Trace contaminant analysis in biodiesel with an Antaris II FT-NIR Analyzer

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Abstract
The ability to quantify trace contaminants in biodiesel is important for optimizing the biodiesel production process and ensuring final product quality. The most commonly used process for making biodiesel is the base-catalyzed transesterification reaction of an oil or fat. The oil (triglyceride) is reacted with excess alcohol in the presence of a catalyst (KOH or NaOH) to produce biodiesel and glycerol. The transesterification reaction is very efficient with yields approaching 100%. If the reaction worked perfectly only biodiesel and glycerol would be present after reaction. Any trace contaminants such as glycerol, glycerides, water, methanol or free fatty acids in the biodiesel indicates that some step in the process is not optimized including the reaction. Contaminants that are of most importance for biodiesel final product quality are free and total glycerol, water, and methanol since they must meet ASTM D6751-07 specifications. This study shows that the Thermo Scientific™ Antaris™ II FT-NIR Analyzer can quickly and accurately quantify the concentration of contaminants in biodiesel.

Introduction
The samples used in this study were from a production process that converts soybean oil to biodiesel, also referred to as fatty acid methyl ester (FAME). The first step in the production process is the transesterification reaction which converts the triglycerides in the oil to a mixture of methyl esters (FAME) and glycerol. Subsequent steps are separation and purification to purify the final product. Separation of the biodiesel from glycerol is commonly done by centrifuge or gravity as a second step. This separation is made possible by the fact that there is a large difference in density between biodiesel and glycerol. If the separation step is not perfect then some amount of glycerol will remain in the biodiesel. The third step is the removal of alcohol from the biodiesel stream by flash evaporation or distillation. Neutralization of the biodiesel is done as part of the alcohol evaporation process. An acid is added to neutralize the base catalyst (KOH or NaOH) and to split any soaps that have formed. One product of this neutralization reaction is free fatty acid (FFA) which shows up in the biodiesel final product. The final step in production is to wash the biodiesel with water to remove residual catalyst, soaps, salts, methanol, and free glycerol. The biodiesel is then dried by a vacuum flash process and sent to storage. Water in the final biodiesel is a sign that the water removal process is not optimized. Methanol in the final product is a sign that the alcohol evaporation and water wash steps failed to remove some amount of methanol from the biodiesel.

There are multiple points in the biodiesel production process where the ability to quantify impurities in-line or online can help optimize the process to improve the yield and purity of biodiesel. NIR technology works well for predicting complex matrices in-line or online, an advantage over traditional lab methods. Multiple key

process points can be analyzed in-line often with a single, centrally located instrument by using fiber optic cables and probes. This eliminates the need for the operator to grab samples and bring them back to a common laboratory for analysis. Since the analysis results are produced in real-time the plant personnel can make adjustments to the process very quickly and often times closed-loop control strategies can be used to automate process adjustments. The real-time process results can also be plotted to show trends or entered into databases for further statistical processing.

The ability to analyze samples for multiple components in seconds by FT-NIR results in a time savings over traditional lab methods. In this study a lab-based Antaris II FT-NIR Analyzer was able to generate results in 30 seconds. The Gas Chromatography method for determining free and total glycerol takes 40 minutes. There are separate ASTM test methods under ASTM D6751-07 for quantifying contaminants present in biodiesel. They all require different equipment, reagents, and supplies which increase the cost and add to the overall complexity of the QA system. Methanol presence is done by a flash point tester or a GC method. The flashpoint method does not allow for exact quantification of how much methanol is present, only that the concentration is above or below a certain threshold. The amount of water present is determined by the % volume of water centrifuged out of a sample. Free Fatty Acid (FFA) levels are determined by a potentiometric titration that is not part of the ASTM test methods.

Experimental

The starting material for preparing standards was a pure biodiesel sample from a plant that uses soybean oil to make biodiesel. This pure biodiesel sample along with 3 biodiesel samples that were saturated with glycerol and/or water were used to form 4 stock standards. The stock standards were combined to produce lots that varied in their amount of biodiesel, water, and glycerol. These lots had differing amounts of Free Fatty Acids (FFA), methanol, tri-, di-, and monoglycerides added to them to produce the standards used in the study. The component concentration in each standard was determined by % weight with each component addition having a mass uncertainty of ± 0.0002. A total of 68 standards were prepared in order to cover a wide range of component concentrations. The values for glycerol and water were determined using accepted industry primary analytical methods. Pure standards of FFA, methanol, tri-, di-, and monoglycerides were purchased for standard preparation in this study.

