# Characterization of Diesel Fuel Using a Modular Raman System

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## Application Note


### Keywords

- Biofuel

### Techniques

- Raman spectroscopy

### Applications

- Compound identification
- Process quality control
- Petroleum analysis
- Authenticity and brand security


Raman spectroscopy is an excellent technique for the identification and characterization of fuels. With no requirement for sample preparation and the power to identify and quantify materials, it is no surprise that Raman has found so many uses in a range of industries.

## Background

In the case of fuel samples, Raman spectra contain a wealth of spectral features due to the presence of different types of hydrocarbons providing a unique Raman fingerprint based on composition.

In addition, chemometrics models can be developed from Raman spectral data to more fully characterize fuels, including determination of critical parameters such as octane and density. Raman spectroscopy also can play a role in the detection of counterfeit fuels through the use of Raman spectral markers added to the fuel to enable rapid field confirmation of fuel composition, quality and source.

Biodiesel is a non-petroleum-based diesel fuel made from vegetable oil or animal fats. It is produced using a process called transesterification, where the oil or fat is reacted with an alcohol to remove glycerin (used in soaps and other products) and produce biodiesel in the form of fatty acid methyl esters. Biodiesel can be used in most diesel engines with little to no engine modification required. It can also be blended with petroleum diesel fuel to provide a cleaner burning, lower emission diesel fuel.

With the trend toward use of renewable energy sources with lower emissions and less toxicity than petroleum-based fuels, biodiesel production is on the rise. As this production increases, there are many opportunities to use Raman spectroscopy during the biodiesel refining process to assess incoming raw materials, monitor the production process and confirm the quality of the final product.

As Raman spectroscopy techniques have grown in popularity, the range of Raman measurement options has expanded dramatically. Today, users can select from handheld systems such as the IDRaman mini; fully integrated systems for the lab including the IDRaman reader; and a "build your own" Raman system toolkit of modular components including spectrometers, lasers, fiber optic probes and sample holders.

If you opt for the modular Raman spectrometer approach, we offer several back-thinned CCD array detector options to get you started, including our Ventana, QE series and Maya2000 series spectrometers. In this application we used the Maya2000 Pro-NIR, which is preconfigured for Raman and low light shortwave NIR applications. The Maya2000 Pro-NIR is configured for the 780-1180 nm region and includes a 760 nm longpass filter, 50 µm slit and gold mirrors for enhanced NIR reflectivity.

## Measurement Conditions

The Raman measurements described here were made with a Maya2000 Pro-NIR spectrometer, a 785 nm Raman laser, a Raman-coupled fiber probe for 785 nm Raman and a sample holder. The 785 nm laser was chosen for Raman excitation to avoid the fluorescence background often seen with shorter wavelength laser excitation. Acquisition parameters were a 500 millisecond integration time with no scans averaged and no boxcar smoothing. Samples of corn oil (sometimes used as a diesel alternative) and petroleum-based diesel were placed in small glass vials for analysis to illustrate the power of Raman to distinguish diesel fuels and to characterize biodiesel raw materials.

## Results

The Raman spectra for corn oil and diesel are shown in Figure 1. While these spectra share some common features due to the hydrocarbon content of the samples, there are also a number of spectral differences observed for these samples in the fingerprint region from 500–2000 cm$^{-1}$. Even though both samples are suitable for use as fuel in diesel engines, they have distinct Raman spectra

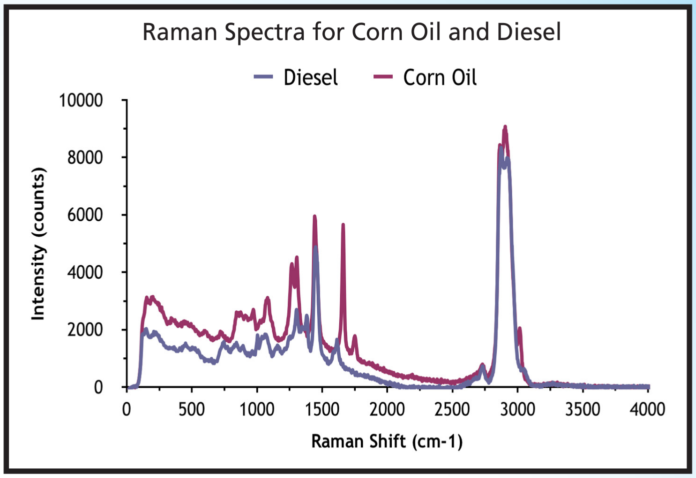


Figure 1. Raman is an excellent method for distinguishing corn oil-based biodiesel fuels from petroleum-based diesel fuel.

that distinguish the corn oil-based biodiesel fuel from the petroleum-based diesel fuel. Note that in addition to identifying the fuel type based on its Raman fingerprint, one could obtain more quantitative information from the spectra — including assessment of critical fuel parameters – by conducting additional analysis and applying the appropriate chemometrics models.

One difference that stands out for the spectrum of corn oil is the presence of stearate (a form of the fatty acid found in animal and vegetable fats and oils) in the region from 1600-1800 cm$^{-1}$. As expected, the stearate peaks do not occur in the Raman spectrum for petroleum-based diesel fuel. While the stearate artifacts and other spectral differences allow for easy discrimination of these fuels, even samples with more closely aligned spectral peaks could be distinguished. Indeed, by using a narrower slit in the spectrometer optical bench, you will achieve a higher Raman shift resolution over a narrower spectral range.

## Conclusion

With their unique hydrocarbon compositions, fuels are well suited for identification and characterization using Raman analysis. The wealth of spectral features in the Raman spectra for fuels can be used in a range of applications including determination of critical fuel parameters, fuel classification and detection of counterfeit fuels. With its great sensitivity in the NIR region, the Maya2000 Pro-NIR is an excellent choice for Raman measurements using laser excitation in the NIR region.

While the setup described here is one possible set of tools for Raman measurements, there are a number of other possibilities, both integrated and modular, to enable a range of measurements for different sample types and conditions. In addition to the Maya2000 Pro-NIR, the Ocean Optics QE series high sensitivity spectrometers are available with a cooled back thinned detector to keep dark noise from interfering with measurements when long integration times (several seconds) are required to detect low intensity Raman scattering. Preconfigured versions of the Maya2000 Pro and QE spectrometers provide optimized Raman measurements; custom configured options allow even more flexibility in tailoring the wavelength range and resolution for specific measurement needs.

There are also a number of Raman excitation laser options available including 532 nm and 785 nm Raman lasers. Excitation lasers and spectrometers can be coupled to a range of Raman probes with built-in laser line filtering and shutters with probes designed specifically for hostile process environments, immersion into samples and various focal lengths for laboratory measurements. Custom flow cells are an option for monitoring Raman in a flowing sample stream.

With all the choices available, the modular approach to Raman measurements provides a nearly endless choice of setups with the ability to change or add components to meet your evolving measurement needs.

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