

## Reproducible sampling and data processing in Laser Induced Breakdown Spectroscopy (LIBS)

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**Executive Summary:** In recent years laser-induced breakdown spectroscopy (LIBS) has shown great potential for rapid qualitative and quantitative chemical analysis of various materials. LIBS is an atomic emission spectroscopic technique wherein a high-power laser pulse is focused onto a sample to create a small plasma region. Emission from atoms and ions in the plasma is collected by a lens and transmitted through an optical fiber to a high-resolution spectrometer. Atomic spectral lines recorded in the spectrum can be used to both identify and quantify the element present in the sample. LIBS is an attractive technique for process analysis and quality control because it is fast, requires no sample preparation and provides rich analytical information.

LIBS has been successfully applied in the pharmaceutical, food, and mining industries, and in a variety of environmental applications. A major challenge with using LIBS for quantitative process analysis is the low reproducibility of measurements obtained when traditional sampling strategies are used. We intend to investigate a variety of optical strategies to improve laser coupling to liquid samples with the overall goal of improving measurement reproducibility and applicability of the technique for online process analysis. Another goal is to improve data processing for faster and more accurate interpretation of LIBS spectra.

**Goals and Objectives:** The goal of this project is to investigate a variety of methods to interface the excitation laser with the sample to improve the analytical performance of LIBS when applied to aqueous solutions. This work will entail optimization of the optical system that we designed recently to generate reproducible plasmas within liquid samples. Additionally, the effects of power density, focal volume, dual-pulse illumination and sample state on the reproducibility of the analytical data collected will be investigated.

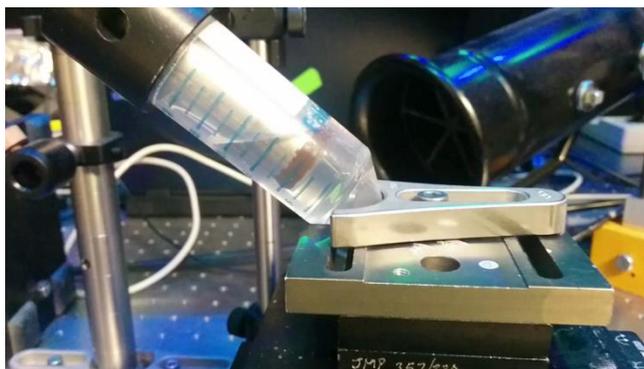
The second objective of the project is to evaluate various data processing methods to maximize the amount of analytical information extracted from LIBS spectra and advance the prospects of quantitative analysis. To achieve this goal, a large number of organic and inorganic samples will be analyzed and classification models will be built using various multivariate methods.

The third objective is to develop automatic algorithms to interpret information-rich LIBS data in order to allow high-speed data accumulation necessary for process control and high-throughput screening. Ultimately, it is desired to implement data fusion of the Raman and LIBS spectra in order to obtain both molecular and elemental composition of the sample in real time. This combination would be valuable in quality control applications where the analyzed product can be contaminated with organic and inorganic entities.

**Budget for 2014-2015:** \$25,000 - Funds would support research staff to support the analytical work and supplies/travel needs for the research.

