Low Level Detection of Biodiesel in Diesel Fuel Using the PAL™ Spectrometer

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Background:

Recent increases in production of biodiesel along with the high cost of crude oil have encouraged some producers to mix biodiesel with regular diesel fuel. Although biodiesel provides some environmental advantages, problems have been reported in the use of mixed fuels in engines designed for petroleum based diesel. Additionally, biodiesel can promote biological growth in the diesel fuel when stored for a period of time. In response to these issues there is a need to determine if biodiesel is present in regular diesel fuel, especially for industries which store large amounts of diesel fuel. The European Union has recently released regulations requiring the measurement of biodiesel in diesel and has issued an analytical test method, EN 14078, for testing.

In the United States, a recent ASTM ruling (D-975) allows shipments of up to 5% biodiesel in fuel without notification to the customer. This notification requirement does not meet the needs of all industries. As an example, the U.S. Nuclear Regulatory Commission (NRC) suggests lower limits for biodiesel in fuel blend for stationary standby diesel engines at nuclear plants because of the potential for instability of the higher percent biodiesel blends resulting from the buildup of oxidation products. These conflicting rulings make it incumbent on the user to verify the level of biodiesel before being placed in long-term storage.

The PAL spectrometer from A2 Technologies provides an easy to use means of measuring biodiesel in diesel. The EN 14078 method comes pre-programmed on the PAL; this method can determine the amount of biodiesel in the range between 1% and 10%. The design is easy to use and provides nearly instant answers. In some cases, however, even lower levels of detection are required. To meet these needs, A2 Technologies has modified the EN 14078 method to provide detection down to 0.025% biodiesel in diesel. The Low Level Biodiesel in Diesel method can quantitatively determine the amount of biodiesel in the range from 0.025% to 5% with the same easy to use PAL system.

Experiment:

Six standards of biodiesel in diesel were made by successive dilution in the range from 0.0 to 1.5 %. Each concentration was measured using an A2 Technologies PAL™ spectrometer with a 100 µm path length Tumbler™ transmission cell; 32 scans were collected at 4 cm^{-1} resolution yielding a 15 second sample measurement time. Measurements were made in triplicate on two separate instruments. A calibration curve was made using the 1745 cm^{-1} carbonyl band specified in the EN14078 method. The EN method specifies peak height but to achieve lower limits of detection the peak area was used in this method.

Results:

Figure 1 shows the carbonyl region of the spectrum of the 6 samples tested plus a blank. The lowest concentration of 0.025% is clearly visible with an absorbance which can be discerned over the blank. The absorbance increases linearly all the way to the highest concentration at 1.5% biodiesel.

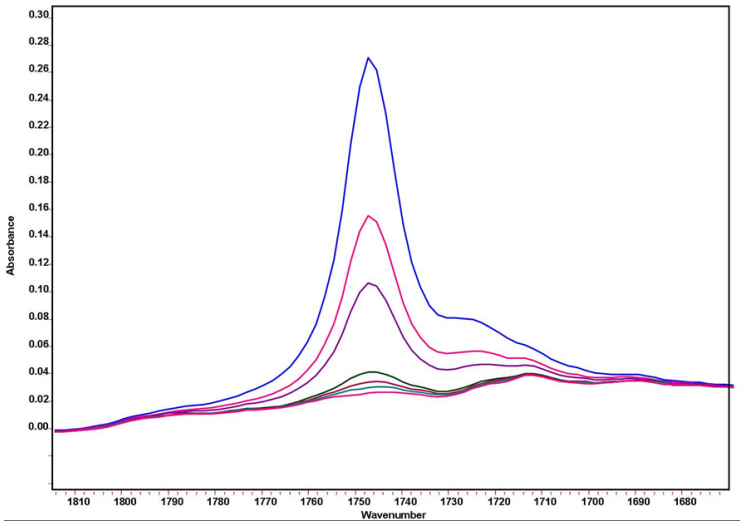

Figure 1: Absorbance at 1745 cm^{-1} of biodiesel in diesel fuel at 0.0, 0.025, 0.05, 0.1, 0.5, 0.8 and 1.5 % (v/v).

The calibration plot of the peak area of the 1745 cm^{-1} band is shown in figure 2. The plot shows an excellent correlation of R^2 = 0.9998.

The data from the calibration was used to generate a method in the MicroLab software. The method is shown in Figure 3.

