ASTM D7806-12 for Biodiesel in Petroleum-based Diesel Fuel Oil

Agilent 4500, 5500, and Cary 630 FTIR

Application Note

Energy and Chemicals

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Introduction

Biodiesel is usually an effective blending component for petroleum-based diesel fuel. However, biodiesel-mixed diesel fuel can be a problem in engines designed for only petroleum-based diesel. Also, blended biodiesel can promote biological growth and increase instability of the diesel fuel resulting from the buildup of oxidation products. Thus, biodiesel-blended diesel fuel can cause issues in stationary standby diesel engines, such as those used in nuclear plants.

The ASTM D7806-12 test method was developed for the determination of biodiesel (FAME) content in diesel fuel oils in the concentration range from 1 to 30% by volume. In this application note, we demonstrate the applicability of any of the three Agilent FTIR spectrometers (4500, 5500, and Cary 630) to this method. The Agilent systems can be used for:

- Quality control in the production and distribution of diesel fuel and biodiesel blends containing FAME
- Routine checks of incoming blended diesel fuels from a distributor

The Agilent FTIR spectrometers demonstrated excellent repeatability (X ± 0.02%), better than X ± 0.3% as defined in the ASTM D7806-12 method, where X is the biodiesel concentration. Whether the biodiesel content of a blended fuel needs to be tested in the lab or in the field, the three Agilent spectrometers provide an easy, accurate, and portable means for measurement. This gives analysts the flexibility to choose the best instrument based on their routine analysis requirements.

Agilent Technologies

Agilent FTIR spectrometers used for biodiesel analysis

Agilent 4500 Series

- Dedicated portable analyzer
- On-site analysis of biodiesels in pipelines and fuel tanks

Agilent 5500 Series

- Dedicated lab analyzer
- Biodiesel analysis in on-site production control labs

Agilent Cary 630

- Highly compact general purpose lab FTIR for QA/QC and methods development

Methods and Materials

Low, high, and ultrahigh cetane diesel check fuels were used to create the calibration standards. The calibration set in the biodiesel concentration range of 0 to 6% and 6 to 30% was used to build the calibration models. The calibration plot for the 0 to 6% range consisted of six calibration standards, and the plot for the 6 to 30% range consisted of 10 standards, for each cetane check fuel. Each cetane check fuel contained 16 standards from 0 to 30% biodiesel for the calibration model. Following ASTM D7806-12, a calibration set for concentration ranges 0 to 6% and 6 to 30% was prepared, where each calibration set contained standards from each of the three cetane check fuel stocks (low, high, and ultrahigh). Eighteen calibration standards were used for 0 to 6% and 30 standards for 6 to 30% biodiesel. In addition to the calibration standards, 20 qualification standards were made with concentrations different to the calibration standards. These qualification standards were used to determine method accuracy and robustness.

All standards were measured in each of the Agilent FTIR spectrometers; the 4500 series with TumbIIR, the 5500 series with DialPath, and the Cary 630 with TumbIIR and DialPath. The spectra were collected using 64 scans and 4 cm^{-1} resolution at specified 100 µm pathlength. A linear regression calibration model was separately developed for the low (0 to 6%) and high (6 to 30%) concentration ranges. As specified in the method, the area from 1,713 to 1,784 cm^{-1}, using a baseline from 1,708 to 1,785 cm^{-1}, was calculated for the low concentration range. Similarly, using a two-point baseline from 1,126 to 1,225 cm^{-1}, the area from 1,126 to 1,220 cm^{-1} was calculated for the high concentration range. The calculated peak absorbance areas were then plotted against the concentration values to generate a linear least squares regression. The resulting calibration constants were then used to add the models into the Agilent MicroLab software.

To provide higher accuracy in the measurement, calibration models were also developed for each cetane check fuel (low, high, and ultrahigh) separately, in the two biodiesel concentration ranges. Six models were generated. Linear calibration models were developed, as specified in the ASTM D7806-12. Also, a quantitative model was developed to predict the cetane index value of the petroleum diesel fuel in which the biodiesel was blended. The cetane index value differentiates the cetane level as low, high, or ultrahigh.

Results and Discussion

The regions of the spectra used to build the calibration models are shown in Figure 1. Biodiesel methyl ester band intensities from 1,713 to 1,784 cm^{-1} (ester carbonyl) and 1,126 to 1,220 cm^{-1} (ester C-O stretch) increase as the concentration of the biodiesel increases in the diesel fuel oil.

