APPLICATION NOTE

FT-IR Spectroscopy

Authors

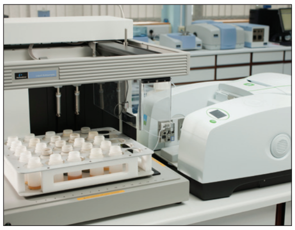
Sharon Williams

Jerry Sellors, Ph.D.

Simon Wells

PerkinElmer, Inc.
Shelton, CT 06484 USA

Biodiesel Concentration Measurements Using OilExpress



Introduction

Reducing our dependence on fossil fuels and our reliance on oil and petroleum supplies are worldwide issues. Many see the increasing use of biodiesel fuel as a key initiative to meet these global needs. However, the move to include proportions of biodiesel in every-day fuel has created a host of unresolved issues for both engine manufacturers and diesel consumers. Uppermost among these are questions concerning the concentration of the biofuel (Fatty Acid, Methyl Ester – FAME) and its quality. This application note describes how infrared transmission measurements can be used to address the concentration measurements.

Biodiesel fuels are often blended compositions of diesel fuel and esterified soybean oils, rapeseed oils, or other potential vegetable oils, as well as fats. The physical and combustion properties of these biofuels have allowed them to achieve similar performance to diesel fuel. However, there are several characteristics (including cetane number, oxidation stability and corrosion potential) that are of concern. These differences, especially the cetane reduction, require that adequate control of the biofuel concentration be implemented.

In addition, there are now tax incentives available in some parts of the world for the use of biodiesel. For example, in the USA this tax credit is presently in the form of a $0.01 per FAME-% per gallon of fuel used. Therefore, the difference between 19% or 20% FAME in diesel fuel can result in a considerable tax value. A recent investigation of commercially available biofuel blends identified that 18 out of 50 splash-blended samples were not the specified 20% FAME value.[1] It can be seen that there are financial justifications for an accurate biofuel concentration determination and characterization.

This work was performed using the Spectrum™ OilExpress™ system* which consists of four elements:

- The PerkinElmer® Spectrum 100 FT-IR spectrometer with high sensitivity, sampling speed, and stability.
- A sealed transmission cell with zinc selenide (ZnSe) windows with a 100-µm pathlength.
- The Molecular Spectroscopy Liquid Autosampler which provides unattended operation and rapid sample throughput of up to 50 samples per hour. The system is fitted with syringe pumps and is designed to handle samples with a wide range of viscosities, ensuring virtually no sample carryover (<0.1%).
- The PerkinElmer infrared quantitative software suite which allows analysis by various methodologies. These include Beer's Law concentration calculations using peak height measurements and full Principal Component Regression (PCR) chemometric analysis.

The primary advantage of this system is the ability to automate the procedure from sample aspiration through report generation, including cleaning between samples. Secondly, the infrared transmission spectra carry the most information-rich data available, enabling more robust methods to be calculated.

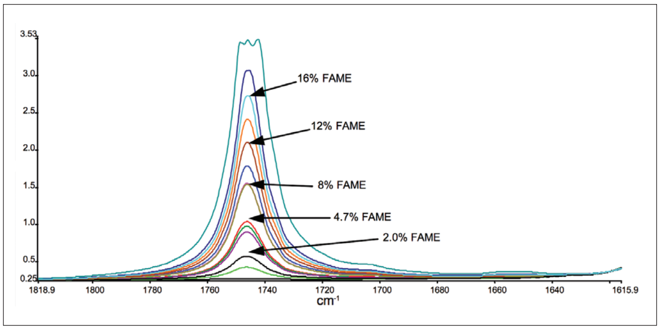


Figure 1. FT-IR spectra of varying FAME concentrations in diesel fuel.

EN 14078 method using Beer's Law

One of the few defined methods for measuring the concentration of FAME is EN 14078 (July 2004) – "Liquid petroleum products – Determination of fatty acid methyl esters (FAME) in middle distillates – Infrared spectroscopy method".[2]

The principle of the EN 14078 method is the application of a simple quantitative model of FAME content using the 1745 cm^{-1} carbonyl absorbance. When using the EN 14078 methods, samples are diluted in cyclohexane to a final analysis concentration of 0-1.14% FAME. This produces a carbonyl peak intensity range between 0.1-1.1 Abs, using a 0.5-mm cell pathlength. The peak height of the carbonyl band at or near 1745 cm^{-1} is measured to a baseline drawn between 1820 and 1670 cm^{-1}. This peak height is used with a Beer's Law plot (absorbance versus concentration) to develop the calibration curve used for calculating the unknown concentrations.

While it is possible to achieve good concentration measurement, the disadvantages of this method are the need for sample dilution and the inability of the simple methodology to cope with variances in the source of the biofuel. An improved solution utilizes the more common 100-µm flow-cell, avoiding sample dilution errors. With the potential for increasing variance in feedstocks used to produce the FAME (namely: soybean, rapeseed, or yellow-grease), peak area is proposed as a preferred calculation technique.

