Laser Induced Breakdown Spectroscopy

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Abbreviations

IB	inverse bremsstrahlung
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP-MS	inductively coupled plasma-mass spectrometry
LIBS	laser-induced breakdown spectroscopy
LSD	laser-supported detonation
LTE	local thermodynamic equilibrium
MPI	multiphoton ionization
UV	ultraviolet

Introduction

Laser-induced breakdown spectroscopy (LIBS) is a powerful analytical technique that can be used for the detection and characterization of materials. In LIBS, a focused laser beam is used to generate a plasma plume on the surface of solid and liquid samples or inside the sample volume of gases, liquids, and aerosols. Each excited atom in the plasma emits a unique set of spectral lines, particularly in the optical region of the spectrum. Therefore, this optical emission can be collected and analyzed to determine the chemical composition of a sample. A LIBS plasma can be generated as a single event using just one laser pulse or using repetitive laser pulses. As a result, localized microanalysis with lateral and depth profiling information is easily obtained. Remote sensing of materials is also possible with LIBS, since only photons need to come in direct contact with the sample. The ability to perform analyses on samples at a standoff distance is especially important when dealing with hazardous materials, samples located in a dangerous environment, or in physically inaccessible locations.

LIBS has a distinct advantage over many other techniques since little or no sample preparation is needed before analysis, and it can be used for rapid real-time analysis in field operations. Quantitative analytical results can be obtained from LIBS by using conventional (one-element) or multivariate calibration. Recently, calibration-free LIBS analysis has been demonstrated as the semiquantitative determination of elements, based on theoretical plasma models. With LIBS, there are no specific requirements for the sample to fluoresce, be Raman-active or infrared-sensitive. It is truly a universal technique, where any sample type can yield a LIBS spectrum.

Theory of Laser-Induced Breakdown Spectroscopy

In practice, LIBS is a very simple spectroscopic technique to implement. A high-powered laser beam (commonly 10-ns pulsed infrared 1.06 μm radiation) is focused through a lens to produce a plasma. The emitted light is collected, often through a fiber optic cable, and directed into a spectrometer (**Figure 1**). However, the physics and chemistry of the plasma initiation, formation, lifetime, and decay are very complicated. Much progress has been made in recent years toward elucidating the physics of the plasma generation processes. Studies that have been performed to characterize the LIBS plasma include local thermodynamic equilibrium (LTE) models, hydrodynamic and kinetic models, nonuniform plasmas, and plasmas generated in a vacuum.

There are two main processes that can initiate ionization of atomic and molecular species in laser-induced breakdown. The first is the direct ionization of the sample by multiphoton ionization (MPI), and the second is the inverse bremsstrahlung (IB) absorption processes. In MPI, atoms or molecules undergo simultaneous absorption of sufficient numbers of photons to cause ionization (or the ejection of electrons from the valence to the conduction band, in the case of metals) (eqn [1]).

$$\mathrm{M} + m(h\nu) \rightarrow \mathrm{M}^{+} + \mathrm{e}^{-} \qquad [1]$$

If ϵ_I is the ionization potential, then m, the number of photons, must be greater than the integer part of $(\epsilon_I/h\nu + 1)$. MPI is only significant at wavelengths that are shorter than $\sim 1\,\mu\mathrm{m}$ and at high laser power, that is, greater than $10^{10}\,\mathrm{W/cm^2}$. When the wavelength is substantially longer than $\sim 1\,\mu\mathrm{m}$, it is statistically unlikely for an atom or molecule to absorb enough photons to increase the energy of the neutral above its ionization potential. This process is also important at low pressures, when few collisions are occurring due to the low particle density of the medium.

