Portable measurement of biodiesel in diesel fuels by ASTM D7371-07 (FTIR-ATR-PLS method) with the Agilent 5500t FTIR spectrometer

Application Note

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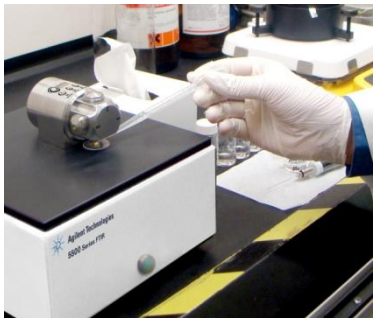

Background

Biodiesel blending with current ultra low sulfur diesel (ULSD) fuels is increasing in popularity for both large scale fleet use and individual small scale consumers. The test method detailed in this application brief can be used for quality control purposes in the production and distribution of diesel fuel and biodiesel blends. The ASTM D7371 method is applicable to 1-100 volume % biodiesel (FAME) concentrations in diesel fuel oils; it applies to all common 5 % (B5), 10 % (B10), and 20 % (B20) biodiesel blends. The ASTM D7371 method coupled with the Agilent 5500t FTIR spectrometer provides an easy, accurate, and portable means for measuring the biodiesel content of a blended fuel with petroleum diesel fuel.

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Experiment

Following the ASTM D7371 procedures, three different diesel fuels are used to create the calibration standards. The cetane index in diesel fuels is varied by changing the relative percentage of aromatic to aliphatic hydrocarbons; higher cetane index fuels have less aromatic compounds. Cetane index is typically lower during cold months. The ASTM D7371 is designed to account for these seasonal differences in the diesel fuels. The ASTM certified B100 Biodiesel was mixed with diesel fuel blended at three different cetane indexes, referred to in the D7371 as diesel cetane check fuel low, high and ultra high. As specified in the method, a total of 70 standards were produced with biodiesel concentrations ranging from 0-100%. In addition to the calibration standards, 21 qualification standards were created with different concentrations than the calibration standards. The qualification standards were used to determine the method's accuracy and robustness.

All standards were measured using the Agilent 5500 Series FTIR spectrometers with an integrated 9 reflection diamond attenuated total reflectance (ATR) sample interface. The spectra were collected using 64 scans at 4cm-1 resolution yielding a 30 second sample measurement time. A partial least squares (PLS) model was developed using Thermo Galactic PLS/IQ software. The model concentrates on the ester carbonyl and other absorbance bands specific to fatty acid methyl esters (FAME). The PLS models were incorporated into Microlab software for an easy end-user biodiesel in diesel fuel application.

Results

A series of spectra from the calibration set are shown in Figure 1. Bands due to biodiesel can be seen both at 1741cm^{-1} and between 1170-1245cm^{-1}; these areas are correlated to the concentration of biodiesel in the D7371 method. The absorbance increases linearly with the concentration throughout the whole range from 0-100 %.

This provides a very accurate and precise measurement using the 5500 Series FTIR spectrometers.

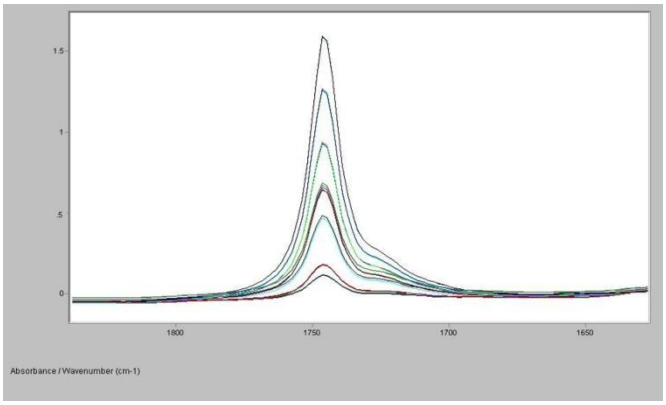

Figure 1. FTIR spectra overlaid of ASTM D7371 standards with biodiesel in diesel at 0, 2.5, 5, 10, 15, 20, 30, 50, 70, and 100 % biodiesel (v/v)

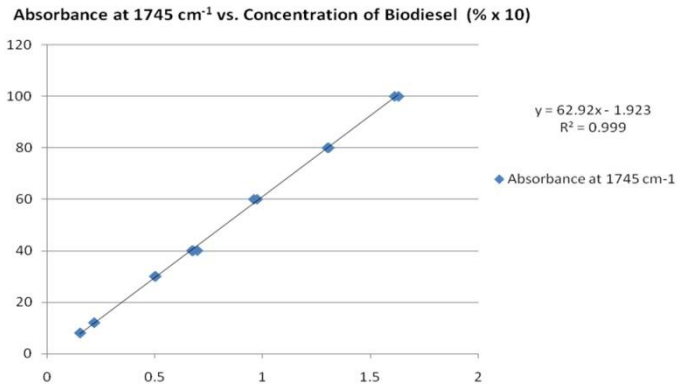

Figure 2. The PLS model's actual vs. predicted plot of biodiesel in diesel, low calibration set (0-10 % biodiesel)

ASTM D7371 specifies individual calibration models for the concentration ranges 0 -10 %, 10 - 30 % and 30 -100 %; each calibration model contains standards from each of the three cetane index diesel fuel stocks (ultra high, high and low). The 0-10 % calibration model results are plotted in Figure 2 as the actual (x-axis) vs. predicted (y-axis) biodiesel concentrations. The correlation coefficient for this model is R_2= 0.999. Results for the 10 - 30 % and 30 - 100 % models were similar. Each model uses 3 - 4 factors on mean centered data.

