SPECTRA OF THE MONTH

UNVEILING THE ELEMENTAL COMPOSITION OF COAL WITH LIBS

CONDUCTED BY: KURT AMEKU

INTRO

BACKGROUND OF APPLICATION

During the Christmas holiday season, many individuals partake in traditions such as giving gifts, putting up and decorating a Christmas tree, enjoying seasonal food and beverages, and spending time with family and friends. While plenty of these activities are fun for everyone, there is one tradition that has been passed along exclusively for naughty children: getting a lump of coal instead of presents. While there a few documented cases of this actually happening to children, the thought of not getting any fun toys and other gifts for Christmas is often enough of a reason for kids to be on their best behavior around the holidays. With this tradition in mind, we at Avantes Inc. thought it would be a fun experiment to perform a spectroscopic measurement on the gift that no one wants for Christmas. While the purpose of the study is lighthearted and themed for the holiday celebration, there are real-world applications for measuring coal, such as determining ways to improve combustion efficiency that can reduce environmental pollution. One of the tools this application employs is a spectroscopic technique known as laser-induced breakdown spectroscopy (LIBS), which can be used to identify the elemental composition of a sample with little to no preparation. This method of analysis is also minimally destructive, leaving only micro-ablations on the measured surface of a sample.

This experiment aims to measure the elemental composition of charcoal using laser-induced breakdown spectroscopy. Three samples were chosen from a bag of charcoal (Figure 1) measured in multiple spots, with the most prominent spectrum being analyzed. Expected elements present included carbon, hydrogen, oxygen, sulfur, nitrogen, and sulfur, among many others.

FIGURE #1: Charcoal samples used for this experiment (from left to right: Sample 1, Sample 2, and Sample 3).

DESCRIPTION OF SPECTROSCOPY SETUP

The setup for this experiment (Figure 2) was based around our AvaSpec-NXS4096CL compact spectrometer, commonly known as the Nexos. The Nexos is our next-generation photonics backbone spectrometer, designed to empower a wide range of applications in various industries. This device is built using our new semi-automated manufacturing technique that ensures higher levels of consistency and reproducibility unit-to-unit. The Nexos offers USB2.0 communication as well as RS232 and SPI communication protocols, a CMOS linear array detector, ultra-low stray light as low as 0.1%, and a signal/noise ratio of 375:1. Furthermore, this spectrometer can be customized with a wide range of gratings (13 total available) and the replaceable slit option is now standard for non-OEM units, which provides even more flexibility for a variety of application needs. Because of the wide range of LIBS peaks in the samples measured, the unit used in this experiment was configured for a board wavelength range of 190-1100 nm wavelength range. A 10-micron slit was used, along with the 4096-pixel detector, to maximize the spectral resolution of the unit to distinguish unique LIBS peaks as well as possible.

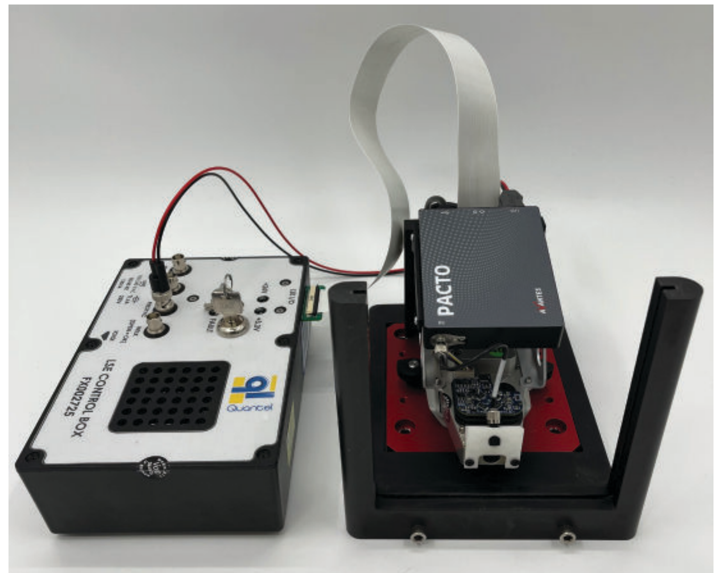

FIGURE #3 Experimental setup for LIBS measurement. The spectrometer is attached to a custom fixture and mounted directly above the laser. The unit measures the LIBS plasma plume generated on the sample surface via a mounted short fiber optic cable.