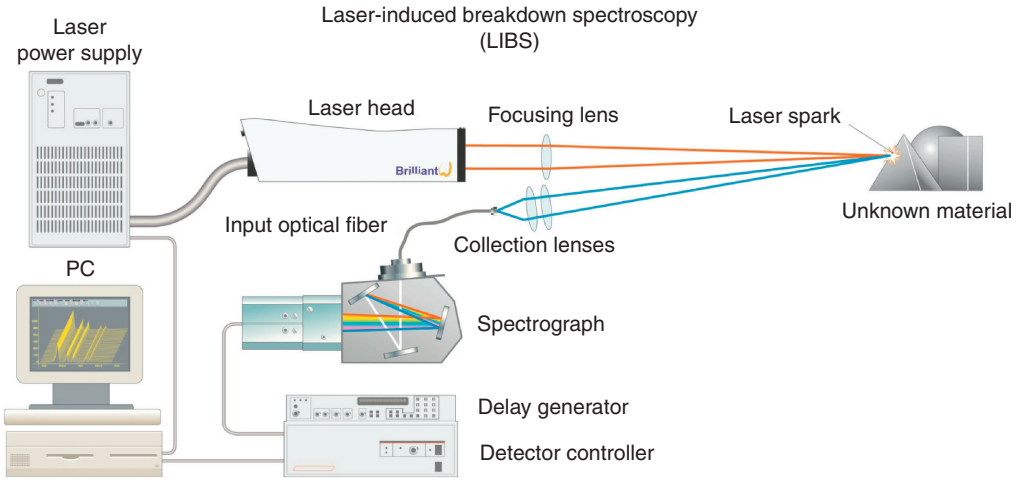

Figure 1 Schematic diagram of a typical lab bench LIBS setup.

IB processes involve the absorption of a photon by one or more seed electrons present in the focal volume at the beginning of the laser pulse. These initial free electrons may be generated through the presence of cosmic rays, or by the Earth's natural radiation. The first few photons in a laser pulse can also produce seed electrons from dust, negative ions, such as O_2^-, organic vapors, or from atoms and molecules present in the atmosphere via MPI. Seed electrons are not necessary for 'pure' MPI processes.

In IB, the absorption of a photon raises the electron energy to a higher state in the continuum. This process must occur in the vicinity of a heavy particle, such as an atom, ion, or molecule so that momentum is conserved. In normal bremsstrahlung processes, high-energy electrons emit radiation as they slow down upon interacting with a gas or a solid. This term comes from the German words, bremsen, which means to slow down, and strahlung, which means radiation. Electrons will typically lose energy by rotational and vibrational excitation of neutral molecules, excitation of electronic states, and by attachment of electrons. However, in IB processes, electrons acquire energy from the absorbance of photons and collisions with atoms, ions, and molecules. If the energy of the free electron is greater than the ionization potential of a neutral species, it can ionize a molecule (M) by colliding with it. This produces two lower-energy free electrons, which can gain more energy from the electric field, causing ionization of other neutrals and two more electrons (eqn [2]).

$$e^- + M \rightarrow 2e^- + M^+ \qquad [2]$$

With the increase in the population of ions and electrons in the focal volume, the probability of electron–photon neutral collisions also increases, resulting in electron multiplication and cascade growth. As more and more electrons repeat the process, there is a geometric growth in the number of free electrons, resulting in cascade ionization. IB processes can be so dramatic that all the species ablated from the surface of the substrate can be ionized causing such an increase in plasma growth that the entire laser pulse can be coupled into the plasma. This results in the plasma becoming so optically opaque that the substrate becomes shielded from the remainder of the laser pulse.

Both MPI and IB absorption can contribute to cascade ionization. The dominant process will depend on the wavelength of the laser radiation, laser intensity, and density of the medium in which the laser breakdown occurs. IB-dominated breakdown is important at high pressures, when collisional effects are strong, and at wavelengths longer than 1 μm. At shorter irradiation wavelengths (<1 μm) or at low densities of molecules, the possibility of electrons colliding with neutral species is small. Therefore, MPI dominates usually at these shorter wavelengths and in low-density media. Cascade ionization continues throughout the duration of the laser pulse and results in the ionization and dielectric breakdown of gases, vaporized particles, and the creation of a plasma.

Plasma Life Cycle

The plasma generated by a focused laser beam in LIBS has a distinct, time-dependent life cycle. For a plasma to be created, the breakdown threshold must be reached. This breakdown threshold is usually defined qualitatively as the minimum irradiance needed to generate a visible plasma. With the exponential increase in the production of free electrons and ions by IB and MPI processes, the plasma begins to expand from the initial focal volume. Ablated materials, such as particulates, ions, molecules, neutrals, and electrons, are also present

in the plasma that forms at the surface of the sample in solids and liquids. The ionization potential of gases is generally higher than that of liquids and solids, but they too can be readily analyzed by LIBS. Using higher-energy densities, gases can be ionized with a tightly focused laser to produce a plasma in the sample volume. A sonic boom is produced from the initial expansion of the plasma. The compression wave front, or shock wave, emanates from the focal volume of the plasma. The wave front is traveling well above the speed of sound, on the order of $10^5\ ms^{-1}$. For comparison, the speed of sound in air is $\sim 345\ ms^{-1}$ at 21°C. As the plasma expands, it continuously emits spectroscopic signals from all constituent components in the sample. When the plasma cools through radiation and other loss mechanisms, the ionized species recombine to form neutral atoms and molecules.

