APPLICATION NOTE

FTIR Spectroscopy

AUTHOR

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Portable Quantitative Biodiesel Analysis Using the Spectrum Two FTIR as per ASTM D7371

Scope

The content covered in this application note describes the process of using portable FTIR spectrometry to quantify biodiesel content in diesel fuel blends. Using three separate partial least squares (PLS) calibration models for low, medium, and high biodiesel concentrations and a suitable attenuated total reflectance (ATR) accessory, an analyst can easily and rapidly collect data in the field. No sample preparation is required, a drop of the neat diesel sample is applied directly to the ATR and results can be recorded in approximately 1.5 minutes including clean-up. In combination with a suite of robust software packages that can process data and update calibrations on the fly, this solution allows for easy quality control of biodiesel content in diesel fuel.

Introduction

Biodiesel, also referred to as fatty acid methyl ester (FAME), is a renewable and biodegradable fuel manufactured from vegetable oils, animal fats as well as recycled cooking greases and oils. These fats consist of triglycerides, a variety of ester derived from glycerol and three fatty acid chains. Biodiesel is synthesized by the reaction of the triglyceride with an alcohol in a process called transesterification. The resultant biodiesel has flow and ignition properties that make it compatible with most diesel engines[1]. Pure biodiesel (B100) is commonly blended with ultra-low sulphur diesel fuel (ULSD) to make up ratios of 5% (B5), 10% (B10) and 20% (B20) biodiesel in the fuel blend. A quick and accurate test method is highly desirable as quality control for producers, blenders and distributors of diesel fuel. ASTM D7371 is a standard test method for determining biodiesel content across the full range of 1 – 100 %v/v biodiesel concentration in diesel fuel blends by FTIR spectroscopy with an appropriate ATR accessory[2]. As the demand for renewable fuels is ever increasing, analysis of biodiesel fuel blends continues to be relevant in today's energy landscape. This application note details how the PerkinElmer Spectrum Two™ FTIR Spectrometer with the PIKE Technologies MIRacle 9 bounce diamond/ZnSe ATR accessory can provide a rugged, accurate and portable analyser to determine biodiesel content in diesel fuel according to ASTM D7371. The calibration models developed for this application can be supplied as a starter calibration with the potential for rapid optimization of an analyser in the field without the need for full recalibration.

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Instrumental

This application was developed using the components listed in Table 1.

Table 1. Application Components

Description	PerkinElmer Part Number
Spectrum Two FTIR with APV and DTGS detector	L160000F
Spectrum Two ATR Biodiesel Application Pack	L1600142

The Spectrum Two FTIR used for this application was equipped with a temperature stabilized deuterated triglycine sulphate (DTGS) detector. The instrument configuration also includes a filter wheel fitted with reference material for automated instrument performance verification. Amongst other reference material, the filter wheel contains a methane cell used for the Absolute Virtual Instrument (AVI) calibration. The AVI algorithm standardizes a measured spectrum of methane against data from the HITRAN database.[3] AVI is used to compensate for instrument – instrument and sampling accessory – accessory variation that can impede the transfer of a calibration between instruments. Using AVI will allow for the potential of calibration transfer between instruments to assist the rapid deployment of instruments for this application[4].

The MIRacle ATR accessory fits easily into the Spectrum Two sampling compartment as shown in Figure 1. Spectrum IR software will automatically detect the MIRacle accessory.

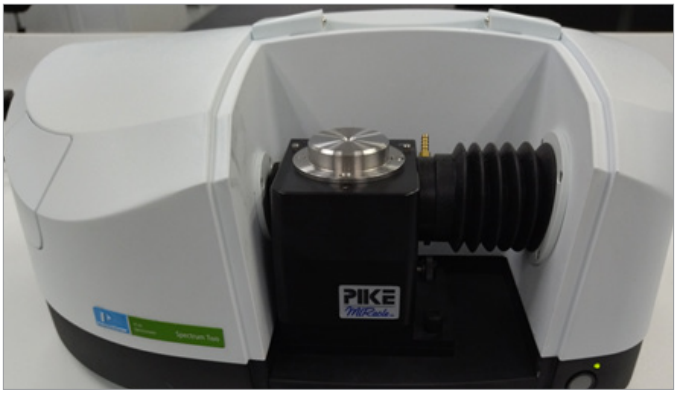

Figure 1. Spectrum Two with PIKE MIRacle ATR with 9 bounce top plate fitted.