The light source used for this experiment was the plasma generated from a DPSS (double pulse, single scan) Nd:YAG laser, courtesy of Lumibird. Lumibird provides a wide range of lasers, with this one in particular built for rugged applications and unpredictable environments where temperature and vibration would destroy most commercial lasers. This laser operates at eye-safe wavelengths, specifically at 1574 nm, with an energy of 4.5 mJ per pulse. Designed for battery operation in hand-held and mobile applications, this compact yet robust laser features maintenance free operation for years of hard use.

Other accessories used for this experiment included a custom short 200-micron core fiber optic cable to directly measure the plasma plume, a Quantel control box (FX002725) to power the laser and sync the laser pulses and spectrometer measurements, a custom interface cable to connect the AvaSpec-PCT4096CL to the control box, and a custom 3D-printed mount to hold the fiber optic cable at the precise angle to line up with the focal point of the laser.

DESCRIPTION OF METHODOLOGY

The charcoal samples used for this experiment were from a 7.7-pound bag purchased from a local grocery store. Three charcoal samples were randomly chosen from the bag. No sample preparation was performed. While pervious research was done to ensure the charcoal would not ignite from the LIBS laser, safety precautions were made during measurements, including using tongs to hold the sample and having an oven mitt on hand if any material was ignited and needed to be moved. Each sample was placed in the firing range of the laser, and the laser was activated using serial commands. The spectrometer was synced to the laser pulses on the hardware side using the Quantel control box and on the software side through defined settings in AvaSoft, our custom software package.

For data analysis, we used the Scope-Minus-Dark mode in AvaSoft. This is a common mode for LIBS measurements, as it subtracts the dark spectrum (what the spectrometer measures with no light source) from the raw counts (i.e., scope mode) for each wavelength. This helps minimize noise in the spectrum and better isolate and identify the plasma plume peaks. We used an integration time of 1 millisecond, which in most cases can be adjusted to increase or decrease the amount of light being measured at one time and affects the overall magnitude of the reported spectrum. For LIBS applications, since the plasma plume is generated and decays at such short time intervals, increasing the integration time will only increase the portion of time where no light is measured and will therefore not affect the measurement amplitude. We set averaging to 1, meaning each measurement corresponds to one plasma plume instance.

TEST DATA AND RESULTS

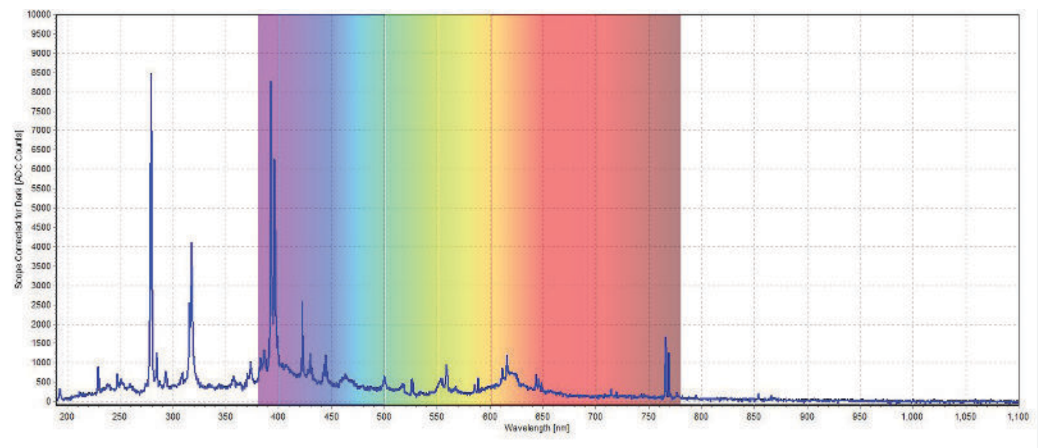

FIGURE #3: LIBS spectrum of Sample 1.

