AVANTES
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APPLICATION NOTE

USING LASER INDUCED BREAKDOWN SPECTROSCOPY FOR SOIL ANALYSIS

INTRO

SPECTROSCOPY METHODS FOR SOIL TESTING

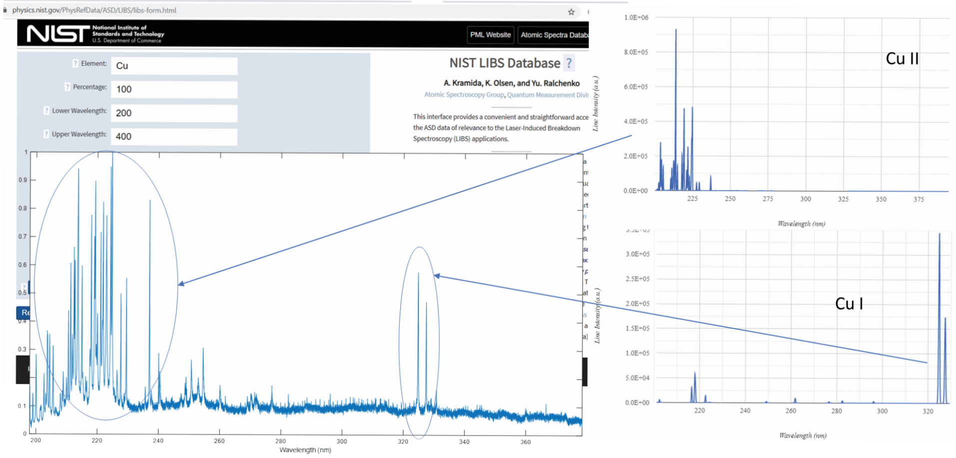
For over 120 years, agriculturalists have been aware of the importance of soil testing, particularly elemental analysis, to ensure the health and productivity of crops. Historically this has been accomplished by randomly sampling soil across a representative region of the field and sending them off to a laboratory to be analyzed using chromatography, mass spectrometry, and various wet chemistry techniques. While precise, the current approach is extremely time-consuming and costly.

Fortunately, recent developments in compact portable spectroscopy instrumentation have made it possible to perform on-site elemental analysis via x-ray fluorescence (XRF) and laser-induced breakdown spectroscopy (LIBS). Not only does portable spectroscopy reduce the time and cost associated with soil analysis. It also enables users to perform smaller-scale localized surveys to help facilitate precision agriculture and improve yield. Of the two methodologies, portable LIBS is generally viewed as the superior tool for soil analysis since XRF cannot measure lighter elements – C, N, Na, Mg, Si, P, and K. All of which are extremely important to determining the health and viability of soil. For example, since N, P, and K are three essential nutrients for plant life, NPK-testing is vital for understanding the proper fertilizer. Traditionally NPK testing is done using a multi-step chemical separation process utilizing various reagents to enable colorimetric and absorbance analysis. By contrast, all three values can be measured simultaneously with LIBS without additional chemical pretreatment. However, it is important to note that while LIBS does not require reagents or filtration, it still requires some sample preparation for use in soil analysis. Since LIBS is a point surface measurement, heterogeneous samples can lead to erroneous concentration values. As a result, it is never advisable to directly analyze soil samples without thoroughly grinding and mixing the samples to ensure homogeneity. While this may seem like a limitation of the technique, it does not serve as a significant impediment since most modern farms already have low-cost portable grinders.

A second note of caution is that while there has been a lot of interest in LIBS as a potential technique for detecting heavy metal contamination in soil, the current state of portable LIBS instrumentation does not yet have the required detection limits. Therefore, laboratory instrumentation such as ICP-MS and benchtop XRF are still the preferred method for heavy metal analysis.

HOW DOES LIBS WORK?

At the most fundamental level, LIBS is an atomic emission spectroscopy (AES) technique. It is often useful to think of this process as a hyper-localized flame test, where a high-energy laser is focused onto the surface of the soil sample creating a localized plasma. When the free electrons recombine with the ionized atomic nuclei and relax back down to the ground state, atoms will emit light. Since each element (and isotope) has unique emission spectra with extremely narrow spectral line width, it is straightforward to deconvolve and identify the different atomic components in a sample by comparing them to known spectra databases, as shown in figure 1.



physics.nist.gov/PhysRefData/ASD/LIBS/libs-form.html

NIST LIBS Database

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Atomic Spectroscopy Group, Quantum Measurement Divis

This interface provides a convenient and straightforward acce the ASD data of relevance to the Laser-Induced Breakdown Spectroscopy (LIBS) applications.

