Application note

Quantitative Measurements of Red Dye in Diesel Through UV-Visible Techniques

Introduction

Diesel fuel for compression ignition engines was first developed by Rudolf Diesel in the late 1800s.[1] Since their invention, these engines have had applications in spaces that include electric generators, buses, farm equipment, semi-trucks, and light trucks. Since diesel has a higher density compared to gasoline, diesel engines work via compression, which differs from gasoline-powered engines that rely on a spark to ignite the fuel. Because of this, diesel engines can be more useful in certain cases compared to gasoline-powered engines. For example, diesel engines are 20% more thermally efficient; this efficiency allows for the higher torque needed to haul heavier loads. Also, diesel engines operate at lower revolutions per minute leading to the engines having longer lifetimes and better fuel efficiency. Thus, they are a good for farm equipment such as tractors or for construction machinery needed to transport heavy loads. They also typically last longer in rough environments.[2]

Figure 1. The Thermo Scientific Evolution One UV-Visible Spectrophotometer.

Because of the high demand for diesel in certain fields that require heavy-duty vehicles, such as agriculture and construction, there is an economic incentive to keep the price of the fuel low for those industries. As such, there are laws in countries like the United States that allow place a lower tax burden on certain vehicles and machinery that run on diesel. There are heavy fines in place if this diesel is used for a purpose that is not allowed.[3–6] To track and enforce the proper utilization of diesel in these markets, a red dye is added to differentiate it from other diesel. According to rules established by the Internal Revenue Service, and as listed by ASTM D6258, the requirement mandates that the fuel contains the dye Solvent Red 164 (and no other dye) at a concentration spectrally equivalent to 3.9 lb of the solid dye standard Solvent Red 26 per thousand bbl (11.1 mg/L) of diesel fuel.[4,7]

ASTM D6258 lays out a method to measure the concentration of the red dye in kerosene using visible spectroscopy that can also be used to measure the concentration of Solvent Red 164 in diesel. Solvent Red 164 is used in place of Solvent Red 26 as it is more cost-efficient and more fuel-soluble. Solvent Red 26 is used to develop the quantitation curve since it is available in its pure form and is very similar in chemical structure to Solvent Red 164. Using the Thermo Scientific™ Evolution™ One Plus Ultraviolet and Visible (UV-Vis) Spectrophotometer (Figure 1) along with the Thermo Scientific™ Insight™ Pro Software, a quant method was developed to determine the concentration red dye in diesel and kerosene.

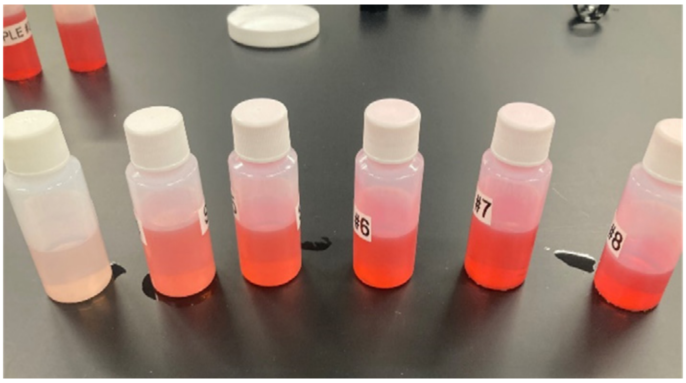

Figure 2. Standards used to develop the quant curve.

Experimental

The procedure for developing the standards and collecting the data is laid out in ASTM D6258.[7] A 1 cm pathlength quartz cuvette was used as diesel is a hydrocarbon liquid that will dissolve polystyrene cuvettes. Data was collected using a Thermo Scientific Evolution One Plus UV-Vis spectrophotometer, from 450 to 750 nm at a scan rate of 120 nm/min and a bandwidth of 1 nm. While the method says to collect at a data interval of 0.11 nm, doing so produced too much noise; thus the interval was increased to 0.5 nm. According to ASTM, "other instrument conditions may be used if they can be demonstrated to give equivalent results to the test method," indicating this change in data interval is still within the method instructions.[7] Using the Thermo Scientific Insight Pro software, a second derivative of the raw absorbance spectrum was calculated. The data was smoothed via a 2nd order polynomial Savitzky-Golay smoothing function to alleviate noise. The amplitude difference between the 538±20 nm valley and 561±20 nm peak of the 2nd derivative spectrum was measured and used for the quant curve as outlined in ASTM D6258. The ±20 nm range accounts for differences in instrumentation and software used. Five standards from 3 mg/L to 15 mg/L of Solvent Red 26 in kerosene, prepared at 3 mg/L intervals of concentration, were used to develop the quant curve. A kerosene sample with unknown dye concentration, used as received, was also measured using the same procedure as outlined for the standards. Pure kerosene was used as a blank for all experiments (Figure 2).

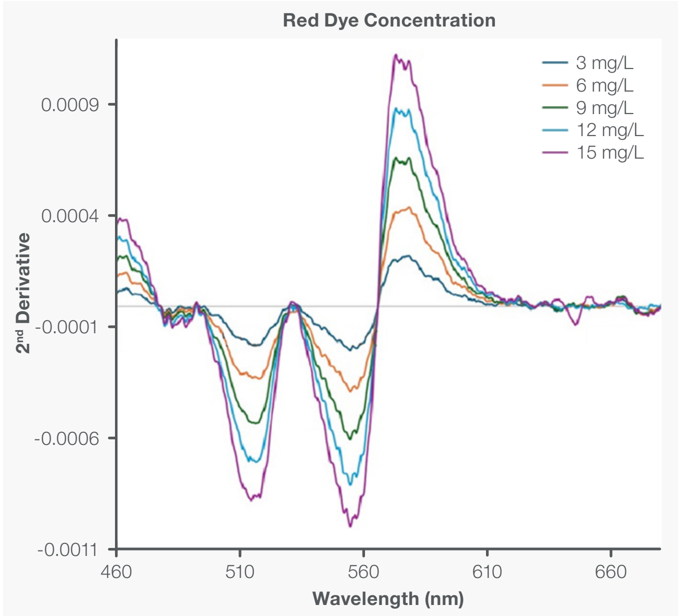

Figure 3. 2nd derivative of red dye spectrum in kerosene.

Results and Discussion

Figure 3 shows the second derivative spectrum of the standards used to develop the quant curve. It is clear that as the concentration increases the difference between the valley at 554 nm and the peak at 574 nm increases as well. As the absorbance is expected to increase linearly with concentration according to Beer's law, the second derivative is also expected to follow this behavior. Typically, one peak is monitored for concentration measurements; however, since there are overlapping transitions, using the second derivative allows for better separation of these overlapping peaks. This is a common practice in UV-Vis spectrocopy.[8]

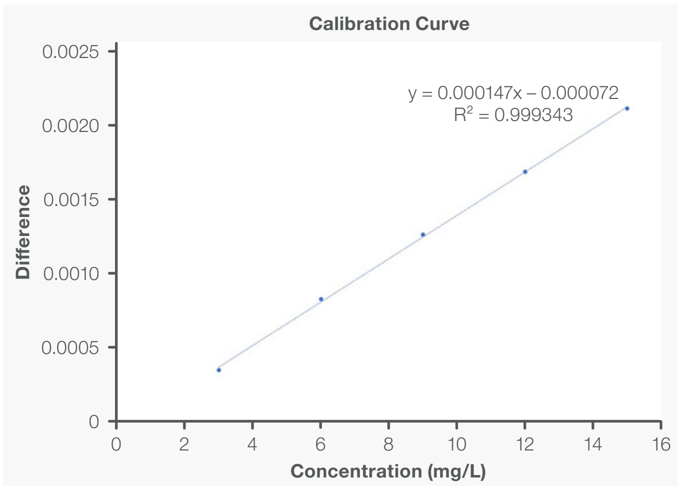

Figure 4. Calibration curve of the difference between 538 nm and 561 nm of the second derivative plots.

The difference between the 554 nm valley and the 574 peak was plotted with respect to the concentration and is shown in Figure 4 to construct a calibration curve for this analysis. The calibration curve has an R^2 of 0.999 showing a good linear correlation between the difference in with the concentration. The calibration curve equation is outlined in Equation 1,

$$y = 0.000147x - 0.000072$$

Equation 1.

where *y* is the difference between the second derivative amplitude at 561±20 nm and 538±20 nm and x is the concentration of Solvent Red 26. An absorption spectrum of a sample of unknown concentration was collected and the second derivative spectrum was calculated (Figure 5). Using Equation 1, the samples were found to have a dye concentration of 14.2 mg/L.

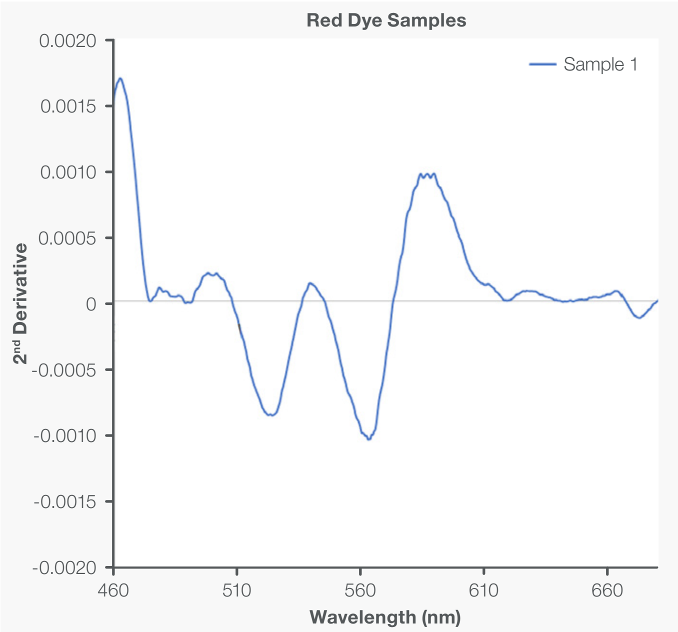

Figure 5. Second derivative of three samples of unknown concentrations.

It should be noted that when developing calibration/standard curves it is best practice to use the same method settings on the same instrumentation, as even minor differences can lead to irregularities in results. This ASTM method does account for any variation between instrumentations, such as the valley and peak having a ±20 nm range, but once a calibration curve is developed it should only be used on the instrument used for development of the curve. It is also best practice to re-calibrate at the start of a new experiment as well to avoid any day-to-day variations that may arise.

While the methods laid out here focused on calculating the concentration of red dye in kerosene, they can be used to measure the concentration of red dye in diesel as well. The use of 1st and 2nd derivative analyses is common in literature; for example, it is used to measure the concentration of materials such as vitamin A content in cod liver oil. The method aids in quantifying analytes with overlapping absorption spectra.[8]

Conclusion

Diesel has many advantages in industrial, construction, and agricultural settings, just to name a few, and as such there is a constant demand for the fuel. To meet standards set by the Internal Revenue Service on tax-exempt red dye diesel, a proper method and instrument is needed to accurately determine the red dye content. Through the Thermo Scientific Evolution One Plus UV-Vis Spectrophotometer, along with the Thermo Scientific Insight Pro Software, development of a quick method to determine the concentration of red dye according to ASTM D6258 is possible.

References

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