# Fuel Analysis with the Agilent 4500 Series FTIR: Monitoring Refinery Formulation to Ensure the Production of FAME-Free Marine Diesel Fuel

Application Note


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## Introduction

Biodiesel (FAME) is increasingly used in diesel fuel formulations, however, even small amounts of biodiesel are not appropriate in certain engine applications. For example, biodiesel in aviation fuel and in back-up electric generators used in nuclear power plants can cause significant issues. Likewise, the presence of trace biodiesel in diesel fuel specified for marine pleasure crafts is problematic. For example, older waterborne craft are often powered by engines that contain elastomeric gaskets that are chemically incompatible with biodiesel. Furthermore, marine engine combustion chambers or fuel supply systems may not be designed for use with biodiesel.

Most of these engines can tolerate trace amounts biodiesel (< 0.1%) with increasing risk of potential failure as the biodiesel concentrations increase. Since refineries formulate fuels for multiple applications, the possibility of contamination from fuels intentionally containing higher levels of biodiesel, such as those used for car and truck engines, is very real. For example, road diesel fuel often contains 5–7% biodiesel, and contamination or inadvertent mixing of this fuel with the fuel designated for marine engines may be highly detrimental.

This application note discusses the use of the Agilent 4500 Series FTIR, equipped with the Agilent-exclusive DialPath sample technology and Biodiesel Measurement Method, by a major UK refinery to ensure that fuel intended for marine application complies with BS ISO 8217 as well as the refinery's own compliance specification for biodiesel levels. The Agilent Biodiesel Measurement Method replaces the conventional FTIR method for measuring biodiesel in diesel fuel, IP 579/BSI 2000:579, since it is easier to use, faster, and more accurate for low level biodiesel measurement.

## Experimental

### Instrumentation

Trace biodiesel in marine diesel fuel is measured using the Agilent 4500 FTIR Series with DialPath technology (Figure 1). The spectrometer is a highly compact, portable system designed and engineered for use in out-of-lab, demanding environments. Powered by an internal battery, the system is not subject to local power fluctuations or interruptions. Though diminutive in size, the performance of the system is class-leading, that is, equivalent or better when compared to classical benchtop QA/QC FTIR spectrometers. The 4500 Series FTIR is able to rapidly obtain accurate, reliable results and enable real-time, actionable decisions to be made about product quality.

The interface between sample and spectrometer is equally critical, and the 4500 Series FTIR uses the Agilent-exclusive DialPath technology to ensure measurement accuracy and ease-of-use. This innovative technology eliminates all of the issues associated with measuring viscous liquids with classical infrared transmission cells.

Turnaround time per measurement consisting of sample introduction, background collection, sample analysis, calculation/display of results, and cleaning the interface is under 3 minutes. This simplicity of measurement, combined with preprogrammed calibration and the "one-button" method in the software, enables a technician to be trained to use the system, for the measurement of biodiesel in marine diesel, within 20 minutes.

*Figure 1. Agilent 4500 Series FTIR with DialPath Technology used for the measurement of FAME in marine diesel and road diesel fuel.*

### Interface for measuring biodiesel in diesel fuel

The Agilent DialPath technology is a proprietary, innovative methodology for measuring liquids that offers many advantages over traditional sealed transmission cells. The DialPath sample interface features an optical head that can be rotated to select one of three factory-calibrated, fixed pathlengths varying from 30 to 200 µm.

To analyze a sample, a drop of the liquid sample is placed on a stationary infrared-transparent window mounted on the top surface of the analyzer, and then a second window is rotated into position, thus sandwiching the sample between the two windows (Figure 2). This creates a highly reproducible, fixed sample pathlength between the two windows. After analysis, a simple wiping cleans the two windows and prepares the device for the next sample. DialPath has many advantages over traditional transmission cell technology:

- It permits nearly instantaneous selection of three different pathlengths as needed.
- No disassembly is required to change pathlengths.
- No spacers are required—cell leakage and fringing are eliminated.
- No syringes are needed to introduce the sample.
- It eliminates the difficulty of sample introduction and cleanup common when using classical IR transmissions cells – especially important when measuring viscous samples such as diesel fuel.
- Since samples are analyzed undiluted, measurements can be made more quickly with no chance that errors are preparation related.
- No supplies or consumables (cell windows, spacers, cleaning solvents, and so forth) are required.

