A Comparison of Standard Test Methods for Determining FAME in Diesel by Infrared Spectroscopy

Ben Perston, Applications Scientist, Molecular Spectroscopy, PerkinElmer
Chalfont Road, Seer Green, Beaconsfield HP9 2FX, UK
Tel: +44(0) 1494 679074 • Email: ben.perston@perkinelmer.com • Web: www.perkinelmer.com

As the importance of sustainable energy production increases, so too does the global commitment to using fuels from renewable biological sources. Biodiesel is one such renewable fuel. Consisting of fatty acids of methyl esters (FAME), it is produced from plant crops by transesterification – a reaction in which natural triglycerides are cleaved and reacted with methanol, producing glycerol and FAME. Rapeseed, soy, sunflower, palm and jatropha are just part of the range of feedstocks used globally in the production of biodiesel.

Biodiesel is intrinsically very low in sulphur, tends to be cleaner-burning than fossil fuel, and can reduce engine wear, all of which are desirable fuel properties. While many diesel engines can run on pure biodiesel, it is more commonly blended into commercial diesel fuel in ratios up to about 30% v/v. 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].

FAME is not recommended for applications where fuel may be stored for a long time, due to concerns about its oxidative stability. As vegetable oils tend to have a degree of unsaturation (which is preserved during transesterification), chemical reactions can occur in which the double bonds slowly undergo oxidation and rearrangement, forming numerous primary and secondary oxidation products. This leads to an increase in the total acid number (TAN) of the fuel, and the formulation of insoluble particulates that can block filters. As such, FAME is not currently seen as a suitable ingredient for power generation, aviation, or marine fuels. However, the widespread use of FAME as fuel for terrestrial vehicles generates an increased risk of inadvertent contamination of mineral fuels. Methods of analysis for trace amounts of FAME are thus becoming increasingly important.

[1] ASTM International D975-09: Standard Specification for Diesel Fuel Oils
[2] BS EN 590:2004 Automotive fuels. Diesel. Requirements and test methods

This article discusses the use of FT-IR spectroscopy for quantification of FAME in fuels, and compares the two current standard test methods, EN 14078 and ASTM D7371, considering their relative merits for both blend and trace analysis.

Standard test Methods for FAME Measurement

An important aspect of the quality control and auditing of blending and distribution operations is the verification of FAME content in diesel fuel blends. Infrared spectroscopy is ideally suited to this measurement as FAME has a strong infrared absorption at around 1745cm^{-1} due to the ester carbonyl bond. This is a region where fossil diesel is transparent (see Figure 1).
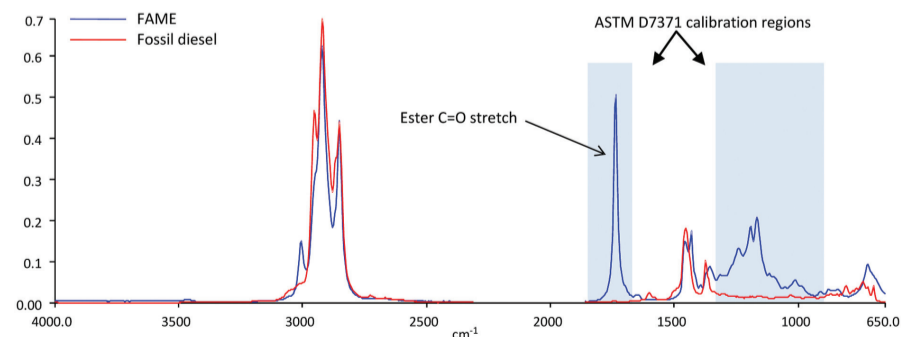

Figure 1: Infrared spectra of FAME (blue) and fossil diesel (red); the shaded regions are used by the ASTM D7371 method.

There are two standard test methods for quantifying FAME in biodiesel blends by FT-IR: ASTM D7371[3] and EN 14078[4]. EN 14078 involves a transmission measurement (with pathlength depending on the concentration) and comparison of the carbonyl peak height measurement against a calibration curve. ASTM D7371, a more recent standard, specifies an attenuated total reflectance (ATR) measurement and a chemometric partial-least-squares (PLS) model.