TEST DATA AND RESULTS

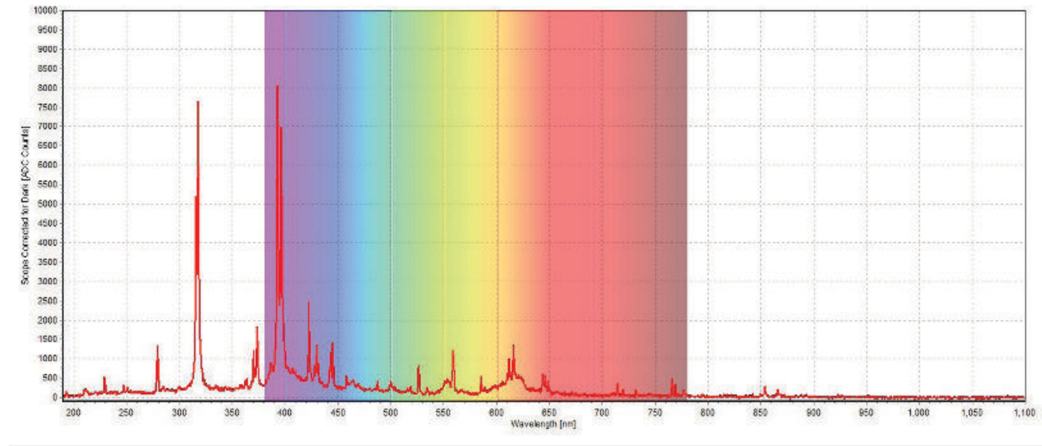

FIGURE #4: LIBS spectrum of Sample 2.

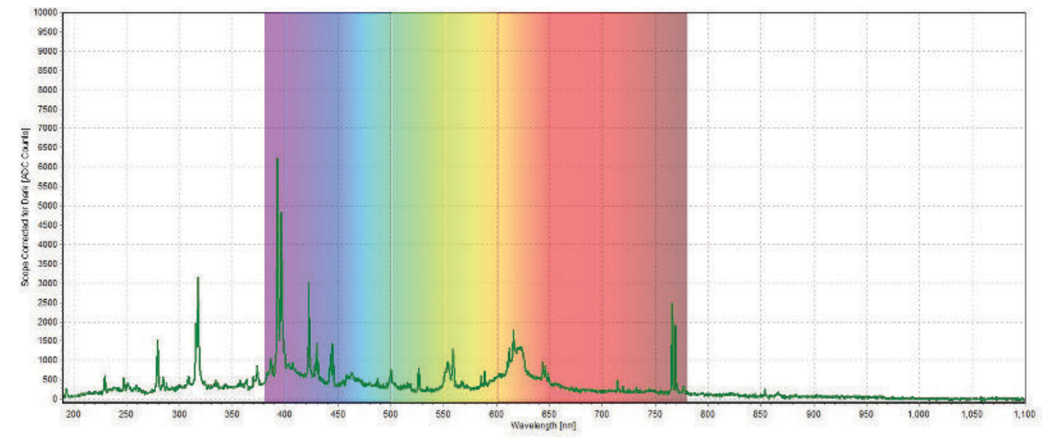

FIGURE #5: LIBS spectrum of Sample 3.

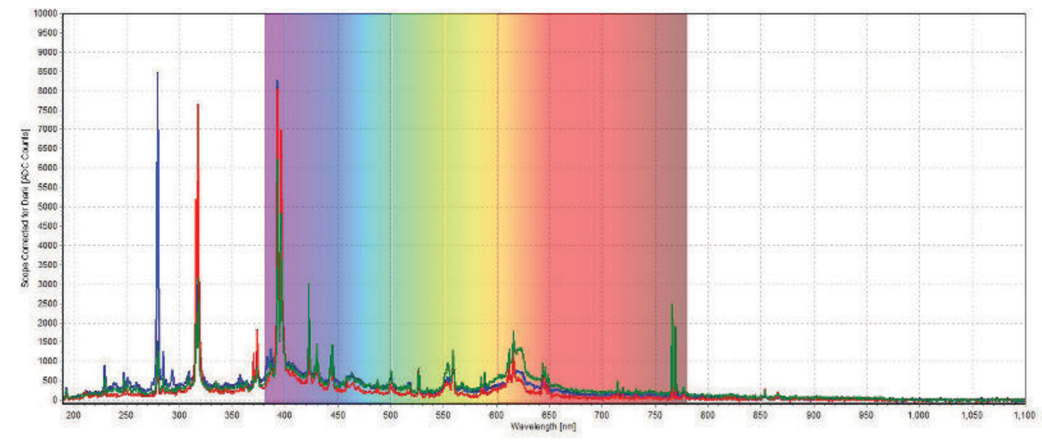

FIGURE #6: LIBS spectra of Sample 1 (blue), Sample 2 (red), and Sample 3 (green), shown together for comparison..