Scanning Parameters	
Spectral Range	4000 – 650 cm^{-1}
Resolution	4 cm^{-1}
Number of Scans	8
Ordinate	Absorbance (AU)
AVI	On

For cleaning the MIRacle ATR, a triple solvent was used as suggested by ASTM D7371, consisting of an equal ratio of acetone, methanol and toluene. Before beginning the analysis and collecting the background spectrum it is important to clean the ATR crystal to ensure no residual contamination or sample carryover remains before analysis. A single drop of triple solvent dispensed with a Pasteur pipette should be sufficient to clean the ATR crystal. After dispensing the solvent, gentle cleaning with a cotton swab will remove any contamination and assist in drying the ATR crystal.

It is vital to repeat the cleaning procedure in-between sample analysis to prevent sample carryover. To ensure no sample carry-over occurs, the monitor function of Spectrum IR software can be made use of to be sure the crystal is clean between sample analysis.

Calibration

The infrared spectra of biodiesel blends exhibit non-linear behaviour with respect to concentration over the full range of 0 – 100 %v/v biodiesel due to interactions between mixture components. Because of this, we cannot create a single linear calibration model spanning the full range. ASTM D7371 specifies that the calibration be divided into three separate PLS calibration models.[2] A low calibration model of 0 – 10 %, a medium calibration of 10 – 30 % and a high calibration of 30 – 100 %v/v biodiesel content. As per the ASTM D7371 procedure, three different diesel fuels are used as matrix for the calibration standards. Low cetane, high cetane and ultra-high cetane index diesel fuel is used to prepare the calibration standards to model for the differences in cetane index that is commonly present in samples due to seasonal differences in the fuel chemistry. The spectral pre-processing parameters were set according to ASTM D7371, which provides specific spectral ranges to include for each of the three calibration ranges. Figure 2 shows an overlay of the standards used to prepare the low calibration model after pre-processing has been carried out by Spectrum Quant software. Most characteristic of the biodiesel present in the sample is the ester C=O stretching vibration at 1745 cm^{-1}.

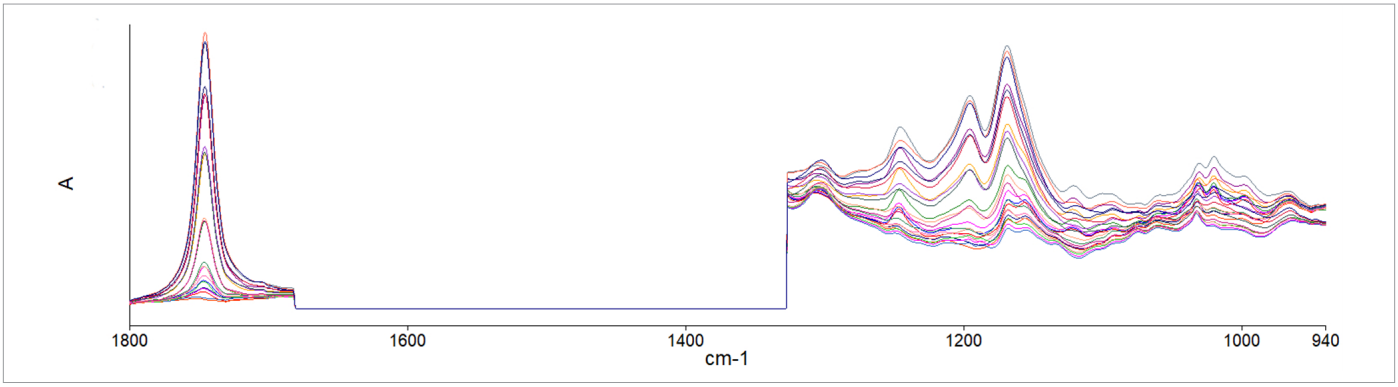

Figure 2: Spectral regions of interest for the low concentration calibration model (0 - 10 %v/v biodiesel).