Triglyceride	Diglyceride	Monoglyceride	FFA
trilinolenin	dilinolein	monolinolein	linoleic
triolein	diolein	monoolein	linolenic
			oleic

Table 1. Pure glyceride and FFA compounds used in method standards.

For each type of glyceride (tri, di, and mono) there were multiple pure glyceride standards used for making the method standards. The glyceride standards differed based on the fatty acid chains that were attached to them. Most naturally occurring fatty acid chain lengths are 16, 18, or 20 carbons. In this study, a fatty acid chain length of 18 carbons was used. Table 1 shows the different pure glycerides and free fatty acids used in the standards.

The NIR spectral acquisition was performed in a laboratory using an Antaris II FT-NIR Analyzer (Figure 1). The spectral data was acquired in transmission using glass cuvettes and a heated cuvette holder set at 30°C. A background was taken in between each sample scan.

Figure 1. Antaris II FT-NIR Analyzer.

Spectroscopic Collection Parameters:

Spectroscopic Range: 10000 to 4000 cm^{-1}

Resolution: 4 cm^{-1}

Co-Averaged Scans: 32 scans

Collection Time: 20 s

Calibration development

The calibration model was developed using the Thermo Scientific TQ Analyst™ software package for quantitative analysis. All spectra were mean centered and converted into their second derivative prior to calibration. This was accomplished using a Norris derivative with a segment length = 5 and gap = 5. A PLS (Partial Least Squares) regression model was developed for this study due to the fact that it gives accurate and robust methods for multicomponent mixtures. The PLS model is a good choice for this application because it calibrates for each component separately and it can effectively handle the high number of sources of variation due to the large number of standards with varying concentrations. Table 2 shows the spectral regions used in the calibration development. TQ Analyst can be set to select spectral regions automatically by using concentration and spectral information of the calibration standards.

Index	Measurement Location / Range
1	4306.27 - 4084.49
2	4450.90 - 4348.69
3	5071.87 - 4556.97
4	5295.57 - 5235.79
5	7133.40 - 6003.32

Table 2. Region selection window in TQ Analyst.

Data analysis and results

The raw spectra for this study are shown in Figure 2. The fact that many of the compounds in this study have the same functional groups makes it hard to see spectral variation among the samples in the raw spectra. For this reason, a 2nd derivative was taken since it increases the spectral peak definition while retaining peak location from the unprocessed spectra. The derivative also removes any baseline due to scattering. Since these samples were liquids run in transmission with a constant pathlength, scattering was not an issue. Figure 3 shows the spectra processed with a 2nd derivative.

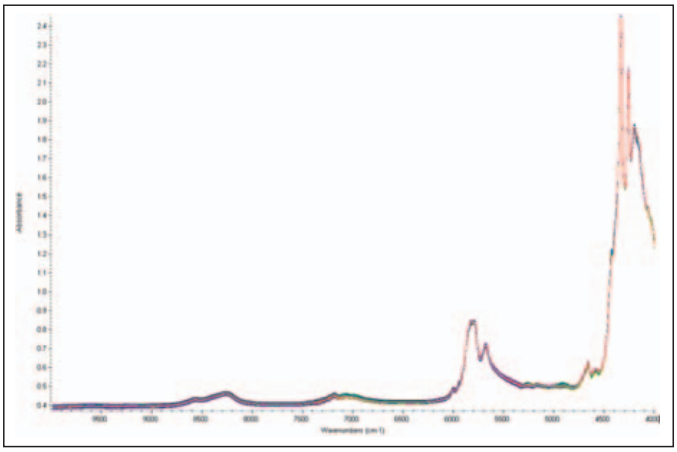

Figure 2. Unprocessed spectra of biodiesel standards.

