

FT-IR Spectroscopy

Authors

Ben Perston

Nick Harris

PerkinElmer, Inc.
Seer Green, UK

Biodiesel Blend Analysis by FT-IR (ASTM D7371 and EN 14078)

Introduction – FAME and FAME Blends

The increasing importance of sustainability in energy production has led to a global commitment to the use of fuels derived from renewable biological sources, such as biodiesel produced from plant crops. Biodiesel consists of fatty acid methyl esters (FAME) and is produced in a transesterification reaction as depicted in Figure 1. A range of feedstocks are used globally, including rapeseed, soy, sunflower, palm and jatropha.

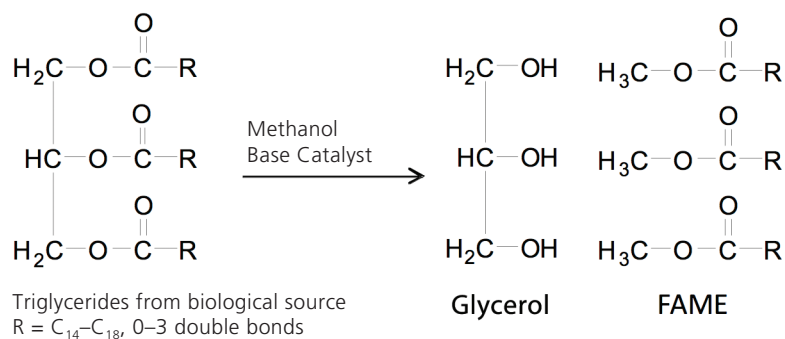


Figure 1. Reaction scheme for the production of biodiesel.

Biodiesel has numerous desirable fuel properties. It is intrinsically very low in sulphur and tends to be cleaner-burning than fossil diesel as well as reducing engine wear. Many modern vehicles can run on pure biodiesel (B100), but it is more commonly blended prior to sale in ratios up to about 30% v/v (B30). According to the ASTM D975 and EN 590 regulations, fuel sold as diesel (without specific biodiesel labelling) in the European Union and United States may contain up to 5% v/v FAME.^{1,2}

Verifying the FAME content of diesel fuel blends is an important aspect of quality control and auditing of blending and distribution operations. Because FAME has a strong infrared absorption at around 1745 cm^{-1} (due to the ester carbonyl bond), a region where fossil diesel is transparent, infrared spectroscopy is ideally suited to this analysis (Figure 2).

There are two standard test methods for quantifying FAME in diesel blends: ASTM D7371³ and EN 14078.⁴ EN 14078 involves dilution in hexane followed by a transmission measurement and comparison of the carbonyl peak height measurement against a calibration curve. The newer ASTM D7371 specifies an attenuated total reflectance (ATR) measurement on the neat fuel blend and a chemometric partial-least-squares (PLS) model.

EN 14078 allows potentially greater sensitivity (for FAME levels below 1% v/v) and a comparatively simple calibration procedure. ASTM D7371 requires a larger number of calibration standards to be prepared, but allows a much more rapid analysis as there is no need for dilution and the ATR crystal is much easier to clean than a transmission cell.

Infrared spectra of biodiesel blends exhibit nonlinear behavior (peak shifts) with respect to concentration, due to interactions between the mixture components. Because of this, it is impossible to have a single, simple linear model spanning the full range of possible blends. In ASTM D7371, this issue is addressed by the use of three separate PLS models, for 0–10, 10–30, and 30–100% v/v FAME.

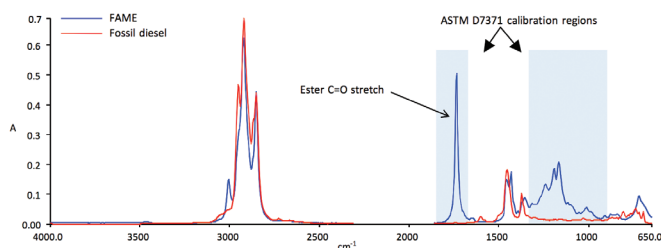


Figure 2. Infrared spectra of FAME (blue) and fossil diesel (red); the shaded regions are used by the ASTM D7371 method.

This application note illustrates how both of these methods have been implemented in the PerkinElmer® EcoAnalytix™ Biodiesel IR FAME Analyzer.

Instrumentation

PerkinElmer's EcoAnalytix Biodiesel IR FAME Analyzer comprises a Spectrum™ 100 FT-IR spectrometer with the appropriate ATR or transmission accessory, and Spectrum Express™ software with a dedicated FAME analysis module that can be configured for either ASTM D7371 or EN 14078. The ASTM version of the analyzer supports either a ZnSe horizontal ATR (HATR) or, for much greater ruggedness and improved cleanability, a Universal ATR (UATR) with a 9-bounce diamond ATR element.

Also included is a starter calibration for the ASTM D7371 method, which can save considerable method development time during deployment. For a given application, this calibration may already provide sufficient accuracy and precision, or it can be optimized further by including spectra of a few calibration standards from the target environment measured on the new instrument.

Detailed standard operating procedures (SOPs) describe how to use the analyzer and how to update the supplied calibrations or to create new ones for strict compliance to the standards.

ASTM D7371 Method Validation

An EcoAnalytix Biodiesel IR FAME Analyzer with a 9-bounce diamond UATR accessory was used for this analysis. A series of 63 validation standards of soy biodiesel in fossil diesel was prepared as described in ASTM D7371, and the spectra were measured as described by the SOP included with the software. Twenty-one of the spectra were used to derive a bias correction to the provided calibration models, as described in the SOP; this calibration transfer procedure is further discussed in a separate article.⁵ The remainder of the spectra was used to validate the performance of the models.

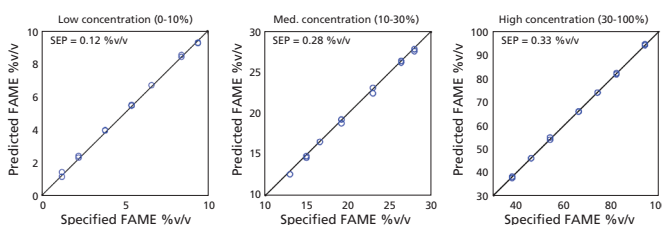


Figure 3. Predicted vs. specified plots for the low-, medium-, and high-concentration models in the ASTM D7371 method.

The FAME volume % was calculated from the measured spectra using the Biodiesel feature in Spectrum Express software. The total analysis time per sample, including clean-up, was around 1.5 minutes.

The results are shown in Figure 3 (Page 2) and summarized in Table 1. The software automatically selects which of the three models is appropriate for the given sample, allowing for very simple routine analysis of a range of different blend concentrations. The use of three separate models provides excellent linearity over the full range of possible blends.

ASTM D7371 specifies that, for an individual instrument to be qualified to perform the analysis, the standard error of prediction (SEP) for samples with <20% v/v FAME must be not significantly greater than the pooled error (PSEP) encountered during their round-robin test. The PSEP was 0.21% v/v,³ and an F-test with the appropriate degrees of freedom sets the threshold for the present system at 0.28% v/v. The measured error of 0.18% v/v is well beneath this limit, indicating that the instrument is qualified to perform this analysis.

Table 1. Summary of the validation results for the three models. The ASTM D7371 qualification criterion applies to samples with <20% v/v FAME, a range spanning all of the low- and part of the medium-concentration bracket. The SEP values are in units of % v/v FAME.

Model	Latent Variables	SEP (Cross-Validation; % v/v)	SEP (External Validation; % v/v)
Low (0–10% v/v)	3	0.08	0.12
Medium (10–30% v/v)	4	0.23	0.28
High (30–100% v/v)	3	0.48	0.33
ASTM qualification (0–20% v/v)			0.18

EN 14078 Method Development and Validation

Five standards were prepared by weighing soy biodiesel into volumetric flasks and filling to the mark with cyclohexane. Four validation standards were prepared as blends of soy biodiesel (5 to 26% v/v) with fossil diesel. These were diluted tenfold in cyclohexane. The concentrations of the standards are given as “undiluted % v/v” in Table 2.

The spectra of the standards were measured using an EcoAnalytix Biodiesel IR FAME Analyzer and a semi-demountable liquid cell with CaF₂ windows and a 0.2 mm pathlength. The spectra were ratioed against a background of pure cyclohexane to approximately cancel absorbance by the solvent. A more careful cancellation of the solvent absorbance was deemed unnecessary because cyclohexane is transparent in the carbonyl absorption region.

The calibration model was built using Spectrum Beer’s Law software, following the parameters specified in EN 14078:2003. The height of the peak at around 1745 cm⁻¹ was determined using baseline points at 1820 and 1670 cm⁻¹. The peak height was correlated against the FAME concentration in g/L, and the calibration and validation results are reported in Figure 4 and Table 2. The linearity over the selected range is very good, as evidenced by the R² value of 0.9996. The validation SEP of 0.43% v/v is very small considering the range of concentrations sampled.

Table 2. EN 14078 calibration and validation results.

Sample	Nominal FAME (% v/v)	Peak Height 1745 cm ⁻¹ (A)	Predicted FAME (% v/v)
Calibration-1	3.30	0.134	3.69
Calibration-2	7.63	0.269	7.48
Calibration-3	13.27	0.467	12.99
Calibration-4	20.28	0.720	20.06
Calibration-5	32.45	1.173	32.72
Validation-1	5.40	0.190	5.27
Validation-2	9.40	0.353	9.82
Validation-3	19.20	0.697	19.44
Validation-4	26.40	0.972	27.10

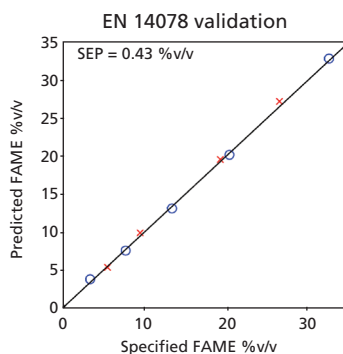


Figure 4. EN 14078 calibration (blue circles) and validation (red crosses) results.

Conclusions

FT-IR spectrometry is a rapid and precise method for quantification of FAME in diesel fuel blends. Using the methodology specified by ASTM D7371 and the streamlined Spectrum Express software allowed for a total analysis time of less than two minutes per sample, and the SEP achieved was 0.18% v/v, well beneath the limit specified by the standard. The use of three PLS models gives excellent linearity and precision for the full range of possible blends. Because the software automatically selects the best model to use, no additional complexity is introduced to the analysis.

The older EN 14078 method requires more sample preparation work, but the calibration is simpler and potentially greater sensitivity can be obtained by varying the path length and dilution factor.

For certain applications, methods somewhat different from the approved standards may be more useful. For example, the EN 14078 peak height calibration can just as readily be applied to ATR data to obtain both rapidity of sampling and simplicity of calibration at a slight cost to sensitivity. Transmission sampling of undiluted fuel blends can provide the lowest detection limit.

Acknowledgements

The calibration models for the ASTM D7371 method were developed for PerkinElmer by Dave Wooton of Wooton Consulting, Beaverdam, VA. Dr. Wooton also supplied the validation standards.

References

1. ASTM International D975-09: Standard Specification for Diesel Fuel Oils.
2. BS EN 590:2004 Automotive fuels. Diesel. Requirements and test methods.
3. ASTM International D7371-07: Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FT-IR-ATR-PLS Method).
4. European Standard EN 14078: Liquid petroleum products – Determination of fatty acid methyl esters (FAME) in middle distillates – Infrared spectroscopy method.
5. “Diamond ATR and Calibration Transfer for Biodiesel Blend Analysis by ASTM D7371” Ben Perston and Nick Harris, PerkinElmer, 2009.