ANALYSIS

All three charcoal samples showed similar LIBS peaks throughout the measured spectral range, though with varying magnitudes (Figures 3-6). The most prominent peaks in the spectra were around 280 nm, 316 nm, 318 nm, 393 nm, 396 nm, 423 nm, 430 nm, 443 nm, 445 nm, 616 nm, 766 nm, and 770 nm. These peaks indicate the presence of elements such as magnesium, sodium, calcium, iron, manganese, oxygen, and potassium. Other elements indicated by the measured peaks include carbon, aluminum, silicon, chromium, and hydrogen. Interestingly, very few carbon peaks were detected in any of the samples, despite typically accounting for 75-80% of the composition of charcoal. Heavier elements are often easier to detect when using LIBS, so it is possible that the peak strength of elements such as sodium, magnesium, potassium, and calcium simply drowned out the carbon detection.

While the three charcoal samples displayed nearly identical peaks in terms of wavelength, the samples had significant differences in the peak magnitudes, which can indicate different percentages of each element in each sample. Because LIBS measurements can vary widely in their overall magnitudes, comparing between peaks within each individual measurement and then comparing the ratio of peaks to separate sample measurements is a more rigorous way of qualifying compositional differences. The peaks at 393 nm, 396, and 423 nm were fairly similar between all three samples, so these peaks were used as the standard to determine if other peaks were within measurement tolerance or could be indicative of differences in composition. Sample 1 showed a significantly higher peak at 280 nm and 285 nm than the other two samples, which could indicate a higher concentration of magnesium in this sample (Figure 3). Sample 2 had significantly higher peaks at 316 nm and 318 nm, indicating this sample had a higher sodium concentration (Figure 4). This sample also had much higher peaks around 370 nm and 373 nm, which can be indicative of iron. Sample 3 had higher peak magnitudes than the other two sample at 766 nm and 769 nm, peaks that are associated with potassium (Figure 5). A plot of all three spectra is also provided to illustrate the differences in peak intensity (Figure 6). While making these comparisons with multiple reference peaks defined, a quantified comparison would require a calibration of the spectrometer, a normalization of the data, and much more post-process analysis. This kind of model is implemented in many applications where precise elemental analysis is needed, such as metal sorting for recycling.

CONCLUSION

In conclusion, the present experiment highlights the use of laser-induced breakdown spectroscopy to determine elemental composition of charcoal as well as perform some minor direct comparisons. More in-depth comparisons would require an irradiance calibration and more complex post-processing. Despite this, the measured peaks still indicated the presence of multiple elements known to be in charcoal. The AvaSpec-NXS4096CL is an ideal solution for OEM applications or any other cases where compact form factor is critical. The Lumibird laser is a perfect pairing with the AvaSpec-NXS4096CL for compact LIBS measurements. Both the custom interface cable and the 3D-printed cable mount highlight the capabilities of our engineering team to provide custom assemblies and solutions for customer needs.

AVANTES
MEMBER OF THE NYNOMIC GROUP

CONTACT

WE'RE HAPPY TO HELP

Curious how spectroscopy can help you reveal answers by measuring all kinds of material in-line, at your production facility, in a lab, or even in the field? Visit our website or contact one of our technical experts. We are happy to help you.

Avantes Headquarters
Phone: +31 (0) 313 670 170
Email: info@avantes.com
Website: www.avantes.com

Avantes Inc.
Phone: +1 (303) 410 866 8
Email: infousa@avantes.com
Website: www.avantesUSA.com

Avantes China
Phone: +86 (0) 108 457 404 5
Email: info@avantes.com.cn
Website: www.avantes.cn

Follow us on social media: