APPLICATION NOTE

FT-IR Spectroscopy

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Detection of trace amounts of biodiesel in diesel fuel using transmission and attenuated total reflection (ATR) sampling

Introduction

Biodiesel is a renewable alternative fuel produced from plant crops by transesterification of the extracted oils. While many diesel engines can run on pure biodiesel, it is more commonly blended with fossil diesel prior to use. In fact, regulations for diesel fuel such as ASTM® D975, used in the USA, and EN 590 in Europe specify that fuel with a content of up to 5% biodiesel may be sold as diesel without any special labelling denoting the biodiesel content.

While the presence of biodiesel does not generally affect the use of the fuel in vehicles, in scenarios where the fuel may be stored for a long time, such as fuel reserves for backup generators at nuclear power plants, there is concern about its oxidative stability. Because vegetable oils tend to have a degree of unsaturation (double bonds in the fatty acid chains), chemical reactions can take place 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 formation of insoluble particulates that can block filters.

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The standard test methods for quantifying biodiesel in fuel by infrared (IR) spectrometry, such as ASTM® D7371 and EN 14078, are intended for use with common blends, usually implying a biodiesel content greater than 1%. However, IR spectrometry is capable of measuring far lower levels of biodiesel. In this note we show that a detection limit of around 0.003% m/m is attainable using the PerkinElmer® Spectrum™ 100 FT-IR and a standard transmission cell. If the ease of sampling provided by Diamond ATR is desired, a detection limit of better than 0.1% is still achievable.

Experimental

Standard solutions of rapeseed biodiesel in diesel were prepared gravimetrically. A stock solution of 2% m/m was diluted to give five standards over the range 0.01–0.2% m/m. The infrared spectra were measured on a PerkinElmer Spectrum 100 FT-IR spectrometer using both a liquid transmission cell with CaF_2 windows and a 0.5 mm pathlength and a UATR accessory with a 9-bounce diamond top-plate. In both cases, the spectral resolution was 8 cm^{-1}. Measurement times were about 30 s for the transmission cell and two minutes for the ATR accessory. Calibrations were constructed by regressing the measured area of the carbonyl band around 1745 cm^{-1} against the concentration, using Spectrum Beer's Law software. Detection limits were calculated as 5 times the standard error of prediction (SEP): this is approximately equivalent to allowing false positive and false negative detection rates (α and β) of 0.05.

Results and discussion

Spectra measured with the transmission cell, and the resulting calibration plot, are shown in Figure 1. Even the lowest-concentration standard is clearly distinct from the blank diesel sample. The standard error of prediction is 0.0005% m/m, indicating a detection limit of around 0.003% m/m. This could be further improved by the use of a longer pathlength (the optimum blank absorbance of ~0.5 would be obtained with a 1 mm pathlength) or by scanning for longer. Note that the blank sample still has some absorption in this region of the spectrum (due to overtones of bands in the fingerprint region of the mineral-diesel spectrum), and care may be required when dealing with samples having varied composition of the base diesel.

The ATR results are shown in Figure 2. Comparing the absorbance values for the 0.2% standard in Figures 1 and 2, the ATR signal is about 40 times weaker, and this is compounded by the increased noise due to the lower transmittance of the accessory. Still, a remarkably good calibration was produced, confidently indicating a detection limit of 0.1% m/m.

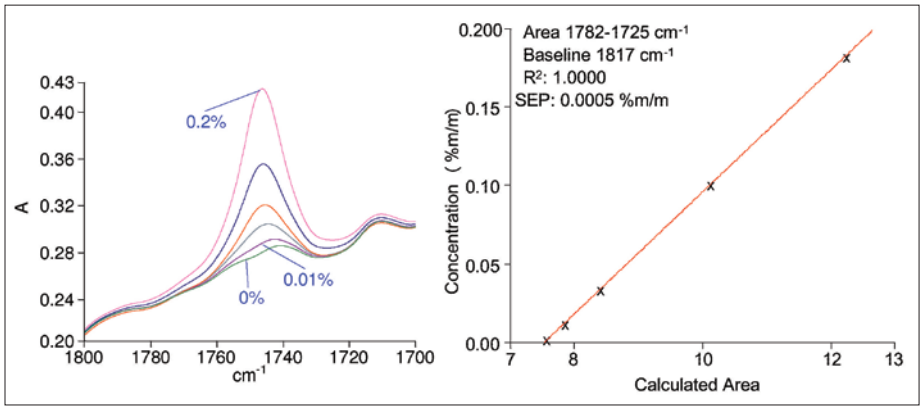

Figure 1. IR spectra of the biodiesel standards measured using the transmission cell, and the Beer's Law calibration plot.

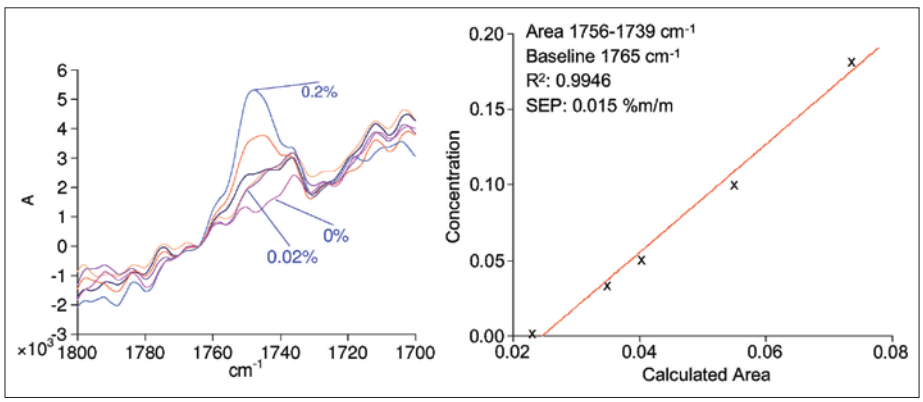

Figure 2. IR spectra of the biodiesel standards measured using the ATR accessory, and the Beer's Law calibration plot. The spectra have been baseline-corrected by subtracting an offset.

Conclusions

Very low levels of biodiesel can readily be detected in diesel samples with the Spectrum 100 FT-IR spectrometer. Diamond ATR provides excellent convenience and ease of use and cleaning, and is suitable for concentrations down to about 0.1% m/m. If greater sensitivity is desired, a standard liquid transmission cell with 0.5 mm pathlength was found to give a detection limit of 0.003% m/m with a 30 s measurement.

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