Ocean Insight

Raman Analysis of Fuel Markers

Spectral Tools to Safeguard Fuel Integrity

Application Note

KEYWORDS

- BPE
- Fuel integrity
- Ocean HDX Raman spectrometer

TECHNIQUES

- Raman
- Surface Enhanced Raman Spectroscopy

APPLICATIONS

- Anticounterfeiting
- Fuel marker detection

Raman spectroscopy is an excellent technique for the identification and characterization of fuels and fuel markers, which have distinct spectral features with unique Raman fingerprints. In the case of fuel markers, Raman is an especially useful tool in detection of fuels that have been adulterated or illegally resold for a profit.

To test the viability of the small-footprint, 785 nm Ocean HDX Raman spectrometer for fuel marker detection, we measured the marker BPE (CAS RN 1437-15-6). BPE is used at very trace levels to prevent damage to engines and other components, making it challenging to detect.

Introduction

Fuel fraud is a significant enterprise, costing businesses billions of dollars annually and adversely affecting regulators and consumers. As a result, the use of technology to ensure fuel integrity has improved in recent years to help thwart various threats to supply chains, with the use of optical sensing techniques playing a key role.

Companies engaged in anticounterfeiting efforts continue to seek spectral sensing tools that are more portable and simpler to use than traditional laboratory benchtop systems, but with comparable performance and reliability. One can imagine the impact of real-time, in situ screening of fuels at various spots along the supply chain, mitigating the need for time-consuming sample collection and lab analysis.

Now, as advances in spectrometer technology and algorithm development have made Raman more accessible and the data more understandable, the idea of using a compact, affordable spectrometer like the Ocean HDX Raman to measure very small amounts of a marker in the field isn't so far-fetched.

Experimental Setup

Equipped with an Ocean HDX Raman spectrometer, we measured 3 ppm BPE in several batches, to demonstrate both the Raman response and reproducibility of the measurements. The rest of the setup comprised a 785 nm Raman laser, a general-purpose Raman probe optimized for 785 nm excitation, a sample holder, and OceanView operating software. To enhance the Raman response, we also used small amounts of Surface Enhanced Raman Spectroscopy (SERS) gold nanoparticles in liquid phase.

Ocean HDX Raman is a compact instrument – at approximately 3.5" x 2.5" x 2.1", it's one of the smallest Raman spectrometers on the market – that unlocks Raman signature data from 150 cm^{-1} to 3400 cm^{-1}. The spectrometer is available with a 25 µm or 50 µm entrance slit, and can be combined with a laser, probe and sample holder to measure solids, powders and liquids. Also, its lower price point makes Ocean HDX Raman more attractive to product integrators and developers than many scientific-grade Raman spectrometers.

Results

After dropping our BPE samples into the SERS nanoparticle suspension, we then put the sample vials into the Raman holder, interrogated them with the laser, and measured the response **(Figure 1)**. Several distinctive Raman peaks were observed in the spectra, and because the BPE was homogeneously distributed throughout the liquid suspension, measurement reproducibility was good.

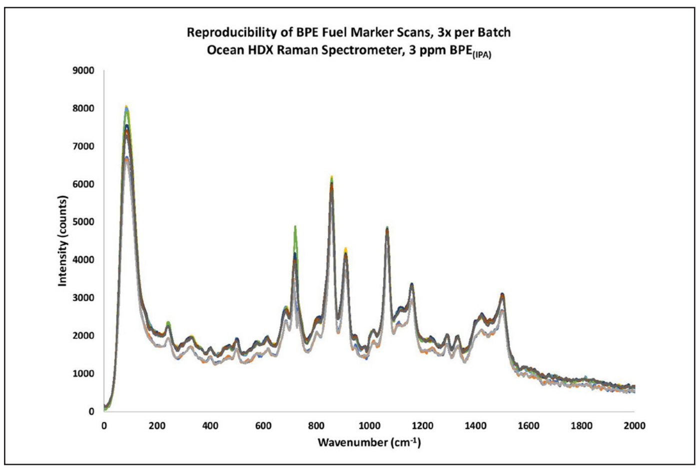

Figure 1. The fuel marker BPE has several distinct Raman peaks.

By adding more analyte to the same sample vial, we could have created a linear concentration regression. If you know the concentration of your analyte, you can create a calibration curve, introduce unknowns, and then calculate the concentration for those samples.

Also, when measuring samples like BPE, it's important to account for any optical shifts by performing a baseline correction. Peak values, or any values in general, may be skewed by environmental influences but can be corrected, based on some region(s) known to be independent of changing parameters. The same can be done for Raman spectra, and is critical to correct if one wishes to extract quantification information.

Summary

Once considered too advanced in both theory and instrumentation for most users, Raman spectroscopy today encompasses simple handheld devices including the Ocean HDX Raman, signal-enhancing SERS chemistries, and advanced chemometrics and machine learning, which have helped to translate complex data into more meaningful answers for a wider range of users.