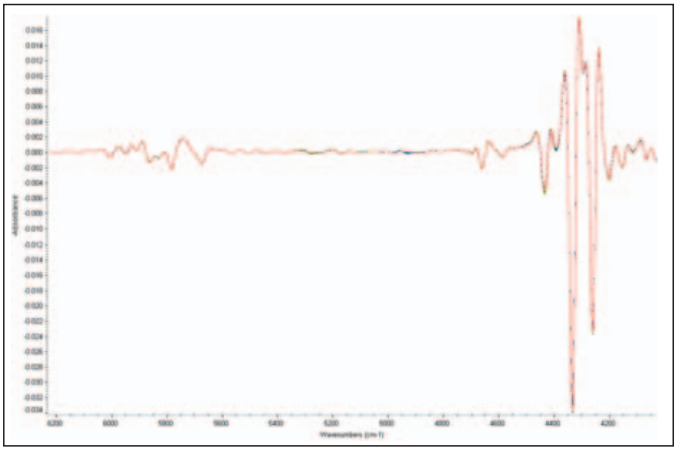

Figure 3: Second derivative spectra of biodiesel standards

Small changes in absorbance and spectral shape can be seen in the 4900-5000 cm^{-1} range (Figure 4) which is the OH combination band. The shift in peak and change in absorbance at 4950 cm^{-1} is due to varying amounts of methanol in the standards. There is a distinct separation between the samples with the highest and lowest concentration of methanol.

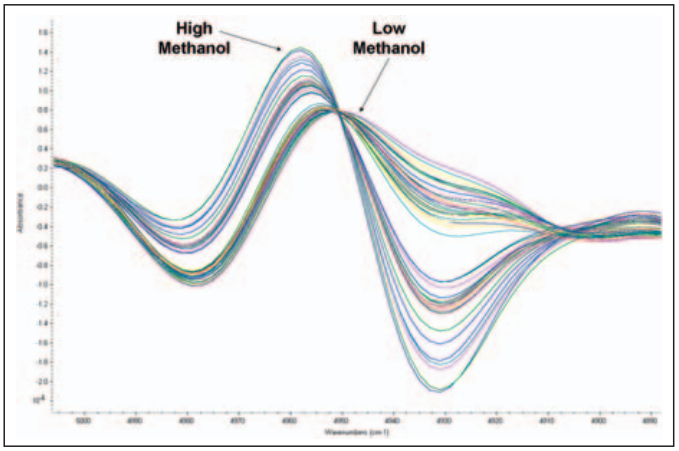

Figure 4. OH combination band showing peak shift for high and low methanol.

The Predicted Error Sum of Squares (PRESS) plot is a good indicator of how well the PLS factors for the model can explain the concentration and spectral information for a given component. Figure 5 shows the PRESS plot for water in biodiesel. The PRESS plot shows an optimum pattern, high PRESS at low factors and low PRESS at a higher number of factors with the curve reaching the minimum with very few factors. In this case the minimum is reached at 4 factors which is very good for a PLS model. TQ Analyst automatically selects the optimum number of factors to use in a PLS calibration.

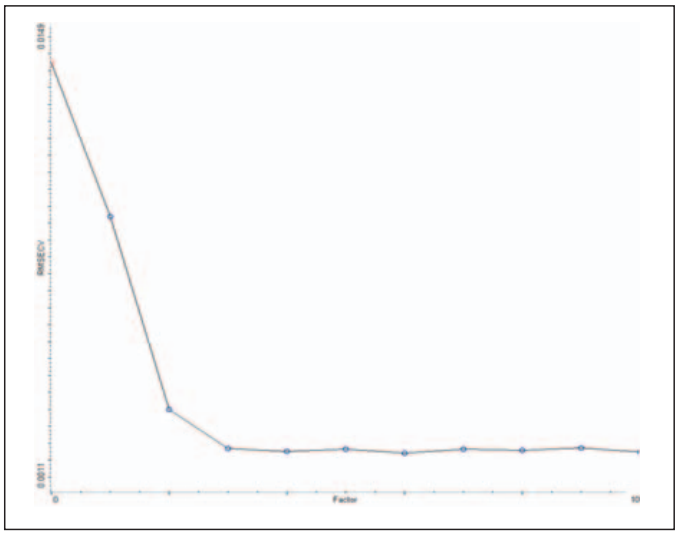

Figure 5. PRESS plot for water.