67 standards were used to create the three starter calibration models. All standards and validation samples were purchased from Spectrum Quality Standards, Houston, USA. Figures 3 – 5 demonstrate the linear PLS curves of each of the calibration models with the standard error of prediction (SEP) and the coefficient of determination (R^2) labelled on the respective curve.

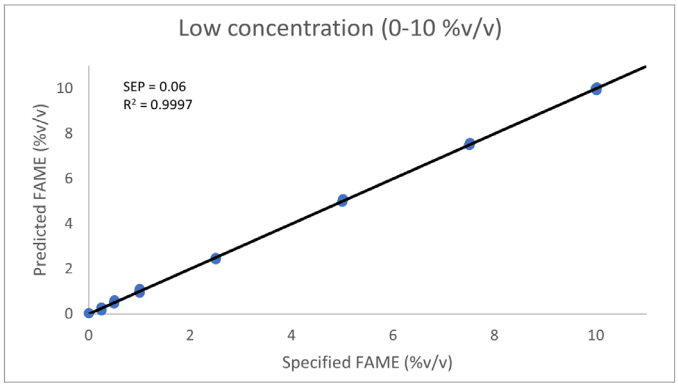

Figure 3. Low concentration PLS calibration curve.

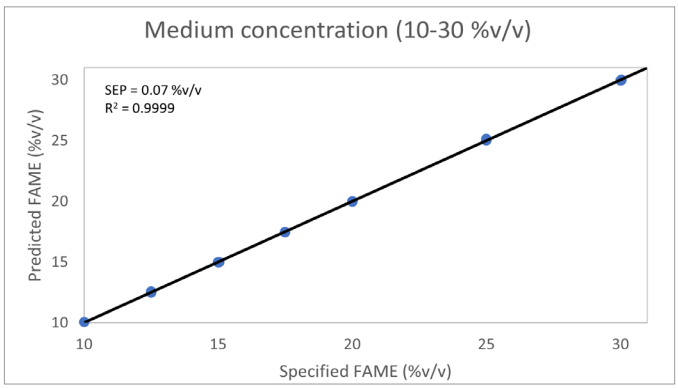

Figure 4. Medium concentration PLS calibration curve.

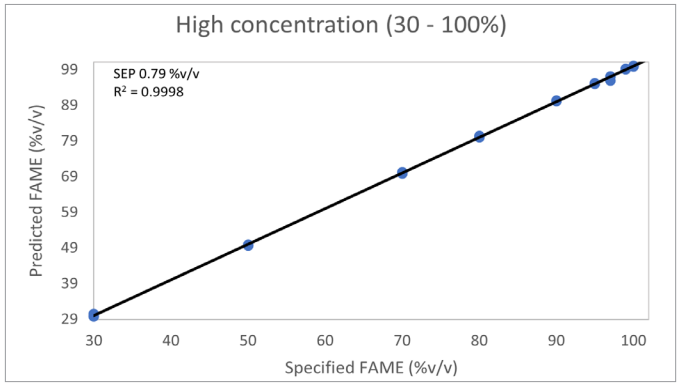

Figure 5. High concentration PLS calibration curve

All models display excellent linearity with an R^2 of at least 0.999 as well as a low SEP providing an indication the accuracy and suitability of the Spectrum Two and MIRacle ATR for this application.

Instrument Validation

To validate the three calibration models created and determine whether the instrument is qualified to perform the analysis, a set of validation standards is needed. A set of 25 validation standards were used spread across all three calibration models. Just like the standards used for calibration, these validation standards were made up in a matrix of diesel fuel of varying cetane index according to the ASTM method.