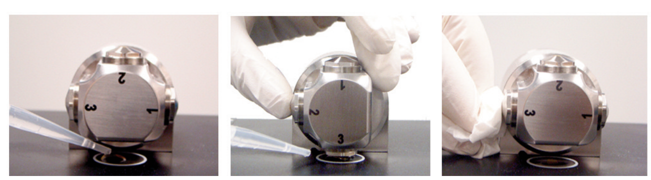

*Figure 2. DialPath operation. Place sample on window; rotate second window into position; analyze sample; clean windows by wiping.*

## Method

The Agilent method for low level analysis of FAME in diesel fuel [1] uses the best concepts contained in both ASTM D7371 (partial least squares regression) and EN14078 (transmission IR). This new approach yields a method that surpasses the capabilities of the earlier methods and achieves a limit of detection (LOD) of 0.025% biodiesel. The spectra of 0–1.5% FAME in biodiesel in the 1,680–1,800 $cm^{-1}$ region (Figure 3) demonstrates that the FAME carbonyl absorbance band is directly proportional to the biodiesel amount present, and is free from interference. The precalibrated multivariate method, which uses the FAME spectrum including the carbonyl absorbance band, is stored on-board, and the highly intuitive software prompts the user with visual commands, explanations, and checks. Moreover, the Agilent method measures the diesel sample undiluted, thus eliminating sample dilution and resultant potential errors.

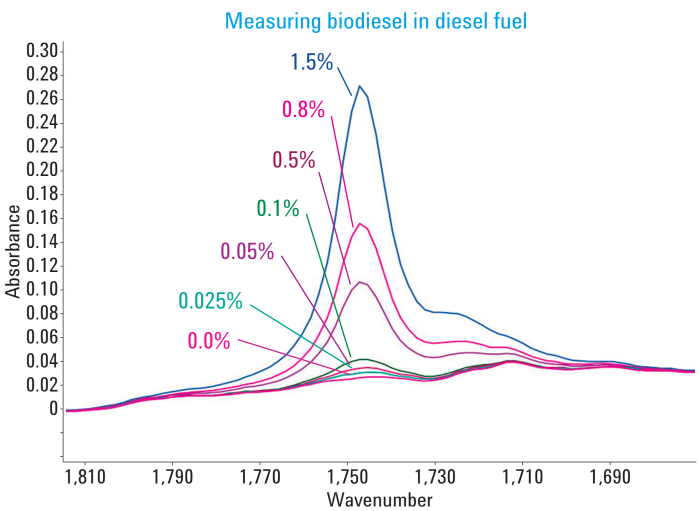


*Figure 3. The carbonyl moiety in FAME has infrared absorbance at 1,745 $cm^{-1}$. The band is free from interferences and is a direct measurement of the amount of biodiesel present.*

## Results and Discussion

For a one-month period, a UK based diesel refinery tested each formulated batch of marine diesel with the Agilent 4500 Series FTIR equipped with DialPath technology and used the Agilent Biodiesel Method. Each batch was tested to determine conformance to BS ISO 8217. These batches are represented by numbered squares (Figure 4) and each square represents a FTIR result from a single batch. The analytical quality control (AQC) samples are at 0.1%, 1%, and 7% in the graph (red circles in Figure 4). It is clear that the tested batches all fall within the acceptable limits for marine diesel (< 0.1% FAME) and the refinery is well within their action level of 0.05% for all their batches.

The inclusion of the measurement for the 1% and 7% standards demonstrates that the same method can be used for different purposes. These levels are used to check that the road diesel has been mixed with the correct level of biodiesel. When the plant is switched over from road to marine diesel, there is a cross over period where the fuel contains intermediate levels of biodiesel (blue triangles in Figure 4).