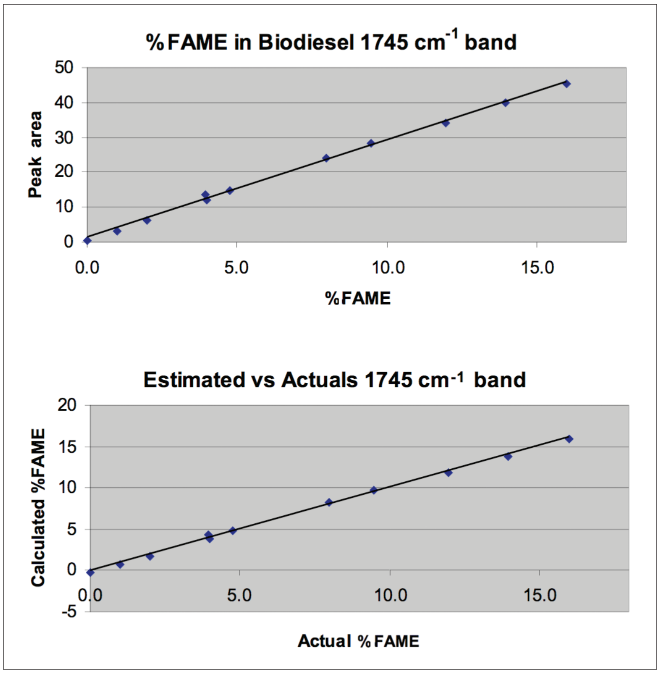


Figure 2. Beer's Law calibration method for 1745 cm^{-1} peak.

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* *The Spectrum OilExpress is superceded by the PerkinElmer Frontier OilExpress system.*

Peak area method

The modifications of this method that were employed in this study included:

- Cell pathlength – 0.1 mm
- Peak area calculation – range: 1820-1670 cm^{-1} with baseline set at the same range.
- No dilution – samples were not diluted to allow for the determination of the usable range.

For a concentration method to be valid, the peak maximum cannot exceed the absorbance range of the spectrometer. Figures 1 and 2 demonstrate that the Beer's Law curve for this spectral region is limited to approximately 18% FAME.

In this study, we took a baseline as defined in the EN 14078 method at 1820-1670 cm^{-1} and a peak area in the same range. The sample concentration range for this method was B0 to B16 (0% to 16% FAME). The method produced a linear graph with a correlation coefficient of 0.9988. Calculating the concentration of the standards by the method yielded a Pearson's correlation of 0.9990 and a standard error of prediction (SEP) of better than 0.30%. These results indicate an acceptable method for the quantitation of FAME up to B16.

Further analysis of the FT-IR spectra shows additional spectral regions attributed to the FAME chemistry; for example 1300-1130 cm^{-1} (Figure 3). The peak maximum for this spectral region does not exceed the system absorbance limit even at 49% FAME. The associated Beer's Law method uses the peak area between 1300 and 1130 cm^{-1}. Figure 4 shows the capability of this method for an extended sample concentration range from B0 to B50. The method produced a linear correlation with a correlation coefficient of 0.9997 and a standard error of prediction (SEP) of 0.38%. This is a capable method for the determination of a wider range of FAME concentrations.

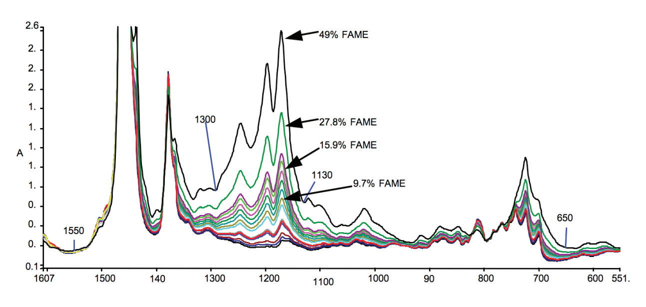

Figure 3. Fingerprint region of FAME/diesel samples.

Principal component regression method

The peak area model is able to yield very capable calculations of the FAME concentration using short ranges of the full IR spectrum. To fully utilize all the relevant information from the whole spectrum, we moved to a chemometric analysis. In this case, we used Principal Component Regression (PCR) to provide a more robust concentration assay. Samples with varying FAME concentrations between 0 and 20% were used in the calibration of the PCR model. The model employed as much of the entire spectrum as available. The quantitative prediction utilized only one principal component (the Regression Spectrum for the method). This spectrum (Figure 5) shows that the entire spectrum was used except the top of the 1745 cm^{-1} FAME carbonyl peak and the C-H peaks at the 2900, 1460, and 1370 cm^{-1} region.

By using the entire spectral region, a more robust model can be generated. The statistics of this model showed a correlation coefficient of 0.9995, Pearson's correlation of 0.9997 and SEP of 0.17%. The actual against predicted results for this model as shown in Figure 6 also confirm a good prediction model.