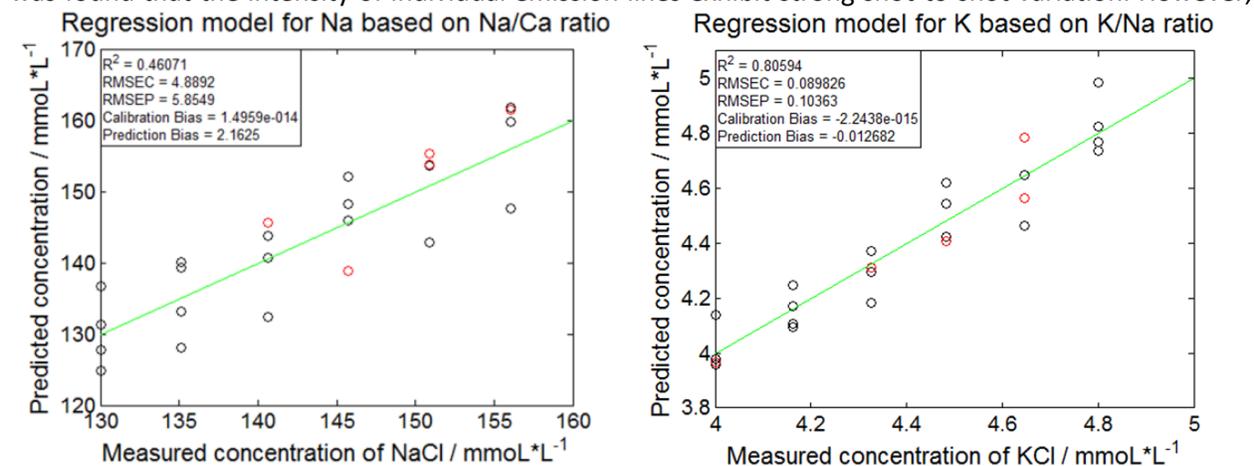
**Background and progress to date:** There is a substantial interest in using LIBS for characterization of liquid samples. Examples include detection of metals in crude oils, toxic catalyst residues in pharmaceutical formulations and heavy metals in water. Plasmas generated in liquids are weak because most of the laser energy goes to breaking intermolecular bonds, heating and evaporation leaving little energy for atomization and excitation of atoms. The weak plasmas can lead to unreproducible and noisy spectra.

Over the last 2 years we demonstrated successful application of LIBS to the classification of liquid samples dried on a metal substrate. Lack of moisture and the presence of metal surface were shown to enhance the emission intensity and improve classification models. Recently we have managed to generate strong atomic emission signal from plasma created directly in aqueous solutions with an immersion probe (**Figure 1**). This preliminary work was a significant milestone with the prospects of performing measurements thousands of times faster with no sample preparation.



**Figure 1. Immersion LIBS probe for direct analysis of aqueous solutions. Sample volume is 12 mL.**

To demonstrate the potential of direct measurements from liquids we prepared a series of calibration solutions with different concentrations of sodium, potassium and calcium varying in a relatively narrow concentration range. The results were consistent with our experience with dried samples. Specifically, it was found that the intensity of individual emission lines exhibit strong shot-to-shot variation. However,



**Figure 2. Regression models for Na/Ca ratio (A) and K/Na ratio (B).**

certain ratios of different lines were much less noisy. For example, the ratio of K/Na emission lines was found to be proportional to the corresponding concentrations with RMSEP values of only 3%. Similarly, the Na/Ca ratio had RMSEP of 5% (**Figure 2**). These results are encouraging although one data point corresponds to an average of 300 measurements (3 minutes). However, it should be noted that the results are preliminary and there are many potential ways to improve the performance. Importantly, the speed

of data acquisition and the decrease of cost have improved several orders of magnitude compared to our previous work with dried samples.

**Proposed work:** The next step in our research is to develop a plan to harness the benefits of our ability to generate LIBS spectra with high speed (1-3 spectra per second) and very low cost. We propose to perform a thorough statistical examination of the signal variability in order to learn how to separate random and non-random noise contributions. Working with random variance can result in significant improvements in reproducibility of measurements by averaging hundreds of spectra which can be obtained in less than 1 minute. The goal is to achieve reproducible measurements that can potentially make LIBS a viable method for real-time quality control applications with the most demanding reproducibility requirements. Working with large amounts of data necessitates a high degree of automation. It includes initial pre-processing, variable selection, detection and elimination of outliers and peak assignment. We propose to automate these steps by developing an algorithm based on NIST atomic emission lines database and the experience we have accumulated over the past several years. Automatic peak assignment will make it possible to generate a complete elemental profile of the sample within a few seconds after measurement – an important requirement for high-throughput process monitoring and quality control applications.