The standards used to develop the calibration model had FAME (biodiesel) concentration that varied from 90.1 – 99.9%. The contaminants made up the remaining weight % of the standard. As can be seen in Table 3 many trace contaminant concentrations in biodiesel can be predicted accurately. The Standard Error of Calibration (SEC) for all the components in the method was less than 0.2% and correlation coefficients were all greater than 0.93. Figure 6 is the calibration plot for total glycerol which is free glycerol plus the bound glycerol portion from the tri-, di- and monoglycerides. The calibration plot is the calculated (NIR model predicted values) versus the actual weight % for each standard. This plot shows good correlation from 0-1%. It also shows the independent validation points predict as well as the samples used for the calibration because they fall as close to the ideal prediction line (slope=1) as the calibration samples. Figure 7 shows the calibration plot for methanol which also shows good correlation from 0-2% and has independent validation points that are predicted very well.

Component	Number of PLS factors	Correlation coefficient	RMSEC	RMSECV
FAME	8	0.9992	0.0866	0.1220
Water	4	0.9926	0.0024	0.0035
FFA	9	0.9924	0.0501	0.0959
Triglyceride	7	0.9923	0.1780	0.2790
Diglyceride	8	0.9338	0.1570	0.2730
Monoglyceride	8	0.9781	0.0961	0.1600
Methanol	4	0.9817	0.0983	0.114
Total Glycerol	8	0.9985	0.0121	0.0224
Total Glyceride	7	0.9975	0.1020	0.1770

Table 3. Statistical summary of component calibrations in biodiesel.

Conclusions

The Antaris II FT-NIR can accurately predict concentrations of FAME and trace contaminants in biodiesel as shown by this study. The ability to quickly quantify multiple trace contaminants allows for process adjustments to be made much more quickly than if samples were run by traditional primary analytical methods. The ability to transfer FT-NIR methods from lab to line using Antaris analyzers gives production facilities flexibility on instrument location and sample presentation. The ability to use FT-NIR inline allows process adjustments to be

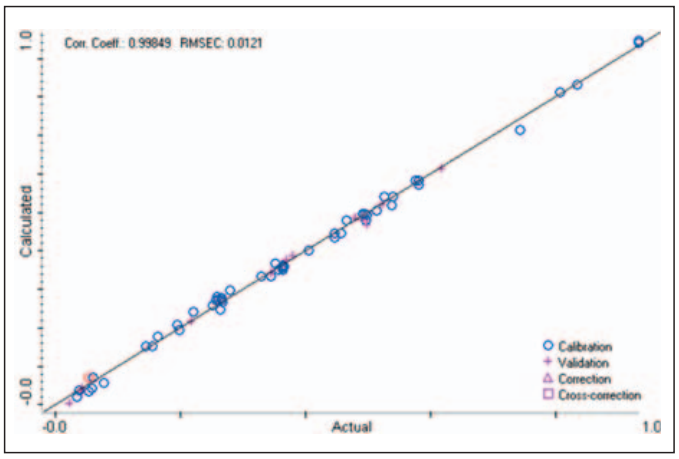

Figure 6. Calibration plot for total glycerol.

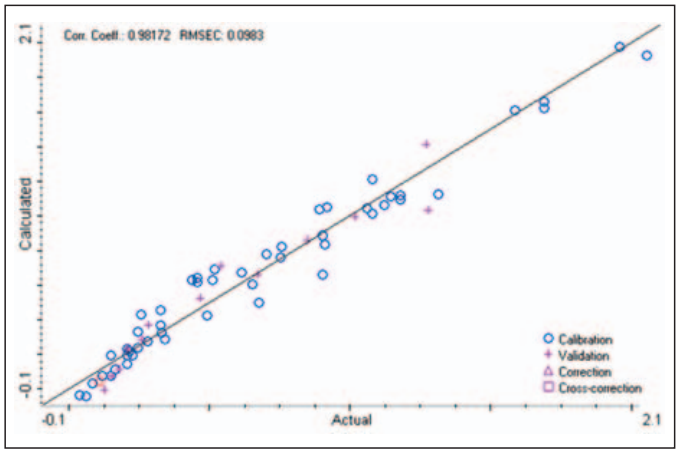

Figure 7. Calibration plot for methanol.

made in real-time using closed-loop control strategies. By optimizing the process, chemical and processing costs can be minimized. The ability to measure multiple sample points simultaneously with a multiplexing FT-NIR like the Antaris MX makes inline measurement more practical and economical since one instrument might be all that is needed for a biodiesel production facility. The use of FT-NIR simplifies the testing protocol for biodiesel process samples since one instrument can replace multiple pieces of equipment and eliminate lab supply costs. This study proves that FT-NIR is a valuable tool for biodiesel process monitoring.

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