26

LIBS Applications to Liquids and Solids in Liquids

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26.1 Introduction

Since its inception, LIBS has become an analytical technique of huge potential for characterization of materials in all three states of matter. It is considered a useful technique for both laboratory and field applications. Qualitative and quantitative analyses can be performed by collecting emission light from the laser-induced plasma of the material. Although LIBS seems to be a very simple technique, it is not fully developed for field measurements. Initially, the technique was studied and applied more for the analysis of solids and gases than for liquids; however, significant progress for the analysis of liquids has been reported in the past few years. Several researchers worldwide are using LIBS and developing methodologies for liquid analysis under various conditions and circumstances. Recent progress in lasers, spectrometers, optics, and data collection and analysis software has tremendously improved the LIBS measurements of liquids. Currently, LIBS analysis of liquids is becoming very useful for many applications, including water-quality assessment, environmental monitoring, subsurface fluid chemistry, and aqueous source characterization of critical materials [1–4]. LIBS measurements of solids immersed inside the liquid can be used for the study of underwater archaeology and oceanic environment assessment [5–7]. LIBS has several advantages over many other analytical techniques because it requires minimal to no sample preparation, provides a rapid sample analysis, and has the capability of real-time continuous measurements and standoff remote measurements [8–10].

Liquids can be in a static or flowing state, may contain completely dissolved, partially dissolved, suspended, or insoluble materials, and may exist in various atmospheric conditions (i.e. temperature, pressure, and pH). Therefore, LIBS instrumentation and measurement methodologies need to be developed depending on specific experimental requirements. Laser–liquid interaction can be either within the liquids or on the surface of the liquids. When the laser pulse is focused on the liquid surface, a plasma is formed at the liquid–air interface and expands into the air where LIBS sensitivity is almost equivalent to that obtained for solids in air. However, splashing of the liquid is a serious issue that could contaminate the optics and result in the reduction of the laser ablation efficiency.

Laser Induced Breakdown Spectroscopy (LIBS): Concepts, Instrumentation, Data Analysis and Applications, *Volume 2*, First Edition. Vivek K. Singh, Durgesh K. Tripathi, Yoshihiro Deguchi and Zhenzhen Wang.

Similarly, shot-to-shot variation due to waves also hinders data precision. Focusing the laser pulse inside the bulk liquid (known as underwater LIBS) has been found to eliminate the splashing completely. In underwater LIBS, the plasma formation, expansion, and emission all take place inside the liquid medium. However, due to the incompressibility of the liquid, the plasma is confined and the expansion and emission efficiency of the plasma is reduced as compared with that in air [11, 12].

In this chapter, LIBS instrumentation and data collection system used for the analysis of liquids and solids in liquids are discussed. LIBS measurements of bulk liquid samples and solids submerged in aqueous media, measurements made by focusing laser pulses on liquid surfaces, and measurements of liquids after various sample treatments are presented. In addition, the working mechanism of NETL-developed field-deployable LIBS sensor and its preliminary performance in field measurements are also reported.

26.2 LIBS Instrumentation for Liquid Analysis

Similar to solids and gases, the LIBS instrumentation for liquid measurements consists of an excitation source, focusing optics, a detection system, and a workstation. Various lasers ranging from UV excimer to IR solid state with fs to μs pulses have been used for the sample ablation. The pulse energy of these lasers can be from 1 mJ to hundreds of mJs and can be selected depending on the threshold of the test samples and the analytical information needed. Generally, Nd:YAG lasers are used more commonly for LIBS measurements as they are convenient and efficient. With a single Nd:YAG laser system, multiple harmonics can be generated to obtain a laser output of UV to IR wavelengths with efficient-energy conversion rates. Tunable lasers are also available providing broad wavelength selection for the particular analytes of interest and required analytical information. Laser properties, such as energy stability, beam quality, wavelength, and pulse duration, are important for the quality of plasma formation and emission. For focusing and collection, lenses and properly coated mirrors are used. Depending on the sample–laser interaction mechanism, single or multiple lenses of appropriate focal length separately or in combination with mirrors can be used. Optical fibers are needed to transfer the collected light to the spectrograph and filters and dichroic mirrors are useful to pass or block selected lights.