This chemometric approach to the analyses is equal to, or better than, the Beer's Law methods. Although this modeling method for developing a calibration of the concentration of FAME in a biodiesel is more difficult to design, it is more robust over larger concentrations. Additionally, it will allow extending the calibration range with additional samples to even higher concentrations.

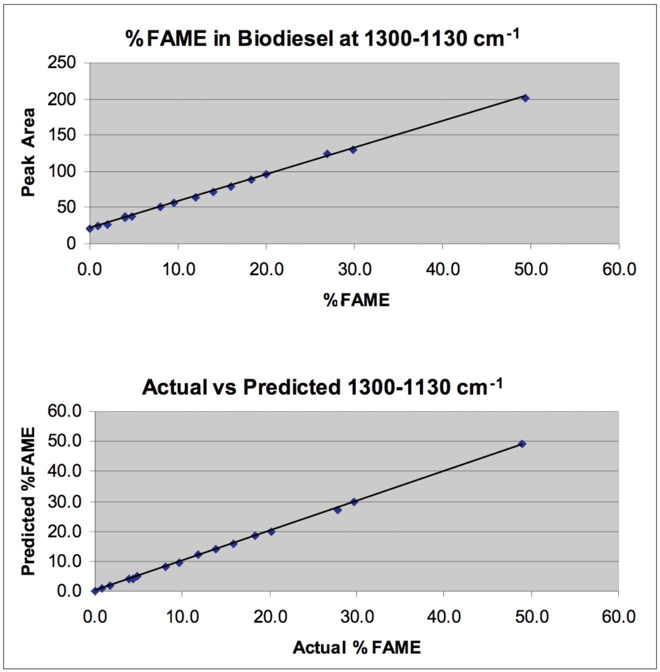

Figure 4. Beer's Law calibration method for 1300-1130 cm^{-1}.

Conclusion

We have shown how infrared transmission techniques can be used to address FAME concentration measurements. All the methodologies presented achieve a standard error of prediction of less than 0.4%.

This compares well with the concentration measurement of FAME in a typical "splash blend" operation, where an error of 0.5% is usually acceptable. Data analysis using either Beer's Law or Principal Component Regression (PCR) is capable of meeting this requirement.

A key advantage to using the transmission cell sampling method is that it allows auto-sampling, which can ease the routine laboratory's manpower needs. The choice of either Beer's Law or chemometrics will be determined by the particular situation.The Beer's Law approach, using peak area, benefits from being a simpler approach and is recommended for situations where there are relatively few standards and low throughput of samples. The chemometrics approach has the advantage of being more robust with respect to known constituents in the blend, better handling of interferents, and reduced effect from noise contributions. Overall, PCR offers higher confidence in the quantitative prediction than is found with the Beer's Law methods.

Note: While the procedures provided in this Application Note may not have yet found their way into methodologies set by standard organizations or government agencies, they have been fully tested and have been demonstrated to provide quality data in numerous laboratories performing routine FAME analysis.

References

1. NREL Technical Report TP-540-38836, Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004; R.L. McCormick, T.L. Alleman, M. Ratcliff, L. Moens, and R. Lawrence (October 2005).

2. EN 14078 Liquid Petroleum Products – Determination of Fatty Acid Methyl Esters (FAME) in Middle Distillates – Infrared Spectroscopy Method (July 2004).

3. ASTM® D7371 Standard Test Method for "Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy".

Acknowledgements

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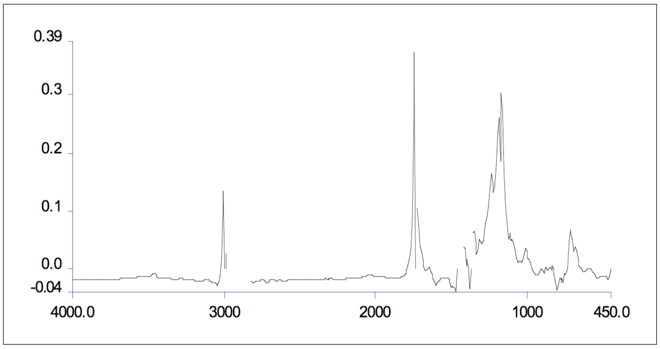

Figure 5. FAME PCR regression spectrum.

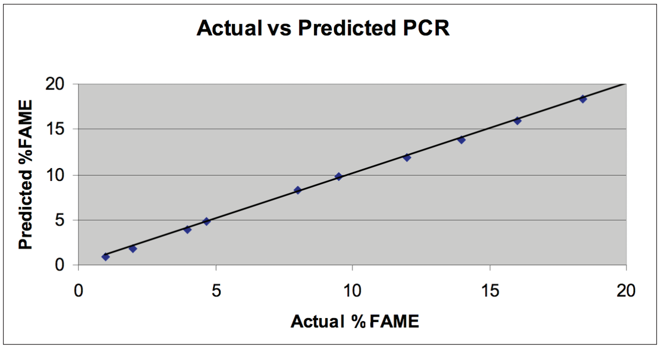

Figure 6. PCR calibration method.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

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