APPLIED SPECTRA

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Application Note # 1001

Petroleum detection using LIBS technology

Summary

Ensuring proper fuel additive levels during fuel storage, distribution and usage as well as in the initial additive injection processes is critical to good performance of the vehicles. Laboratory analysis of fuel properties includes at least 100 ASTM POL specific test methods. Implementation of these analytical systems at the petroleum sites and transport lines can help identify fuel quality before use of the product. However none of the current employed methods are designed to detect dissolved particulate contaminates. Furthermore, none of the current tests will assess additive concentrations, or monitor adjustment of these concentrations on an As Needed Basis.

Applied Spectra performed LIBS test on various petroleum products and successfully demonstrated the capability using LIBS to identify different petroleum products. LIBS tests was able to provide these testing capabilities, in real-time and without consumables. When bulk petroleum products are sampled by LIBS methodology and compared to a resident data base, a unique "Bar Code type signature" helps to identify the materials of interest and their concentrations.

Process

A dedicated LIBS system was built to demonstrate several proof of concepts for LIBS for real-time petroleum analysis without sample preparation. The work used an Echelle spectrometer with broadband detection and enabled identification of carbon, hydrogen and oxygen as well as other elements simultaneously. A Nd: YAG laser at the fundamental wavelength (1064 nm) delivered the laser beam to the sample using an optical mirror. The laser-induced plasma was imaged onto the entrance slit of the spectrometer/ICCD system through an optical fiber.

C, H and O are the major elements in the petroleum products; their LIBS spectral ratios provide distinct signatures for analysis. The LIBS signatures appear similar and difficult to discriminate by eye because of common spectral lines and bands. However, these LIBS spectra can be computer analyzed to show differences.

Note

1. LIBS Spectrum of petroleum products

Some preliminary LIBS tests on the fuel additives have been conducted to detect fuel additive. Diesel fuel from gas station and NIST standards was tested with fuel additives including icy inhibitor, lubricity improver and Cetane boost from Amsoil. Normalized LIBS spectral lines of diesel fuel and the additives were shown in Figure 1. Variations in C, O and H values can be used to identify difference of the fuel type and additives. Figure 2 represents relative strength of C, O and H from diesel fuel and additives. Via building a spectral library and optimizing the LIBS parameters for different fuel additives, LIBS will be able to determine the concentrations of each fuel additives in the military fuel.

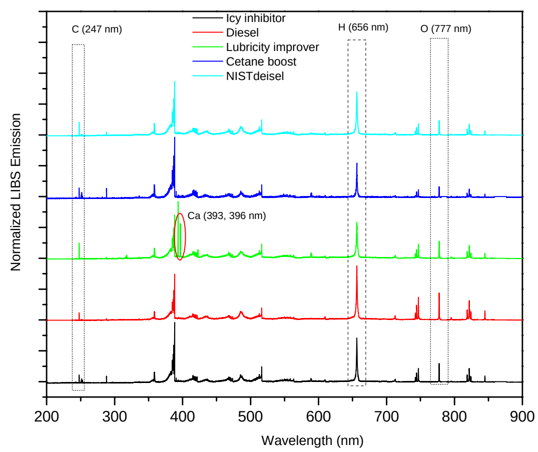

Figure 1 LIBS spectra diesel fuel and fuel additives

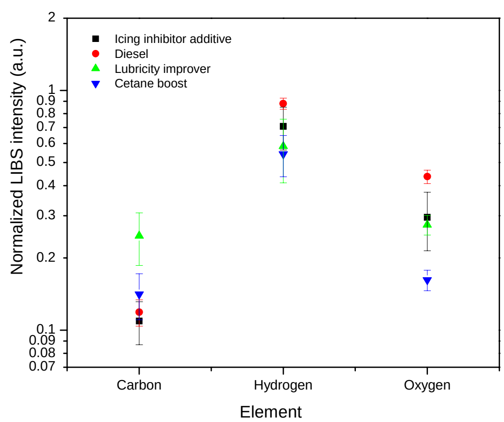

Figure 2 LIBS signal strength for C, O and H from diesel fuel and fuel additives

2. Detection of impurities in petroleum products using LIBS

LIBS easily verified the existence of vanadium in a crude oil sample from NIST (RM 8505). The concentration of vanadium in this sample was 390±10 μg/g (390 ppm). Figure 3 shows the measured LIBS spectra for V in crude oil; all the V ion lines can be clearly identified. The detection limit (DL) can be determined as 40 ppm. Even for these preliminary experiments, we can measure ppm level of metal impurities in petroleum. Further optimization of the system will result in better performance.

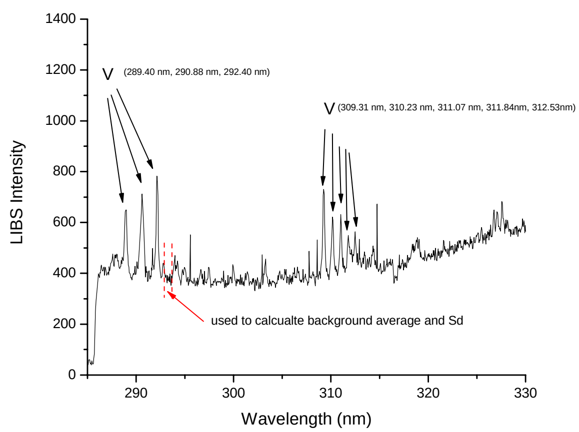

Figure 3 LIBS spectra of NIST RM 8505 crude oil at center wavelength

3. Sample identification

A Partial Least Square Discrimination (PLSD) algorithm is used to discriminate the different petroleum and additive components. The table shows our preliminary validation of LIBS for identifying typical additives:

