

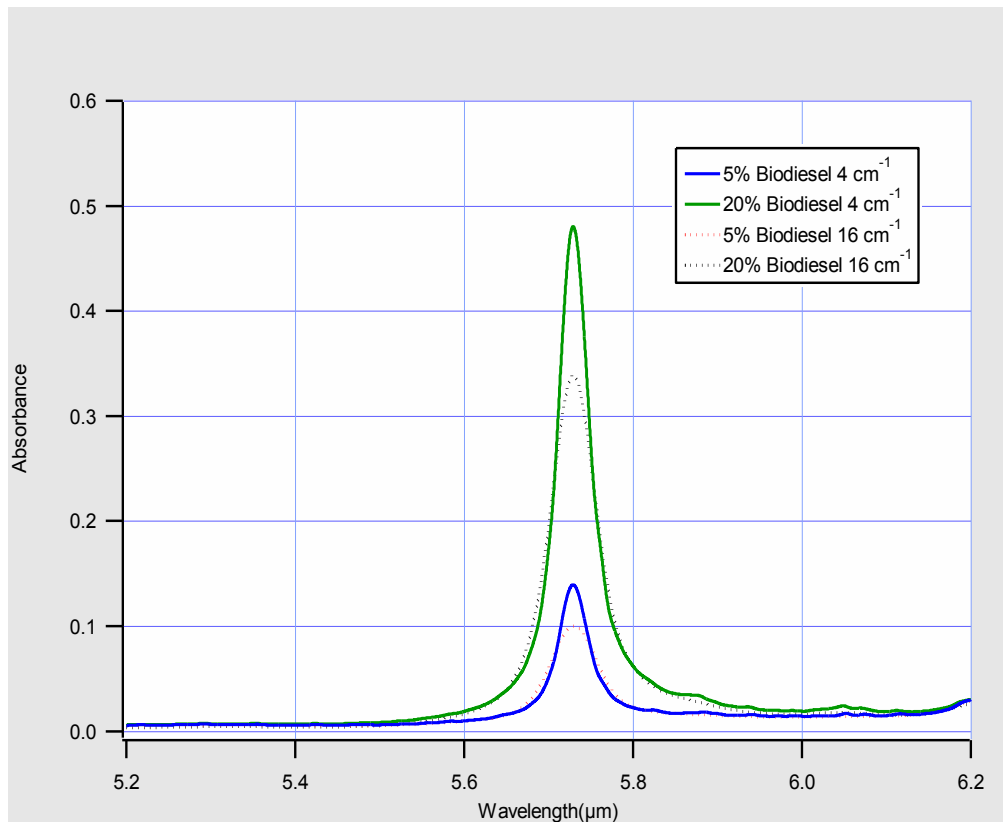
## **Lower Resolution Infrared (IR) Spectroscopy Can Provide Higher Performance for Quantitative Biodiesel Measurements**

Resolution is often used as a yardstick of instrument performance in Infrared Spectroscopy. This is especially true when the measurements are energy limited as they are in the mid-infrared. For example, in both the European and ASTM standards - EN14078 and ASTM D7371 - for the determination of biodiesel in diesel fuel, a  $4\text{ cm}^{-1}$  resolution is specified which is a relatively high resolution. Resolution is important to qualitatively examine specific components and attributes of a sample, but quantitative analysis does not always benefit from higher resolution. In fact, as has been pointed out in the past by Hart and Griffiths, a lower resolution instrument will actually perform better for quantitative measurements where absorbance peaks are well defined and not overlapping<sup>1</sup>. This can be demonstrated with the following example of biodiesel in diesel.

In this study, mixtures of biodiesel in diesel were measured on a Nicolet FT-IR spectrometer, Model 5-PC. This instrument is capable of analysis at multiple resolutions. The samples were collected at  $4\text{ cm}^{-1}$  and  $16\text{ cm}^{-1}$  using a 10 bounce Attenuated Total Reflection (ATR) sample stage. Figure 1 shows the carbonyl stretching absorption for 5% and 20% biodiesel samples measured at resolutions of  $4\text{ cm}^{-1}$  and  $16\text{ cm}^{-1}$  which occurs at approximately  $5.7\text{ }\mu\text{m}$  ( $1745\text{ cm}^{-1}$ ). Note the broader and less intense peaks associated with the lower resolution spectra.

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<sup>1</sup> "Effect of Resolution on quantification in Open-Path Fourier Transform Infrared Spectrometry under Conditions of Low Detector Noise: I. Classical Least Squares Regression," B.K. Hart and P.R. Griffiths, *Env. Sci. Technol.*, 34, 1337-1345 (2000).



**Figure 1: 5% and 20% Biodiesel in Diesel Spectra**

From the spectra alone, it looks as if the higher ( $4\text{ cm}^{-1}$ ) resolution spectra would give the best results in a quantitative analysis. In fact, the opposite was found to be true. The collected spectra were used to generate a calibration using a measurement area including half the maximum peak intensity on either side of the carbonyl peak. A baseline correction was applied at either end of the peak.