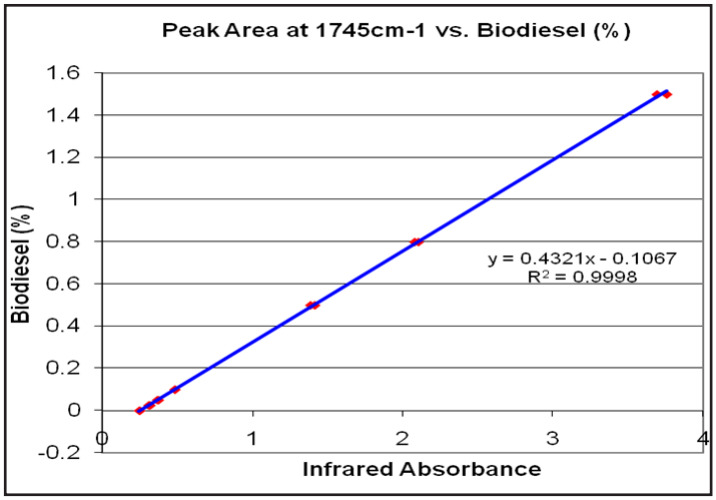

Figure 2: Calibration plot of biodiesel in diesel fuel showing linear fit of absorbance from 0 to 1.5 % (v/v).

Actual %	Peak Area Abs at 1745	Predicted %	Error (%)
0	0.245	0	0.0
0.025	0.307	0.025	0.0
0.050	0.365	0.049	2.0
0.100	0.482	0.101	1.0
0.5	1.385	0.491	1.8
0.8	2.078	0.790	1.3
1.5	3.691	1.488	0.8
3.0	7.122	2.971	1.0
5.0	11.674	4.938	1.2
	Average Error:	1.0	
	Maximum Error:	2.0	

Table 1: Results from samples measured with the biodiesel method in the MicroLab software.

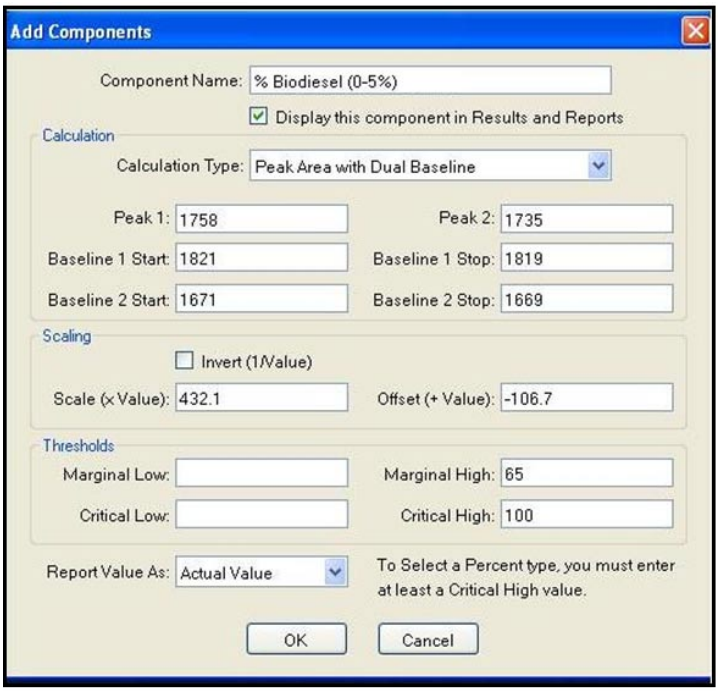

Figure 3: Biodiesel method in MicroLab software.

This method was used in the MicroLab software to predict the concentration of a separate validation set. The validation set ranged from 0 to 5% biodiesel in diesel. The average relative error was 1% with a maximum relative error of 2%. These results indicate that the same method can be used to predict concentrations at least as high as 5%. The results are shown in Table 1, and an example of the MicroLab software results screen is shown in Figure 4.

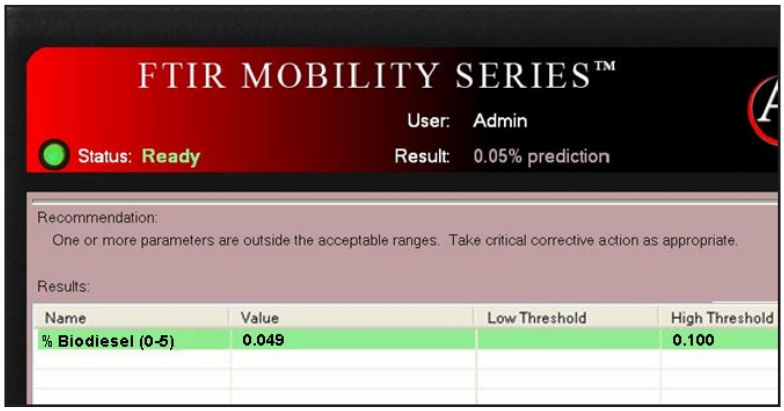

Figure 4: MicroLab results screen for a 0.05 % sample of biodiesel in diesel.

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