For underwater LIBS, generally short focal length lenses are used to obtain better ablation efficiency. Collection optics can be set in confocal, orthogonal, or transverse configurations to collect plasma emission and the detection of the signal is usually obtained using a time-resolved intensified charge coupled device. The diagrams for the benchtop LIBS setup used in our laboratory for underwater measurement under high-pressure conditions and surface measurement on laminar liquid jet are shown in Figure 26.1a and b, respectively. For measurements without taking pressure into account, the liquid sample can be placed in a simple cuvette and the laser can be focused at a certain depth from the surface through the cuvette or on the surface of the liquid.

Multi-pulse LIBS systems have been used for signal enhancement and hence detection sensitivity improvement. Multiple pulses in the system can be generated either with the same laser source or multiple lasers employed in various geometrical configurations. Since inter-pulse delay has a significant effect on the signals, a good synchronization of laser

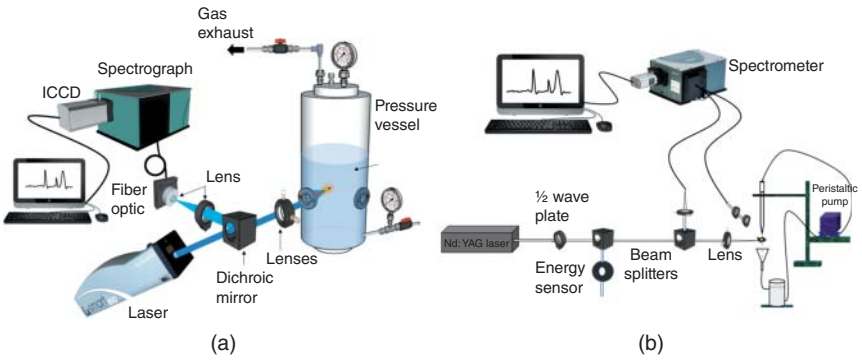

Figure 26.1 LIBS setups for (a) underwater measurements; (b) surface measurements on a liquid jet. Source: Hewlett-Packard Company; QSMART and Oxford Instruments.

pulses and control of the pulse gap are essential for the system optimization. Microwave and laser-induced fluorescence (LIF) have also been used for signal enhancement purposes by many researchers. In microwave-assisted LIBS, the plasma is heated by the microwave radiation through antennas or an enclosed microwave cavity system. Use of microwave heating results in increasing the plasma lifetime and hence the analytical signal. LIF can be achieved by using an optical parametric oscillator (OPO) in concert with a pulsed laser. The OPO/laser pair can be tuned at a specific wavelength corresponding to the emission line of an analyte are focused on the plasma and, consequently, a significant enhancement in signal strength is obtained.

26.3 LIBS Measurements

LIBS can perform both qualitative and quantitative analyses. Spectral signatures of elemental species in the LIBS spectra are used to provide information about their presence in a test sample. For quantification of the analytes, a proper calibration method is required. Analytes in liquids might be either completely or partially dissolved or could be in a solid form inside the liquids. LIBS measurements in liquids can be executed either by focusing a laser beam into the bulk liquids or onto the liquid surface. Due to low compressibility of the liquid, the plasma produced in a liquid environment generally gets confined significantly and hence the electron-ion recombination rate increases. Also, the plasma persistence time is significantly reduced, and the broad band continuum may overwhelm the emission signals with the radiative recombination and Bremsstrahlung emission.

Although both underwater and surface measurements are used for analyte characterization in liquids, they follow two different mechanisms. While the whole process of laser–matter interaction, plasma formation, and plasma expansion takes place inside the liquid during underwater measurements, the surface measurements involves laser–matter interaction taking place at the liquid–air interface and the other two events occurring in the air. While performing the trace element analysis in liquids, single-pulse LIBS may not always be able to detect analytes due to the quenching effect and low emission signal intensity. Therefore, various signal enhancement techniques have been employed by

researchers for a low-level analysis [13]. Similarly, sample pre concentration and hyphenated techniques are also applied to improve analyte detection sensitivity [14, 15]. The remainder of this section will discuss underwater LIBS measurements of bulk liquids and submerged solids, measurements on the liquid surface, and measurements on pretreated samples.