The calibrations were analyzed using leave-one-out cross-validation, which involves removing all samples of a given concentration level, then generating a calibration without the excluded samples, and finally predicting the concentration of the excluded samples. This is done in succession with each concentration of biodiesel. Leave-one-out cross validation allows a prediction to be made as to how robust the calibration is since it forces a calibration to predict samples not seen in the calibration set. Both the cross-validation results and the Standard Error of Cross Validation (SECV) can be found in Figure 2 below.

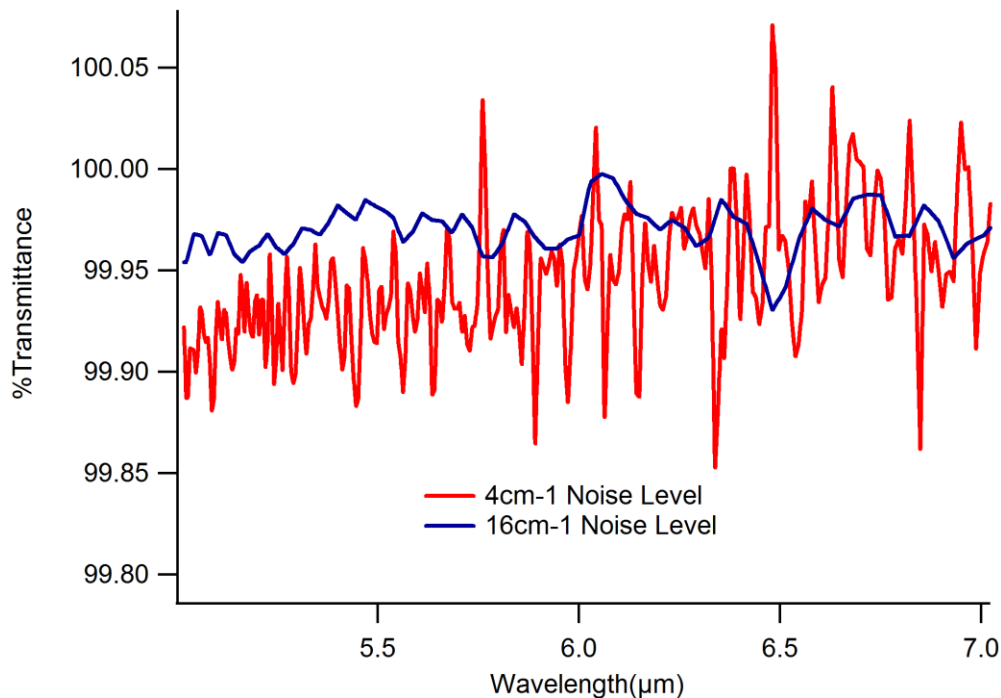
Sample	4 cm <sup>-1</sup> Cross Validation Result	16 cm <sup>-1</sup> Cross Validation Result
0.00	-0.02	-0.15
2.00	2.08	2.11
5.00	5.00	5.05
10.00	9.93	9.97
15.00	14.59	14.76
20.00	20.33	20.12

25.00	25.36	25.19
30.00	29.20	29.66
<b>SECV</b>	<b>0.36</b>	<b>0.18</b>

**Figure 2: Cross Validation Results**

As the above table shows, the low resolution calibration performed better on most samples than the high resolution samples. The SECV of the low resolution sample was calculated to be half the SECV of the high resolution.

The data shown seems to contradict the spectra shown in Figure 1, since the high resolution spectra had a more visibly intense and clearly defined peak. When using high resolution, however, there is a trade off in the signal-to-noise ratio. Typically, instruments operating at a lower resolution will have a higher signal to noise ratio. Figure 3 shows the noise level of the FT-IR used in this study at both the 4 cm<sup>-1</sup> and 16 cm<sup>-1</sup> resolution. It is clear that the noise level is significantly lower when the instrument is operating at low resolution. This lower noise level results in a higher degree of precision in the spectra, which translates to a better performing calibration.



**Figure 3: Noise Levels of the Nicolet FT-IR at 4 and 16 cm<sup>-1</sup>**

It has been shown here that the resolution of an infrared instrument does not have to be extremely high in order to obtain good quantitative results. In fact, the higher resolution can be a detriment in some cases due to a decrease in signal to noise level -- since as the resolution increases, the noise level typically grows as well. While both the ASTM and EN biodiesel blend methods set a requirement of 4 cm<sup>-1</sup>, it is clear that this restriction is not necessary and in fact may hinder the method performance. Since lower resolution infrared instruments can be made with few or no moving parts, they can be ruggedized and made portable. This allows for a portable instrument having performance similar to that of a lab-based instrument and ideally suited for dedicated or simple on-site quantitative analysis. The InfraSpec VFA (Variable Filter Array)-IR Spectrometer, manufactured by Wilks Enterprise, Inc., is a typical example of an

instrument that provides very good signal to noise in a compact low resolution design capable of accurate, on-site quantitative analysis.