Element: Cu

Percentage: 100

Lower Wavelength: 200

Upper Wavelength: 400

FIGURE 1: Comparison of NIST LIBS database spectra of Cu^{+1} and Cu^{+2}, with LIBS spectra of Cu measured using the Avantes LIBS demonstration kit.

For complex heterogeneous samples, like soil, there are matrix effects which can slightly alter the LIBS emission spectra. While this complicates the analysis process, as Yu, Zhao, and Liu showed in their 2016 article in Nature Scientific Reports [1], multivariate chemometrics can be employed to discriminate various classifications of soil (see figure 2). While slightly more computationally intensive, this allows for a two-step analysis process where the variety of soil is identified and then used to determine the proper libraries that should be used.

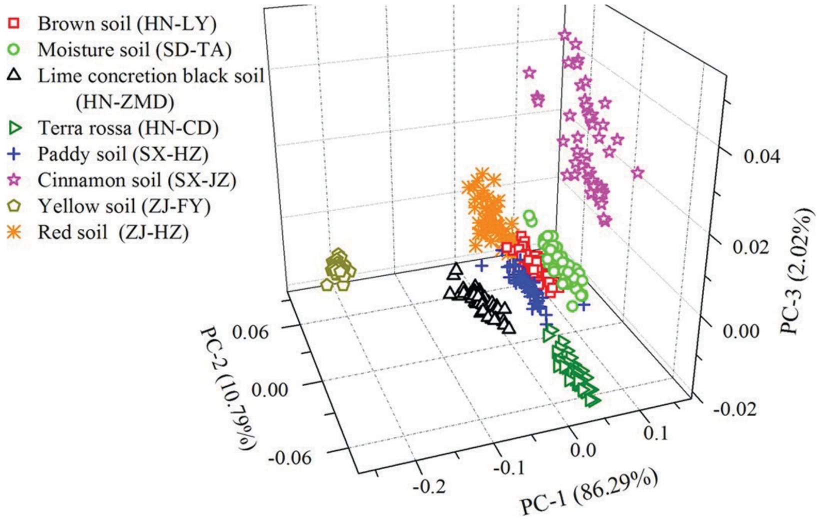

FIGURE 2: The scores plot for eight unknown soil samples from different regions of China. From ref. 1, shared under the Creative Commons License.

SPECTROMETER REQUIREMENTS FOR LIBS SYSTEMS

From a high-level perspective, LIBS systems are straightforward. First, a high-energy q-switched laser is focused on a sample, then the light from the plasma plume is measured with a spectrometer and processed via an identification or classification algorithm. But, as with most spectroscopic applications, the devil is in the details, and for LIBS, the most crucial details are related to the triggering electronics and spectral resolution.

As stated above, LIBS measures the AES of the soil sample, but unlike traditional flame tests, pulsed laser ablation is transient in nature. This results in what is commonly referred to as the plasma continuum, whereby the emission spectra rapidly evolve throughout the plasma's lifetime. While the exact underlying physics surrounding the plasma continuum is still an active area of research (see ref. 2), the fundamental behavior of the plasma is fairly well characterized.

The free electrons released during the ionization process dominate the plasma emission spectrum within the first microsecond after ablation. After this time, there is a roughly 10 µs window where the electrons recombine with the nuclei, emitting their characteristic atomic emission lines. This is followed by a prolonged 100 µs period where vibrational energy dominates the emission spectra, leading to broader band molecular emissions. As a result, LIBS instrumentation requires exceptionally tight control of the delay time between the laser pulse and the spectrometer acquisition and the integration time. Not only must the spectrometer's electronics handle sub-microsecond trigger delay times, but the trigger jitter must be on the order of nanoseconds to ensure that the integration window is consistent from measurement to measurement. Figure 3 shows a graphical representation of the plasma continuum with the laser pulse, trigger delay, and integration window overlaid. While this diagram is not perfectly accurate, it serves as an excellent visualization of the process.

Additionally, it is also imperative that the triggering electronics can communicate across multiple spectrometers simultaneously. This requirement is primarily driven due to the extremely high spectral resolution required for LIBS instrumentation. It is relatively common for LIBS systems, both portable and benchtop, to incorporate multiple spectrometers, each with a high spectral resolution (0.1 – 0.2 nm) but a limited spectral range (~200nm).   As a result, LIBS instruments often rely on multiple miniature spectrometers with offset spectral ranges to ensure broad spectral coverage.

