Rapid measurement of gasoline (petrol) in diesel fuel using portable FTIR spectroscopy

Application Note

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Introduction
Gasoline contamination in diesel fuel is a growing problem as diesel and alternative biodiesel blends are becoming more popular for commercial and personal fuel consumption. Gasoline can contaminate diesel fuel stocks in transit from the refinery to the final destination via tanker trucks, railcars, pipelines, or cargo ship. Gasoline contamination of diesel fuel can also occur in underground storage tanks at distribution facilities or end user filling stations. Some South American countries are experiencing problems with gasoline dilution of diesel to increase profits due to the lower cost of gasoline relative to diesel in certain markets. Some individual diesel owners mix gasoline into diesel to prevent gel formation in very cold winter locations.

Gasoline consists of light distillates with hydrocarbons in the C7-C11 range. Most hydrocarbons in gasoline are straight or branched chained aliphatics; although, 25-30 % of the hydrocarbons are aromatics consisting of hexagonal rings. Aromatics are more volatile and have lower flashpoints than their aliphatic counterparts, and high octane gasoline contains more aromatics. Additionally, gasoline in North America also contains 7-10 % ethanol (oxygenate), which lowers the smog emissions of gasoline engines.
Diesel fuels are middle distillates from the refining process and consist of hydrocarbon chains greater than C12. These longer hydrocarbon chains result in more energy per unit of volume; furthermore, the diesel combustion process is about 20% more efficient than a spark ignition combustion engine. Both these properties make turbo diesel powered vehicles travel ~40% further than an equal sized gasoline powered vehicle on the same volume of fuel. A gasoline contaminant in diesel fuel creates a mixture with less energy content, lower cetane value, and lower lubricity compared to straight diesel. This can cause coke formation (carbonization) on diesel fuel injectors and can also cause excessive wear on injectors, pistons, and other fuel contact engine parts. This is especially problematic for ultra low sulfur diesel (ULSD) due to its lower lubricity compared to agricultural diesel. Furthermore, gasoline can cause varnish deposits on diesel fuel filters to be washed off the filter and into the engine, which could clog injectors and contaminate other critical engine parts.

Diesel fuel does contain heavy aromatics, such as naphthalenes and other condensed ring compounds, but their infrared bands do not overlap the aromatics present in gasoline. The intensity of an infrared absorbance band is proportional to the concentration of that component in a mixture, as stated in Beer’s Law. This relationship allows the Agilent 5500t FTIR spectrometer to accurately measure gasoline in diesel fuels. The sensitivity of the 5500t FTIR allows gasoline to be measured down to 0.025% in diesel. To demonstrate this, several concentrations of gasoline (87 octane) are carefully prepared in ultra low sulfur diesel (US, Danbury CT). The samples were prepared with 0%, 0.0269%, 0.2669%, and 1.0586% gasoline in diesel. The FTIR spectra were measured on the 5500t spectrometer and the gasoline absorbance results are plotted against their concentrations in Figure 2. This gasoline absorbance plot indicates a very good linear correlation with concentration. This linear correlation is common in spectroscopy and can be easily added to 5500 FTIR methods. Multiple components can be reported from a single 3 minute analysis, such as gasoline in diesel, biodiesel in diesel, oxidation, and water.

The chemical differences between gasoline and diesel can be seen in the infrared spectrum of each. Figure 1 shows a comparison between the infrared spectra of gasoline and diesel highlighting the ethanol and aromatics in gasoline. Neither ethanol or light aromatics present in gasoline are observed in the diesel fuel spectrum; in fact, the spectrum of diesel fuel is similar to mineral oil.

Figure 1. The IR spectral overlay of gasoline (Blue) and diesel fuel (Red) using the Agilent 5500t FTIR spectrometer, 100 µm pathlength
Fuel analysis using the Agilent 5500t FTIR spectrometer has been shown to accurately measure gasoline in diesel fuel from 0.025-100% gasoline. This ability coupled with the 5500t FTIR’s industry established measurement of biodiesel in diesel, provides highly sensitive on-site and field portable diesel contamination analysis. Oxidation and water contamination are also accurately measured using the same 5500t instrument.

The instrument can be operated from a laptop (5500t) or the Agilent 4500t FTIR which is a fully field portable version with an onboard battery and operated from a hand held computer (PDA). The instrument software is simple to use with little to no sample preparation. The instrument is not harmed by humidity or other outdoor conditions, weighs 8lbs, and takes up less bench space than a laptop computer.

**Figure 2.** The IR absorbance vs. concentration plot for gasoline in diesel, Agilent 5500t FTIR 100 um pathlength

**Conclusion**