26.3.1 Bulk Liquids

When a laser beam is focused within a liquid, laser-induced breakdown occurs by multiphoton absorption or cascade ionization, followed by the formation of a plasma attaining high temperature and pressure [11, 16–23]. Elevated temperature and pressure within the plasma causes expansion at supersonic velocities to create a shock wave and acavitation bubble that contains liquid vapor. Subsequent cooling and decay of the plasma occurs due to energy loss to the shockwave emission, spectral emission, and loss to surrounding liquids. During cooling of the plasma, the reduction in interior pressure takes place and the cavitation bubble collapses. However, a bubble with high energy may create a second shock wave [24, 25]. The evolution of the bubble in liquids generally depends on experimental parameters, such as laser pulse duration, wavelength, and focusing lens. In fact, the breakdown threshold in a liquid is significantly higher than that in solids because a significant part of the energy is utilized in overcoming the associated mechanical effects. The threshold is even higher in gases [26, 27]. Plasma emission in liquids is of a shorter duration and the intensity is lower than that in air due to fast quenching and confinement effect.

After initial liquid LIBS work by Cremers et al. [28], in 1984, the technique in bulk liquids has been widely applied for the study of analytes in ocean environment and subsurface liquids. The experimental parameters and conditions have been demonstrated to play a crucial role in underwater LIBS measurements [29]. Since the plasma persistence time is significantly shorter in liquids compared with gases, plasma emission at an early gate time delay will produce higher signal intensity. Moreover, the persistence time of atomic lines is longer than ionic lines because more atoms are produced due to the recombination of ions and electrons during plasma cooling [30, 31]. Michel et al. [32] evaluated the dependence of plasma emission on major experimental parameters at pressure conditions similar to those at the sea level. Higher excitation energy levels can lead to unfavorable effects such as plasma shielding. A moderate energy level appears to be sufficient to create a plasma and is appropriate for underwater LIBS measurements.

Many dissolved analytes (i.e. Li, Na, K, Ca, Mn, and Zn) in liquids have been studied by the underwater LIBS technique and the results have demonstrated the capability of LIBS for detecting and quantifying these and other elements in hydrothermal and subsurface liquids [12, 33, 34]. Guo et al. [5] used a LIBS prototype (LIBSea) in hydrothermal experiments at a depth of approximately 1800 m and detected major metallic ions, including Na, Ca, K, Mg, and Li. Bhatt et al. [30, 35] performed LIBS analyses of two rare earth elements (Eu, Yb) in an aqueous solution under high-pressure conditions. Underwater LIBS has also been used for colloid determination in aqueous solutions [36, 37].

For LIBS measurements in the marine environment, the effect of surrounding conditions, such as pressure, temperature, and salinity, play an important role on plasma emission. Li et al. [38] studied the effect of temperature (in 5–60 °C range) on the underwater plasma

emission and reported an increase in the intensity of Ca emission with increasing temperature. A gradual increase in plasma temperature and electron density was also observed by these authors. While Goueguel et al. [39] and Li et al. [40] reported the effect of salinity, the others studied the effect of pressure on plasma emission during underwater LIBS analysis [34, 41–47]. It was observed that the pressure effect on the plasma emission depended on the analytes, emission lines, elemental composition of solution (matrix), and experimental conditions (temperature, laser energy, gate delay). Some of these studies did not indicate any notable change while others reported minimal to significant changes in the intensity and width of analyte lines with increasing pressure. The observed differences are attributed to the differences in experimental conditions and measurement approach.