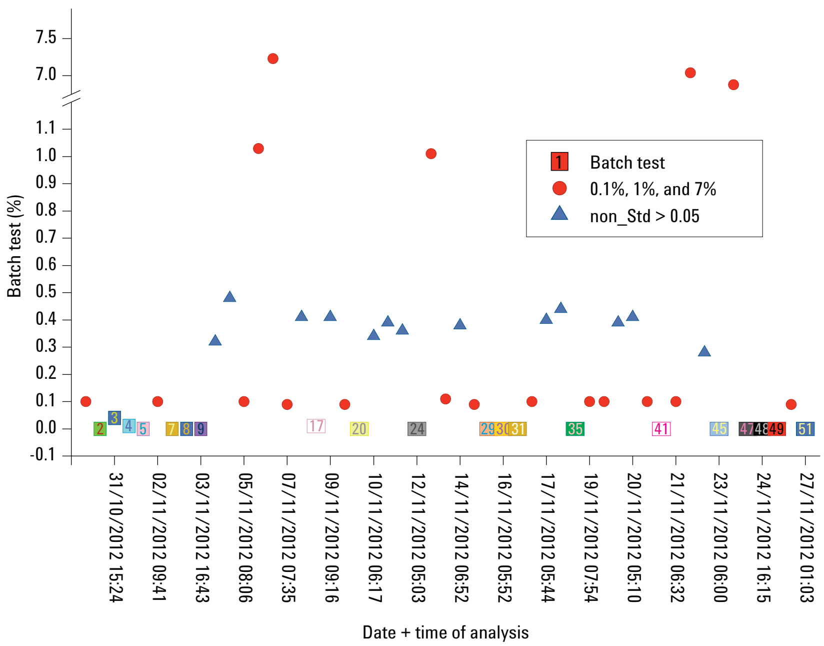


*Figure 4.* *Marine diesel batches tested for FAME level (numbered squares). Analytical quality control standards are shown as red circles. Intermediate samples from switch over from road diesel formulation to marine diesel are shown as blue triangles. Higher level analytical standards (1%, 7%) are shown as well.*

Occasionally, the amount of FAME in reformulated marine diesel may lie within the acceptable regulation limits of < 0.1%, but may exceed the refinery's own specifications of 0.05%. Because of the excellent analytical performance of the Agilent 4500 Series FTIR, those cases (Batch 3 in Figure 5) can be detected and decisions made about acceptability of a specific batch.

## Conclusion

A FTIR based method that combines the most appropriate aspects of the EN14078 and ASTM D7371 methods was used to test each individual batch of biodiesel (FAME)-free marine diesel. This method is far easier to use and implement than the traditional IP 579 method, and validates that each individual batch meets BS ISO 8217 standards.

The method uses the Agilent 4500 Series FTIR equipped with DialPath technology. This eliminates the need to use standard IR transmission cells and also eliminates a number of steps including dilutions and more involved cleanup of glassware and cells. Sample measurement time from introduction to full analysis and preparation for the next sample takes under 3 minutes and the precalibrated method is executed with a simple command so that user training takes less than 30 minutes.

This method enables the refiner to quickly determine switch over times as well as check each individual batch to ensure that marine diesel is FAME-free. The same method is used to check that road diesel reformulation contains correct levels of FAME as well as for a number of other time and cost saving functions. The portability, accuracy, and ease-of-use enable measurement in virtually any location whether a refinery's lab, harbor, or storage depot.

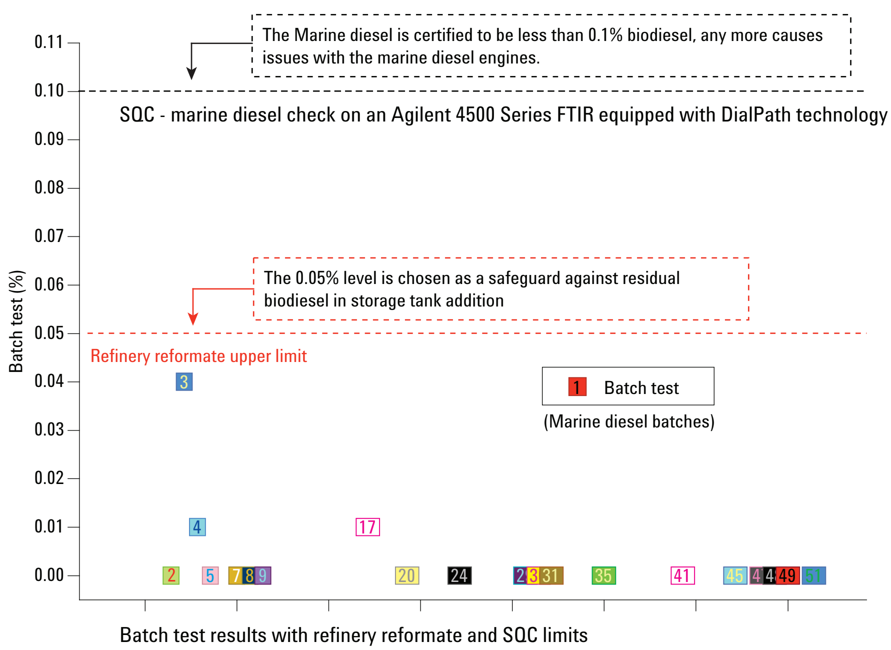


*Figure 5.* *FAME in marine diesel. Switch over from road diesel to marine diesel are within regulation limits, however, Batch 3 shows FAME levels approaching refinery specification limits.*

## Reference

1. J. Seelenbinder, F. Higgins, "Test method for low level detection of biodiesel in diesel using the Agilent 5500t spectrometer", Publication Number 5990-7804EN, May 1 2011.

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