Throughout the lifetime of the plasma, the emission spectrum changes as a function of time. In the earliest phase, there is a strong white light component, which contains little useful spectroscopic information. This continuum light consists mainly of bremsstrahlung and recombination radiation. Recombination radiation is caused by the recombination of free electrons and ions. As stated earlier, bremsstrahlung radiation is caused by the decrease in the translational energy that occurs when ions and electrons slow down upon collision with a gas or solid. This is in contrast to IB processes, which cause cascade ionization during the initial breakdown event.

After the laser pulse, the continuum gradually fades allowing the weaker spectroscopic signals from the elements of interest to be detected. This occurs in a time frame that is much longer than the laser pulse duration, which in a nanosecond laser is on the order of 10 ns. Since the weaker signals only appear as the continuum fades, the collection of the spectroscopic signal of interest should be delayed.

Time parameters in LIBS are important considerations when obtaining emission spectra. At low laser pulse energies, that is, several millijoules, the time delay may need to be less than 1 ns in duration to obtain an optimal signal. With higher laser powers, the delay may be several microseconds. Too short a gate width will not allow enough signal to be processed across the detector. Too long a gate width will allow too much ambient light to enter the detector thus adversely affecting the signal to noise ratio. Optimization of the time delay and gate width should be performed on the individual samples to maximize the relative intensities of the emission lines for the signatures of interest. Sample properties, such as substrate, matrix, and concentration, and experimental conditions such as laser power, wavelength, and pulse width, can all influence the temperature and energy density of the plasma (**Figure 2**).

LIBS Emission Signal Enhancement – Background Gas Effects

Different background gases are often utilized to enhance the quality and intensity of the LIBS plasma, especially for the analysis of complicated or difficult samples. The use of argon gas is a common technique to effectively enhance the LIBS emission signal. In this method, a steady stream of gas is directed toward the focal volume of the plasma. This increases both the intensity and quality of the signal by displacing the background air and making it easier to generate a plasma. Calculations of electron densities and plasma temperatures of plasmas created in difference background gases show that argon produces the highest temperatures and electron densities, followed by ambient air. Helium is associated with the lowest temperatures and densities.

When laser ablation is performed in a vacuum, lower temperatures are attained and lower concentrations of electrons are seen in the plasma volume than in a gaseous environment. Since there is no pressure counteracting free plasma expansion in the vacuum, the expansion rate is increased whereas the cooling rate is decreased as compared to expansion in a gas. This decrease in cooling rate of the excited electrons can be explained by the dominance of elastic collisions. Since cooling is inversely proportional to the mass of the background gas, heavier gases like argon have a less efficient cooling capacity than helium or air. Therefore, using argon will produce higher plasma temperatures with greater electron density than one produced in ambient air or gases with lower atomic masses, like helium. Argon also displaces the nitrogen and oxygen molecules in the air. This effectively eliminates any interference from these molecules in the analysis of species that contain nitrogen and oxygen atoms, including organic compounds.

When argon gas is utilized, a laser-supported detonation (LSD) wave can be observed at the tip of the vapor plume 3 ns after the laser pulse. An LSD wave occurs when a shock wave front, expanding at supersonic speeds, is transmissive enough to allow the incoming laser energy to penetrate the boundary of the plasma and the surrounding atmospheric gases. The shock wave is powerful enough to compress and heat the gases surrounding the plasma, thus allowing for strong optical absorption of the incoming laser radiation. The compression of background gases by the shock wave enhances the conversion of kinetic energy into thermal energy in the vapor plume by slowing the rate of vapor plume expansion. As a result, the vapor plume generated with a background gas of argon continues to increase in temperature and electron number density after the laser pulse ends. The LSD is thought to create an area of high temperature and low gas density above the vapor plume, which allows the expansion of the plume to continue, in