Table 2 shows the prediction results for two validation standards from each of the three calibration models. The results indicate a high level of agreement between the reference and predicted values for all three calibration models.

Table 3. Selected validation results from the three calibration models.

Description	Reference Biodiesel Conc. (%)	Predicted Biodiesel Conc. (%)
Sample 1 (low calibration)	1.30	1.27
Sample 2 (low calibration)	4.50	4.43
Sample 1 (medium calibration)	12.00	12.17
Sample 2 (medium calibration)	25.00	25.13
Sample 1 (high calibration)	40.00	40.22
Sample 2 (high calibration)	96.00	95.85

ASTM D7371 states that for an instrument to be qualified to perform this analysis, the standard error for the calibration range of 0 - 20 %v/v biodiesel must not be greater than the pooled error (PSEQ) specified in the ASTM method[2]. The PSEQ is specified to be 0.21 % v/v in the ASTM method and the measured error of 0.18 calculated from the results collected on the Spectrum Two and MIRacle ATR indicates that the instrument is qualified to perform this analysis.

Table 3 summarizes the results of the calibration and validation for the three calibration ranges as well as the standard error calculated for the range of 0 – 20 %v/v biodiesel.

Table 4. Validation results.

Model	R^2	Latent Variables	SEP (Cross Validation)	SEP (External Validation)
Low (0 - 10 %v/v)	0.9997	3	0.13	0.15
Medium (10 - 30 %v/v)	0.9999	4	0.10	0.19
High (30 - 100 %v/v)	0.9998	4	0.93	0.46
ASTM qualification (0 - 20 %v/v)	0.9994	3	0.20	0.18

Analysis Workflow Options

For collecting and processing data on the Spectrum Two and MIRacle ATR, there are three software options to implement the calibration models and analyse samples. These are as follows:

- From within Spectrum Quant using the Predict function.
- From within Spectrum IR software by using the calibration models created in Spectrum Quant.
- By incorporating the Spectrum Quant models in a Spectrum Touch macro.

The calibration models can be edited in Spectrum Quant software where a user may create a fresh calibration using the spectra of a new set of standards prepared according to ASTM D7371. Existing calibrations can be updated with a bias correction or improved by adding spectra of additional standards. Spectrum IR allows for the collection of standard or sample spectra and the processing of these spectra with the Spectrum Quant models. Finally, Spectrum Touch allows for the collection of sample spectra as well as the prediction of biodiesel content from these spectra in the same software workflow.

Ease of Analysis Workflow with PerkinElmer's Spectrum Touch Software

For ease of analysis the calibration models can be incorporated in a Spectrum Touch macro to provide step by step guidance for an analyst with the added benefit of being able to include an SOP for sample/standard preparation and analysis procedure. The benefit of this a streamlined workflow for quick and easy analysis. Figure 6 shows detail of the results screen from Spectrum Touch, displaying the results table and spectrum of a sample. Results can then be included in a .pdf report file or exported in .csv format for further data processing.

Figure 6. Results from the Spectrum Touch macro.

Conclusion

The PerkinElmer Spectrum Two in combination with the PIKE MIRacle 9-bounce diamond/ZnSe ATR provides a robust, portable, and accurate solution for biodiesel quantification as per ASTM D7371. Analysis of diesel samples on the Spectrum Two and MIRacle ATR is easy and accurate with all three PLS calibrations displaying excellent linearity. The external validation SEP achieved in the 0 – 20 %v/v biodiesel concentration range was 0.18%, below the limit specified for by the ASTM method and therefore indicating the instrument is qualified to perform this analysis.

Spectrum IR, Spectrum Quant and Spectrum Touch software provide a robust suite of tools for acquiring and processing data as the user requires. The calibration models can be used for the purpose of bias correction or as a template for updating with spectra collected from the users' own standards. The standards used for the creation of the calibration models for this application all made use of biodiesel from the same source. As such biodiesel from a different source could yield spectra with differences that could require further calibration model adjustment or recalibration with the relevant standards.

References

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