In our laboratory, underwater LIBS was demonstrated as a potential tool to detect CO_2 leakage in carbon sequestration [4, 48–50]. Leakage of CO_2 gas from the storage sites could attack the formation rocks and transport leachates to increase the concentration of certain elements in the overlaying groundwater. The changes in elemental composition of groundwater can be measured by LIBS and could provide an early indication of leakage from the CO_2 storage sites. Bhatt et al. [4] measured the dissolution of carbonates at increasing CO_2 pressures using underwater LIBS. Carbonate pellets were inserted into water solution containing Ba as an internal standard and CO_2 was injected to raise the pressure level to 50, 100, 150, 200, and 250 bars. Carbonic acid (H_2CO_3) is formed due to the interaction of CO_2 and water, which subsequently decomposes into H^+ and HCO_3^- ions. The carbonates are converted into bicarbonates because of the interaction with the H^+ ions and dissolution occurs. With the increase in pressure, pH decreases and causes more and more dissolution of carbonates. LIBS spectra were recorded from samples before injecting the CO_2 and at each pressure level after injecting the CO_2. Emission lines of mineral elements were detected in the spectra obtained at higher pressures, indicating the dissolution of carbonates with the application of CO_2 pressure as shown in Figure 26.2. Emission lines were more intense at higher pressures stressing the fact that the more rapid dissolution of carbonates occur at increasing CO_2 pressure. These results of carbonate dissolution demonstrate the possibility of using LIBS as an indirect detection system indicative of CO_2 leakage from the geological carbon storage.

26.3.2 Submerged Solids

It is not always practical to extract submerged solids from liquids for laboratory analysis. In addition to the complexity of a separation process, there may be a need for real-time analysis of materials in their original state and environment. In this case, LIBS can be an appropriate technique as it can operate easily in an underwater environment to generate real-time results. As per the literature, underwater LIBS has successfully been used for obtaining critical information about the sea floor, analysis of solid wastes in the sea, archaeological materials submerged in lakes and ocean, and solids of forensic importance present in liquids [6, 7, 51, 52]. When a submerged solid is ablated by a laser pulse of sufficient energy, a plasma is created on its surface. Because solids are more dense in nature, their ionization efficiency is relatively better than that of liquid solutions. However, the plasma expansion and emission processes are similar to those found in bulk liquids and the plasma plumes