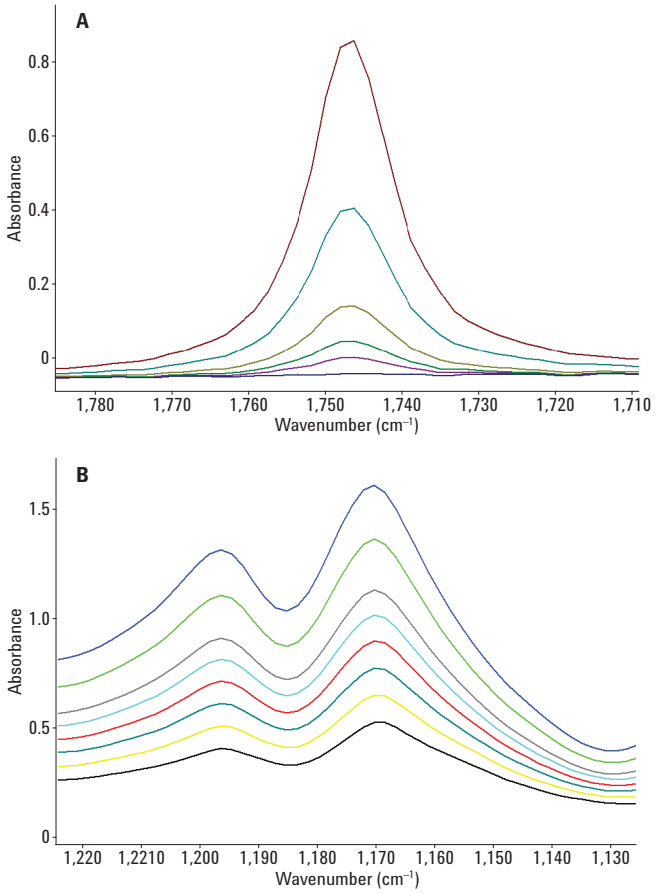

Figure 1. Overlaid IR spectra of diesel fuels with various biodiesel concentrations in high cetane diesel fuel (A) absorbance region 1,713 to 1,784 cm^{-1} used in the calibration for the concentration range 0 to 6% and (B) absorbance region 1,126 to 1,220 cm^{-1} used in the calibration for the concentration range 6 to 30%.

The 0 to 6% and 6 to 30% biodiesel calibration plots in high cetane check fuel are shown in Figure 2. Results for the low cetane and ultrahigh cetane check fuels are similar. Two models were developed for the two concentration ranges for each of the three cetane check fuel stocks. Similarly, two models in the concentration ranges were developed using all the cetane check fuels, as specified by ASTM D7806-12. All models were incorporated into a single method within the MicroLab software.

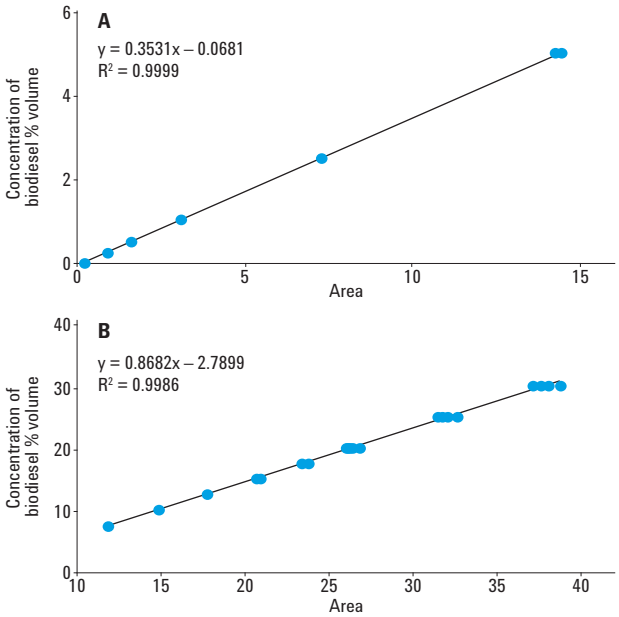

Figure 2. Calibration plot of high-cetane diesel fuel with different biodiesel concentrations (A) 0 to 6% and (B) 6 to 30%.

Based on conditions set by the cetane index value and biodiesel concentration, Agilent MicroLab Software automatically chooses the correct calibration model and provides accurate measurement of a sample (Figure 3).

