Beers Law; however, the full spectrum technique better accounts for baseline effects and interferents. In addition to the different algorithm, the ASTM method specifies a large collection of samples. The samples cover the entire calibration range and are made in three different diesel formulations: low, high, and ultra high Diesel Cetane Check Fuel (DCCF-Low, DCCF-High, and DCCF-Ultra High). The DCCF basestock fuels and biodiesel B100 used to create the biodiesel calibration and qualification

standards are in compliance with specifications described in Annex 2 (A2.1, A2.2.1, A2.2.2, and A2.2.3). Varying the aromatic content of the diesel fuel used in the calibration and qualification sets creates a more robust and accurate PLS model.

Agilent's transmission IR based method incorporates 3 calibration models similar to the ASTM 7371 method; the Microlab software automatically selects the result from the correct calibration to display without any user input. The calibration ranges are 0.025-1 %, 1-10 %, 10-25 % biodiesel in petroleum diesel. The PLS model for the low biodiesel range (0.025-1 %) consisted of 70 spectra preprocessed with mean centering, baseline correction, and thickness correction and uses a portion of ester carbonyl region of the mid IR spectrum (1950-1720 cm^{-1}) similar to the ASTM 7371 method.

The calibration for the second range (1-10% biodiesel) consists of 46 spectra preprocessed with mean centering and baseline correction. The model uses a portion of ester carbonyl region of the mid IR spectrum (1800-1720 cm^{-1}) similar to the ASTM 7371 method. The third calibration (10-25 % biodiesel) uses 40 spectra preprocessed with mean centering and baseline correction preprocessing. Three spectral regions are used : the ester carbonyl at 1846-1758 cm^{-1} and 1738-1719 cm^{-1}, and the ester C-O stretch at 1327-1119 cm^{-1}

Method Performance

Each calibration model was tested with both a cross validation (leave one out) and a separate validation set. The cross validation data was used to calculate the standard error of cross validation (SECV) and to prepare an actual versus predicted plot. The correlation of the actual versus predicted plot was also calculated. The results of each model are listed in Table 2. All models produced a correlation greater than R_2= 0.999 and an average relative error for the separate validation set of less than 1.5%.

The Agilent method was compared to the ASTM 7371 method by two other analytical labs in a blind round robin experiment initiated and conducted by a third party. Twenty samples were received with no identification of their composition and run with the 5500t FTIR. The Agilent method performed the best of all six biodiesel methods, including the ASTM 7371 methods. The total average relative error was only 2.1% (all samples, 2-20% range), the low level accuracy was much better than any other method at only 1.1% relative error.

Range	SECV	R^2	#Validation Samples	Avg. Relative Error
0.025 - 1 %	0.0016 %	0.9999	29	1.37 %
1% - 10 %	0.0164 %	0.9999	12	0.06 %
10% - 20%	0.04 %	0.9999	8	0.57 %

Conclusion

Two established standard techniques exist for measurement of biodiesel in fuel by infrared spectroscopy: ASTM D7371 and EN 14078. Unfortunately, both of those methods are focused on measurement of levels consistent with blended fuels; they do not address the needs of users who need to minimize the amount of biodiesel in their fuel supply. Agilent Technologies, employing its 5500t FTIR system, combines the transmission sample interface specified in the EN 14078 method with the algorithm and standards specified in ASTM E7371, yielding a method that accurately predicts the percentage of biodiesel in diesel fuel in the range from 0.025 % to 20 %. The accuracy of this method has been tested and found to be superior to other methods, especially for low levels of biodiesel. Thus, users who must quickly and accurately detect low level biodiesel contamination in their diesel fuel supply will find this new technology and methodology of great value.

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