The three models based on the ASTM D7371 method were incorporated into a single method within the Microlab software. A screen shot showing one of the calibration definitions definition is shown in Figure 3.

The Microlab software also contains logic to report only the result from the correct model.

Using the "Component Reporting" feature, shown in Figure 4, which result will be shown to the user based on the predicted result. Using this feature, a single, correct result is present to the user even though results from three methods are calculated. This reduces confusion and allows samples to be measured by untrained users.

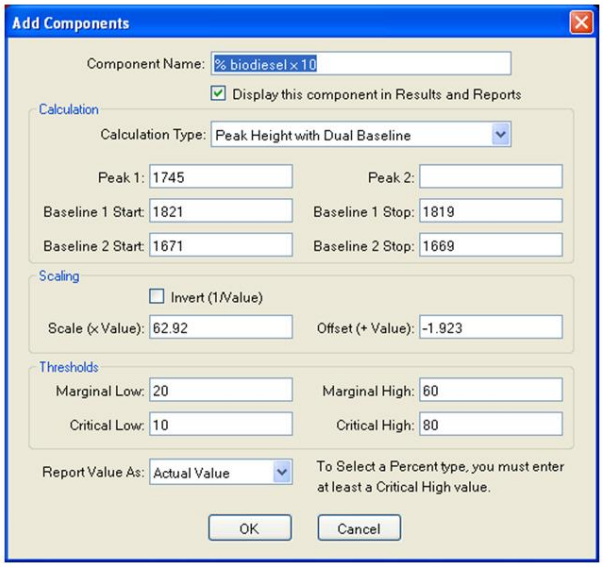

Figure 3. The Microlab methods editing feature where the 1-10 % biodiesel model is assigned

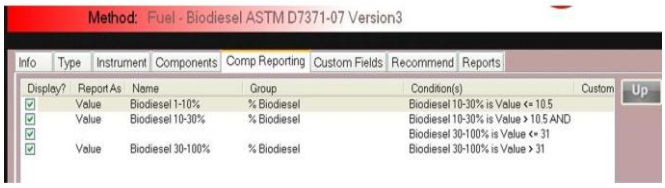

Figure 4. The conditional reporting setup window from the Microlab PC software, which determines the model results to be displayed when running a sample

The Microlab ASTM D7371 method was used to predict the concentrations of a separate qualification set. The qualification set covers the entire 0-100 % range of biodiesel in diesel, and the different cetane index diesel fuels were also used to make the qualification samples. The average relative error (1-100 % range) is 0.47 % and the maximum relative error is 1.56 %. The results of the separate validation are shown in Table 1. It should be noted that the standard error of qualification calculated for these tests is less than half the acceptable standard error of qualification listed in the ASTM method. A screen shot showing the software display for a 2.5 % biodiesel validation sample is shown in Figure 5.

Figure 5. Microlab results screen for a 2.50 vol % sample of biodiesel in diesel

Table 1. The results from the qualification set samples measured with the ASTM 7371 method in the Microlab software

Qualification Sample	Predicted Biodiesel (Vol %)	Actual Biodiesel (Vol %)	Error (%)
Q1	0.77	0.71	8.61
Q2	5.98	5.95	0.55
Q3	13.14	13.14	0.01
Q4	26.50	26.44	0.24
Q5	59.05	58.73	0.54
Q6	92.12	92.07	0.05
Q7	97.73	97.77	0.04
Q8	0.36	0.36	0.77
Q9	1.64	1.66	1.56
Q10	5.91	5.94	0.49
Q11	38.51	38.69	0.47
Q12	84.16	84.39	0.27
Q13	95.74	95.88	0.14
Q14	99.11	99.30	0.20
Q15	0.35	0.36	1.09
Q16	3.60	3.55	1.28
Q17	8.35	8.31	0.43
Q18	13.15	13.10	0.39
Q19	21.17	21.49	1.50
Q20	73.70	73.65	0.06
Q21	95.66	95.49	0.18
		Average Error Total (%)*:	0.47
		Maximum error (%*):	1.56
		Standard Error of Qualification (SEQ):**	0.08
		ASTM D7371 SEQ Limit (PSEQ):	0.21

Conclusions

This set of experiments show the ability of Agilent 5500 Series FTIR spectrometers with 9 reflection diamond ATR sample interface to meet the ASTM D7371 method. The method file which calculates the concentration in all ranges from 1 % to 100 % biodiesel and selectively reports the correct concentration is standard with all 5500 FTIR and 4500 FTIR systems. The results from a separate validation show that the instrument and method are very accurate while being very simple to use.

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