As an example, a screen display of results (Figure 4) shows both visually (green) and numerically that the biodiesel value is within the preset threshold limit. This contrasts with another sample that is beyond the threshold limit, indicated in red. Threshold values can be defined for the method as their analysis demands.

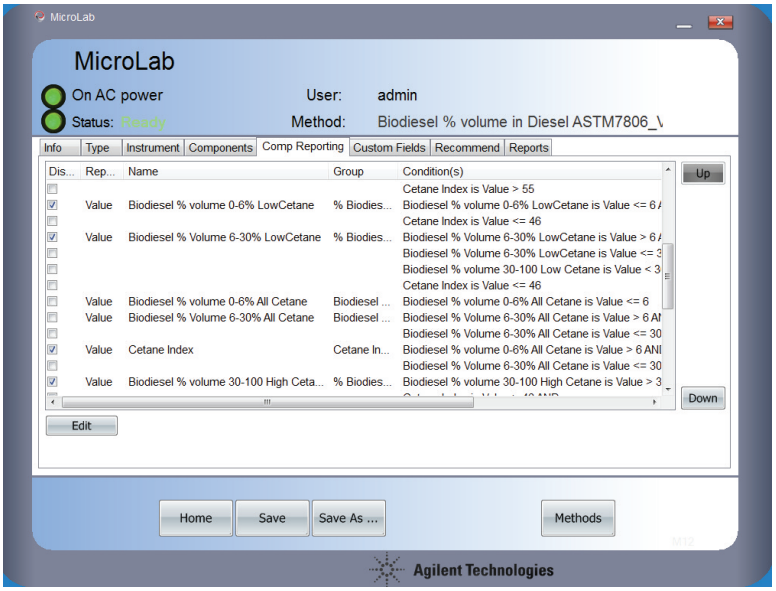

Figure 3. The component-reporting feature in Agilent MicroLab Software sets the proper conditions in the method.

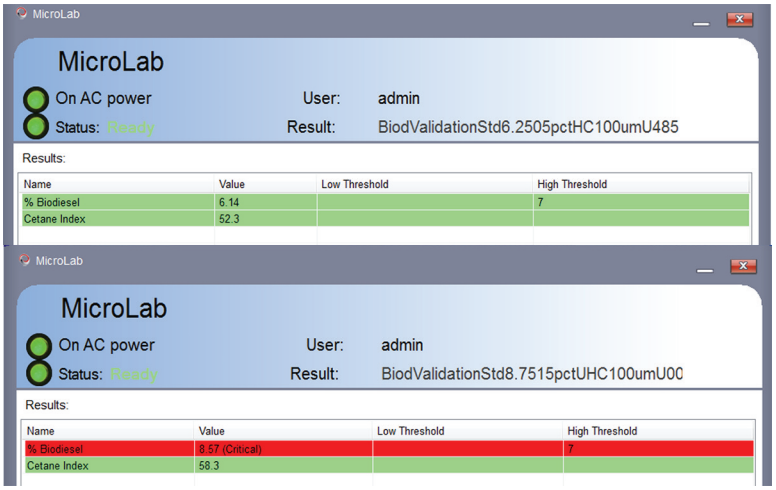

Figure 4. Agilent MicroLab Software display with the threshold setting in the method.

The advantages of Agilent MicroLab Biodiesel Analysis Software

- An intuitive, push-button operation executes preloaded and precalibrated methods.
- A single method contains the calibration models required to cover the 0 to 6% and 6 to 30% ranges specified by ASTM D7806-12.
- A unique conditional reporting feature picks the right calibration model for the biodiesel concentration range.
- Color-coded results alert you if your sample exceeds threshold limits (that is, out of specification).
- You can define threshold limits.

The MicroLab ASTM D7806-12 method was used to predict the concentrations of a separate qualification set. The set included the qualification standards from all cetane check fuels, and covered 0 to 30% biodiesel. The results of the separate validation are shown in Table 1. One important consideration in the ASTM D7806-12 method is its applicability to concentrations from 1 to 30% biodiesel. The MicroLab method can predict biodiesel concentrations below 1%, and above 30%, but the relative error is greater. A separate calibration model is added to the method for the biodiesel concentration prediction from 30 to 100%.

Table 1. Qualification set samples measured using the ASTM D7806-12 method in the Agilent MicroLab Software.