Training Sets / Test Sample	alcohol	Diesel	Lubricant additive	Methanol	Motor Oil	Cetane Booster
alcohol	0.597647	0.005531	-0.09782	0.29348	-0.03297	0.234125
Diesel	-0.07689	1.155526	0.042903	-0.07933	-0.01942	-0.0228
L lubricant additive	-0.31801	0.072139	0.72058	0.291005	0.077979	0.156307
methanol	0.30008	0.062214	0.085423	0.713371	0.00651	-0.1676
Motor oil	0.162648	0.066277	0.009905	-0.2451	0.966647	0.039618
Cetane Booster	0.228905	-0.15144	0.162901	-0.40867	0.093119	1.075182

The numbers in the table represent the similarity of the test sample to the training set; values close to one represent a match. **Alcohol and methanol have very similar signatures (Figure 2) yet the algorithm was able to discern the differences**. The identification algorithm is still in the development stage for further accuracy improvement.

4. Comparison of LIBS signatures in lubricants

LIBS spectra were measured from new and used motor oil, and show difference in the primary species making up the molecular structure. The used oil was from a 2003 vehicle with ~5000 miles before the oil change. Figure 4 shows broadband LIBS spectra. Metal residues are commonly found in used motor oil. Mg was present in the new motor oil, but a significant difference in the ratio of elements and strong Mg line emission in the used motor oil is obvious. **These data demonstrate the potential of LIBS as the tool to perform oil sample property test and determination of metal wear in the power system.**

LIBS measurements also were made from four different commercial motor oil samples (Chevron, Shell, Valvoline and Mobil) with grade of 10W-30. The normalized (by the strongest CN intensity) spectra are shown in Figure 5. As plotted in the figure, although the strength of CN and C_2 spectral peaks was similar, the difference in the element peaks was significant. For example, only Mobil motor oil contained Na, not the other three. Chevron motor oil produced the strongest peaks for O, N and H, but did not contain Mg. All four motor oils contained calcium; the Ca peaks in the Valvoline motor oil were the strongest (almost double the line intensity compared to the other three brands). Using the same algorithm, the four different motor oil can be easily identified (Table 2).

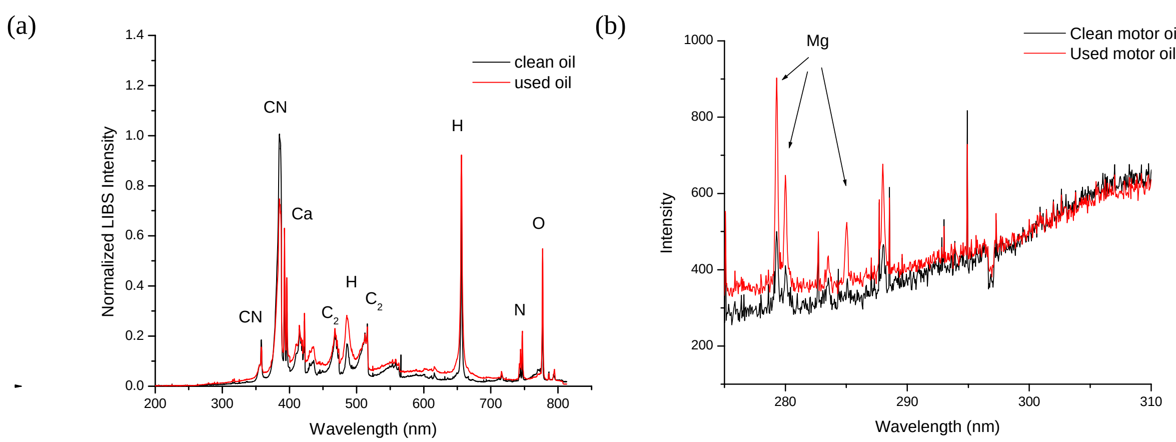

Figure 4 LIBS of clean and used motor oil. (a) Broadband and (b) high resolution.

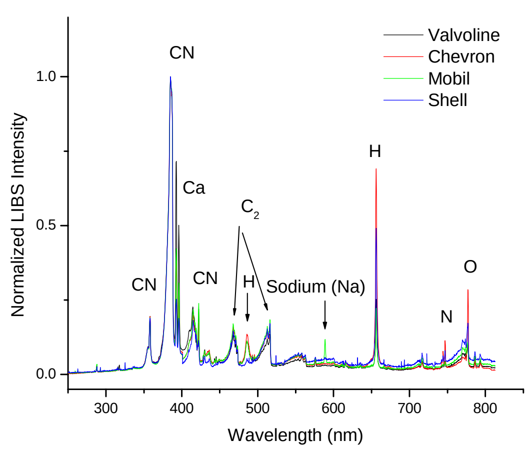

Figure 5 LIBS of different motor oil.

Training Sets / Test Sample	Chevron	Mobil	Shell	Valvoline
Chevron	**0.910115**	0.030373	0.060773	-0.001260
Mobil	0.045872	**1.098783**	0.136103	-0.280757
Shell	0.277781	-0.035519	**1.162941**	-0.405203
Valvoline	-0.088101 -	0.124879	0.007161	**0.970383**

Table 2. Matching coefficients for each motor oil sample type against different training sets.

Conclusion

In the preliminary tests, Applied Spectra demonstrated LIBS can successfully detect ppm levels of contaminants and fuel additives in the petroleum products. Fuel qualities can be monitored by LIBS technology for improving vehicle performance. LIBS applications in petroleum products can be used both in storage facilities and field vehicles.