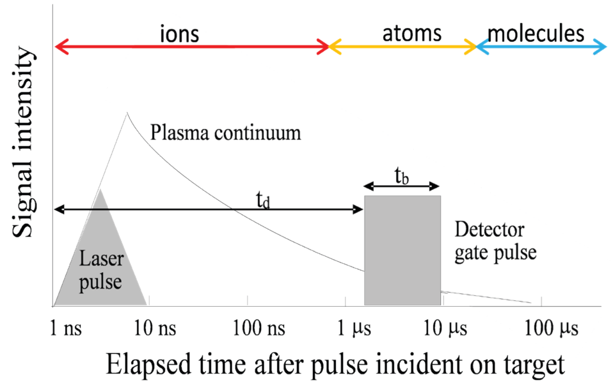

FIGURE 3 Graphical representation of the plasma continuum overlaid with typical laser and spectrometer trigger delays .

FINAL THOUGHTS

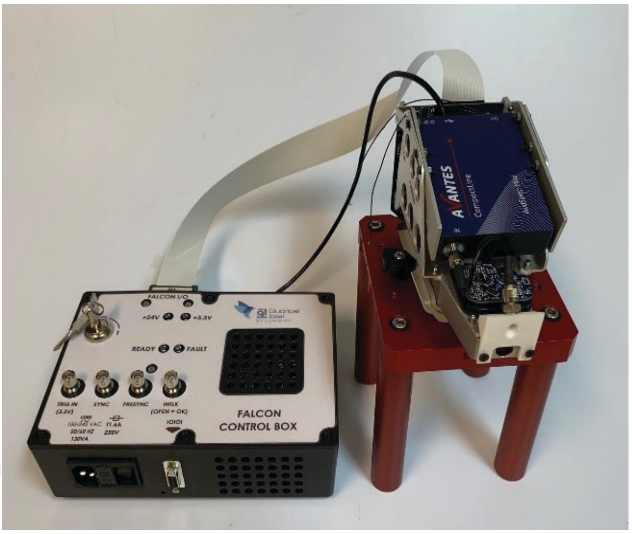

FIGURE 4: LIBS evaluation kit.

Between Avantes' proprietary high-resolution spectrometer design based on crossed Czerny Turner architecture and advanced electronics boards, Avantes spectrometers are specifically designed to meet the demanding needs of LIBS. The AvaSpec-Mini2048CL provides sub-nanometer spectral resolution and integration times as short as 30 µs, all within a 95 x 68 x 20 mm footprint weighing only 175g. With five digital programable bidirectional input/outputs and an analog input and output, the AvaSpec-Mini2048CL is ideal for integrating portable and handheld LIBS instrumentation. In addition, Avantes has partnered with Lumibird to develop a LIBS evaluation kit that combines AvaSpec-Mini2048CL with compact q-switched laser source into one easy-to-use package, as shown in figure 4.

For more demanding applications, Avantes offers the AvaSpec-ULS2048CL-EVO, with 12 digital programable bidirectional input/outputs, two analog inputs and outputs, and integration times as low as 9µs. Avantes Starline spectrometers such as the AvaSpec-ULS2048CL-EVO are the most commonly used instruments for LIBS applications but the instrument size and weight specifications are larger 177 x 127 x 44,5 mm (1 channel), 1135 grams). All Avantes spectrometers allow for multiple units to be combined into one easy-to-use desktop or rack mount multi-spectrometer system containing up to 10 different spectrometers with a single USB or ethernet output, shown in figure 5. Using the Avantes AvaSpec DLL package, with sample programs in Delphi, Visual Basic, C#, C++, LabView, MATLAB, and many other programming environments, enables users to develop their code.

FIGURE 5: Avantes Multichannel Spectrometer .

Contact us

For more information about the full range of spectrometer options available from Avantes for LIBS, please feel free to visit the website at www.avantes.com or give us a call at +1 (303)-410-8668 where our knowledgeable applications specialists are standing by to help.

References:

[1] Yu, KQ., Zhao, YR., Liu, F. et al. Laser-Induced Breakdown Spectroscopy Coupled with Multivariate Chemometrics for Variety Discrimination of Soil. Sci Rep 6, 27574 (2016). https://doi.org/10.1038/srep27574

[2] A. De Giacomo et al. Spectrochimica Acta Part B 65 (2010) 385–394 https://doi.org/10.1016/j.sab.2010.03.016

CONTACT

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Curious how spectroscopy can help you reveal answers by measuring all kind of materials, in-line, at your production facility, in a lab or even in the field? Please visit our website or contact one of our technical experts, we’re happy to help you.

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