[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 (FTIR-ATR-PLS Method)
[4] European Standard EN 14078: Liquid petroleum products - Determination of fatty acid methyl esters (FAME) in middle distillates - Infrared spectroscopy method

ASTM D7371 offers a stated reproducibility of around 0.8–1.7 %v/v for samples between 1 and 20 %v/v, while EN 14078 has reproducibility of 0.02 – 1.6 %v/v over the range from 0 to 20 %v/v. Both methods divide the calibration into several ranges.

EN 14078 allows potentially greater sensitivity (for FAME levels below 1%v/v) and a comparatively simple calibration procedure. ASTM D7371 however, 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.

Performance and Method Validation for Blend Measurements ASTM D7371

The ASTM D7371 method was evaluated using a PerkinElmer Frontier™ FAME Analyser consisting of a Frontier FT-IR spectrometer equipped with a 9-reflection diamond UATR sampling accessory. Sixty-three validation standards of soy biodiesel in fossil diesel were prepared, and the spectra were measured as described by the SOP included with the software. Twenty-one of the spectra were used to derive bias corrections to the supplied calibration models and the remainder were used to validate the performance of the models.

The volume percentage of FAME was calculated from the measured spectra using the biodiesel feature in Spectrum software. Including clean-up, the total analysis time for each sample was approximately 1.5 minutes.

ASTM D7371 specifies that, for an individual instrument to be qualified to perform biodiesel 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. Well beneath this limit, the measured error of 0.18 %v/v indicates that the instrument is qualified to perform this analysis, as shown in Table 1.

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

Table 1: Summary of the validation results for the three models. The ASTM 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 valves are in units of %v/v FAME.

EN 14078

Calibration standards were prepared by diluting rapeseed biodiesel in mineral diesel fuel and two ranges were used: Range A (0–2 %v/v) and Range B (0–20 %v/v). The spectra of the standards were measured using a PerkinElmer Spectrum Two™ FT-IR spectrometer equipped with a Fuels FT-IR Analysis Pack. The liquid cell had BaF2 windows and a pathlength of 0.5 mm for Range A and 0.05

mm for Range B. For Range A, mineral diesel was used for the background while for Range B, the open beam was used. The flow cell was drained between samples and then rinsed with approximately 3 mL of the next sample prior to use. This rapid cleaning procedure reduces carryover to negligible levels and allows a total sample measurement time of about 2 minutes.

The calibration model was built using Spectrum Beer's Law software following the parameters specified in EN 14078:2009. The results are shown in Figure 2. Excellent linearity and precision were obtained over both ranges, and the SEPs were about a factor of 2 – 3 better than obtained with the ASTM D7371 method.
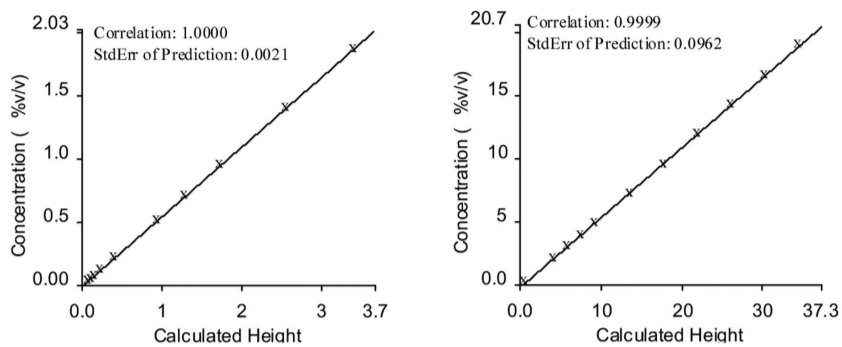

Figure 2 Calibration results for EN14078 using the Spectrum Two FT-IR spectrometer.

Both of these methods provide excellent performance for blend analysis. EN 14078 offers slightly better precision and a simpler calibration procedure, but at the cost of slightly greater analysis time per sample.

Detection Limits: Suitability for Trace Analysis

EN 14078 affords excellent sensitivity by the use of a long pathlength transmission cell. Spectra of some low-concentration samples are shown in Figure 3. The difference between 0 and 0.01% FAME is clearly visible, and the detection limit estimated as 5 × SEP is 0.003% (30 ppm). However, this assumes that a suitable FAME-free reference is available, and the real detection limit may be somewhat higher if variability in the mineral fuel is encountered.
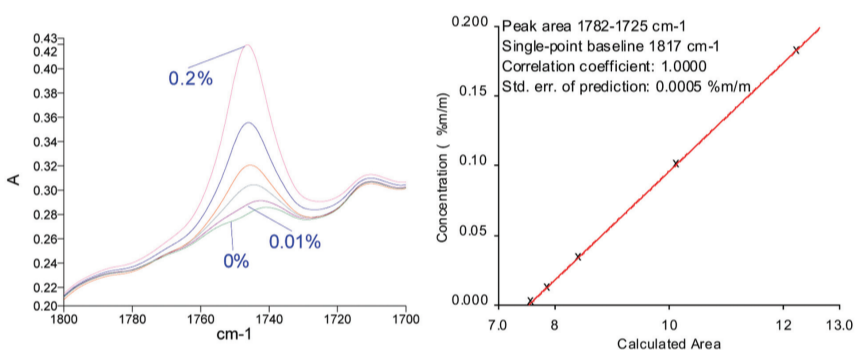

Figure 3. IR spectra of the biodiesel standards measured using a PerkinElmer FT-IR spectrometer and Fuels FT-IR Application Pack.

ASTM D7371 specifies the concentration ranges that must be used for the calibration. The resulting calibrations are not suitable for routine measurement of concentrations below 1%. However, good spectra of significantly lower concentrations can be measured using an ATR accessory, as shown in Figure 4. A realistic detection limit for this method is approximately 0.5%
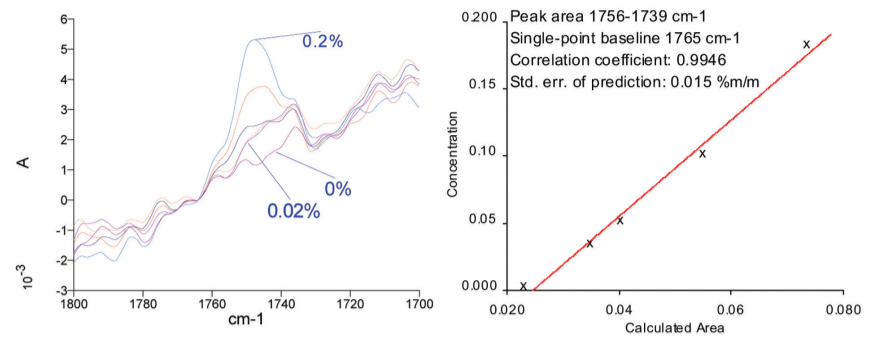

Figure 4. IR spectra of the biodiesel standards measured using a PerkinElmer Biodiesel IR FAME Analyser system with 9-reflection diamond UATR accessory, and the Beer's Law calibration plot.

Other Considerations for Method Implementation

For routine use, the ATR accessory permits slightly easier sampling in practice than other methods, since only a very small volume of sample is required and the accessory is easy to clean. The transmission method can be streamlined significantly by using a flow cell and disposable syringes. Initial qualification of the ASTM method requires measuring a large number of standards in order to verify that the chemometric model is performing adequately.

Conclusions

Analysing the concentration of biodiesel in distillate fuels is becoming increasingly important, both to verify blend concentrations and to detect trace levels of FAME in supposedly pure distillate. As such, a rapid and precise method quantification of FAME in diesel fuel blends is essential - FT-IR spectrometry offers just that. As demonstrated here, very low levels of biodiesel can be detected in diesel samples using FT-IR spectroscopy. Although both ASTM D7371 and EN 14078 methods are equally effective for standard blend measurements (1% to 30%), the better sensitivity attainable with a transmission measurement gives EN 14078 the edge over ASTM D7371 for trace measurements, with a detection limit of tens of ppm demonstrated here. Both methods are very easy to use with support from modern instruments and intuitive software.