

Laser-Induced Breakdown Spectroscopy for In Situ Chemical Sensing

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Over the past two decades, a new spectroscopic technique called laser induced breakdown spectroscopy (LIBS) has been developed that is rapidly gaining favor for *in situ* field measurements in hostile environments. The LIBS technique utilizes a high power laser (usually a >100 mJ Q-switched Nd:YAG solid state laser with 1064 μm fundamental wavelength and a pulse length of 5-10 ns) focused to a beam of order 10 mm in diameter to create a plasma or “laser spark” once the power density exceeds the breakdown threshold of the material (typically, a few MW/cm^2). A gated spectrometer (typically, a diffraction grating coupled to an intensified charge-coupled device (ICCD) detector) covering part or all of the ultraviolet through near infrared range (nominally, 200-1000 nm wavelength) is used to capture the plasma spectrum. The plasma radiates both a continuum component which decays relatively rapidly and an emission line component which decays more slowly; the latter provides information about atomic composition. The spectral line wavelengths and intensities obtained from plasma ablation can be compared with standard atomic line references and/or calibrated against samples of known makeup to determine the chemical composition of a sample. This relatively simple apparatus yields simultaneous sensitivity to virtually all elements in the parts-per-million (ppm) or better range in solids, liquids, gases and aerosols. LIBS is effectively non-invasive due to very small sampling regions (typically, pg to ng of material are ablated), requires no sample preparation, and can be used in a stand-off mode without perturbing the target. It is also fast, requiring under 1 s for a cycle, and hence is essentially a real-time measurement. These characteristics are some of the greatest advantages of LIBS compared to other analytical approaches; no other sensor is capable of detecting all classes of chemical compounds and all types of matter. They are also the sort of characteristics required for *in situ* chemical sensing in the ocean. It should be emphasized that a vigorous sensor development effort is required for *in situ* chemical and biological sensors, as is recognized in the reports from recent ocean sciences meetings.

For the past two years, the PI and graduate research assistant Anna P.M. Michel have made significant progress in adapting LIBS to operation in the ocean. Exploratory high pressure (it should be noted that LIBS had previously only been used at atmospheric pressure) LIBS experiments on bulk aqueous solutions have been completed using apparatus in Mike Angel’s laboratory at the University of South Carolina. However, the competing interests of Angel’s graduate students and postdocs make it difficult to continue this work, and hence establishment of a LIBS laboratory at WHOI has become imperative. Under previous DOEI support, an Echelle spectrometer was acquired. The present funding has supported the purchase of a dual wavelength (1064 and 532 nm), dual head laser to complete the LIBS apparatus.

The key scientific issues to be addressed include optimization of LIBS system parameters for detection of a set of critical (to hydrothermal vent studies) elements (Na, Mg, K, Ca, Mn, Fe, Si, Cl, Br, Cu, Zn, with others added as appropriate) at elevated pressure, building on the completed studies. Single pulse laser work will first be explored for its ability to detect the elements over a range of pressures from 1 to ~300 atm. Laser pulse energy levels will be varied to find levels that maximize the signal intensity for each element. Double pulse work will then be initiated to study the signal intensity enhancement that can be gained. The parameters that can be varied are molarity, pulse energies, gate delay, the interpulse delay, and the gate time. The multivariate influence of changing concentrations of more than one element at a time on high pressure LIBS will also be studied. Experiments will initially be carried out with pairs of elements at varying

concentrations and then proceed to artificial vent fluids with known element concentrations. The studies of artificial fluids will be carried out over a range of pressures and temperatures to create calibration curves for a series of vent fluid compositions. Experiments will also be conducted using real seawater and real vent fluids. Meeting these goals will yield a breakthrough result for in situ sensing at hydrothermal vents, which is presently seriously impeded by sensor issues. Once this work is completed, NSF funding for the construction and deployment of a field system using the ROV Jason will be vigorously pursued.

On a longer term basis, the adaptation of LIBS to work in the ocean will enable a broad range of oceanographic research applications, and certainly has a more extensive range of uses than hydrothermal vent studies. In addition to these scientific impacts, the successful development of a marine LIBS capability will facilitate a wide range of applied oceanography. For example, in the environmental area, LIBS should be capable of rapid classification of oil spills or heavy metal pollution of sediments at sewage outfalls or dump sites without extensive and time-consuming laboratory analysis.