Qualification sample	Predicted biodiesel (vol %)[a]	Actual biodiesel (vol %)	Error (%)
Q1	3.76 ± 0.08	3.76	0.00
Q2	11.28 ± 0.38	11.27	0.09
Q3	15.97 ± 0.50	15.85	0.76
Q4	22.18 ± 0.70	21.99	0.86
Q5	1.76 ± 0.06	1.75	0.57
Q6	6.13 ± 0.18	6.25	1.92
Q7	13.88 ± 0.38	13.75	0.95
Q8	18.86 ± 0.52	18.75	0.59
Q9	27.55 ± 0.80	27.51	0.15
Q10	3.73 ± 0.10	3.75	0.53
Q11	8.75 ± 0.26	8.75	0.00
Q12	13.85 ± 0.40	13.75	0.73
Q13	16.45 ± 0.48	16.25	1.23
Q14	22.57 ± 0.66	22.51	0.27
		Average error (%)	0.62
		Maximum error (%)	1.92

[a] Average of 14 measurements from three instruments ± two standard deviations.

Based on the validation set results (Table 1), the average relative error was 0.6%, and the maximum relative error was 1.9% from 1 to 30% biodiesel. The average relative error increased to 4.3%, and the maximum error was 7.7% for the qualification standards from 0 to 1% biodiesel. The quantitative model in the method calculates and reports the correct cetane index value of the diesel fuel until the biodiesel blend mix reaches 30% by volume. The cetane index value, which discriminates the cetane check fuel as low, high, and ultrahigh, is used to choose the correct model among those developed for each cetane check fuel. The main advantage of using the calibrations developed for each cetane check fuel separately, compared to the calibrations that are built using all the cetane check fuels together, is lower relative error. Due to the difference in aromaticity and density of the cetane check fuels, the model developed separately provides more accurate measurement, when compared to models developed with all cetane fuels together (Table 2). When the models are built using all levels of cetane fuels, the results are biased and tend to favor high-cetane check fuels. In the MicroLab method, the default is setup for the calibrations that are built separately. However, you can choose the calibration build for all cetane check fuels together, if necessary.

Table 2. Comparison of calibration model built using cetane check fuels together or separately.

			All cetane check fuels together calibration		Each cetane check fuel separate calibration	
	Qualification sample	Actual biodiesel (vol %)	Predicted biodiesel (vol %)[b]	Error (%)	Predicted biodiesel (vol %)[b]	Error (%)
Low cetane	Q1	3.76	3.8 ± 0.08	1.06	3.76 ± 0.08	0.00
	Q2	11.27	11.71 ± 0.36	3.90	11.28 ± 0.38	0.09
	Q3	15.85	16.35 ± 0.54	3.15	15.97 ± 0.50	0.76
	Q4	21.99	22.49 ± 0.70	2.27	22.18 ± 0.70	0.86
High cetane	Q5	1.75	1.76 ± 0.06	0.57	1.76 ± 0.06	0.57
	Q6	6.25	6.15 ± 0.18	1.60	6.13 ± 0.18	1.92
	Q7	13.75	13.91 ± 0.36	1.16	13.88 ± 0.38	0.95
	Q8	18.75	18.91 ± 0.52	0.85	18.86 ± 0.52	0.59
	Q9	27.51	27.62 ± 0.80	0.40	27.55 ± 0.80	0.15
Ultrahigh cetane	Q10	3.75	3.68 ± 0.10	1.87	3.73 ± 0.10	0.53
	Q11	8.75	8.3 ± 0.26	5.14	8.75 ± 0.26	0.00
	Q12	13.75	13.42 ± 0.40	2.40	13.85 ± 0.40	0.73
	Q13	16.25	16.03 ± 0.48	1.35	16.45 ± 0.48	1.23
	Q14	22.51	22.19 ± 0.66	1.42	22.57 ± 0.66	0.27
Average error (%)				1.94		0.62

[b] Average of 14 measurements measured with three instruments ± two standard deviations.

Conclusions

The results demonstrate that Agilent 4500, 5500, and Cary 630 spectrometers, equipped with Agilent proprietary TumbIR and DialPath sampling technology, easily meet the requirements of ASTM D7806-12. The method file includes an added feature, which calculates concentration not only from 1 to 30% biodiesel as indicated in ASTM D7806-12, but also below 1% and above 30% for each diesel cetane check fuel. The average relative error as determined by the method was 0.62% for 1 to 30% biodiesel. The method also reports the cetane index value, which aids in identifying the diesel cetane fuel. The qualification standard results show that the instruments and method are accurate and precise.

These Agilent spectrometers are available for lab or field use, without compromise in performance and ease-of-use, enabling you to choose the system that best meets your requirements.

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