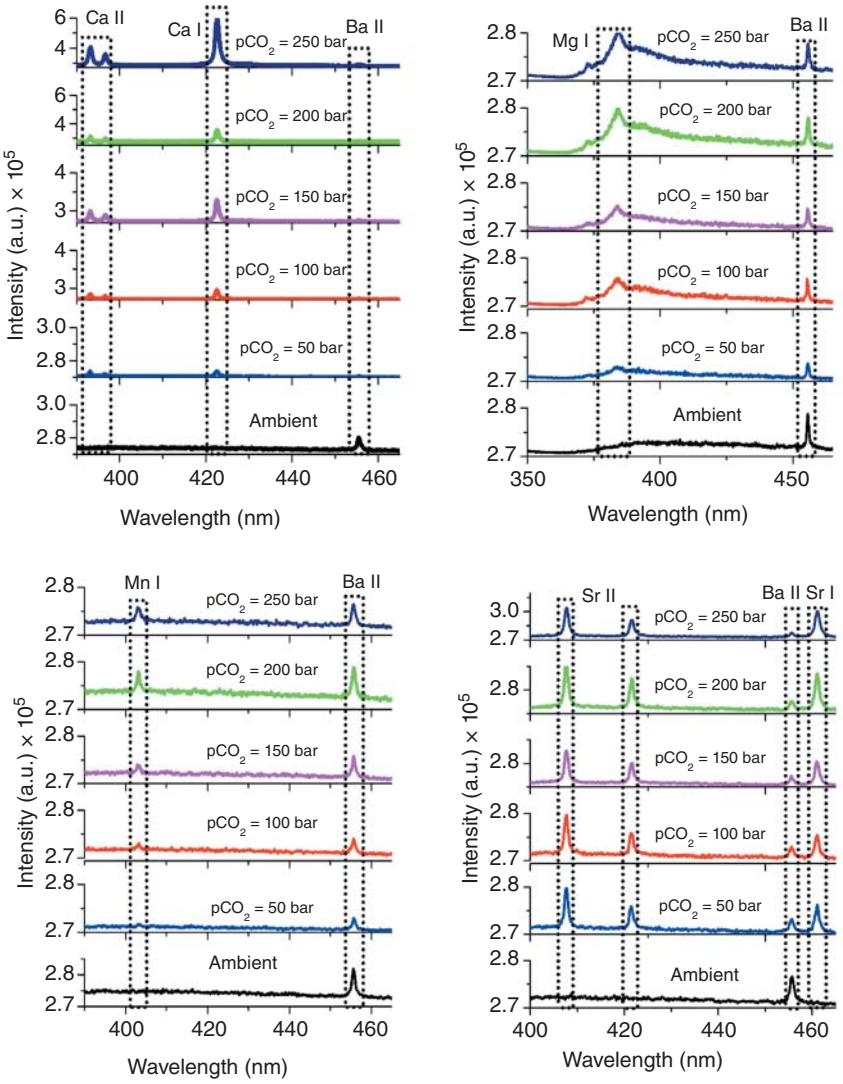

Figure 26.2 LIBS spectra showing dissolution of carbonates with increasing CO_2 pressure.

generated from the laser–solid interaction in a liquid are smaller than that in air as can be seen in Figure 26.3 [53].

Since pressure and depth have a directly proportional relationship, the ablation and characterization of solids submerged deep under water are highly affected because of the high-pressure environment. Both chemical and physical effects of external pressure are imminent on the plasma depending on the source and amount of the pressure, which can suppress or enhance the signal intensity [54]. Cavitation bubble dynamics and plasma emission from the laser interaction with the solids submerged in pressurized liquids have been studied by several research groups [51, 55–57]. During the ablation of a silver target submerged in water, Dell'Aglio et al. [55] observed a strong dependence of bubble

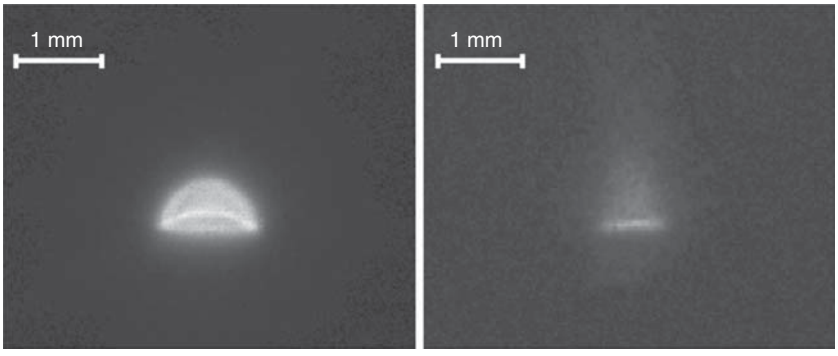

Figure 26.3 Images of plumes generated on the surfaces of solids in (a) air and (b) water at atmospheric pressure. Source: Thornton et al. [53], reproduced with permission from IOP Publishing.

dynamics on the applied pressure; however, the electron density and plasma temperature remain unchanged in the pressure range of 1–150 bar. In addition, a decrease in the bubble collapsing duration with an increasing pressure was observed in these experiments. Sasaki et al. [56] irradiated a titanium target immersed in pressurized water by perpendicularly focusing a laser beam on the target. The authors concluded that the cavitation bubble dynamics can be controlled by applying an external pressure to the liquid. However, the bubble temperature at the maximum size was found to be independent of external pressure in this study, which satisfies the scaling law. Additionally, a shorter lifetime of the cavitation bubble with the increasing pressure was observed and a second bubble was induced by the collapse of the first cavitation bubble. This second bubble was extinguished into the surrounding liquid when the external pressure exceeded 30 bar and a third shock wave was observed when the pressure was increased to 300 bar. Thornton et al. [57] investigated the characteristics of the plasma plume generated from the submerged material at increased hydrostatic pressures up to 300 bar. Surprisingly, no significant effect of the pressure on the density of the plasma plume was observed in this study at the early stages (prior to 600 ns) of laser ablation.

Sakka et al. [58] and Thornton et al. [51] also examined a long-duration laser pulse for underwater LIBS measurements of solids and found that the long pulse resulted in an increase in plasma emission efficiency and emission line narrowing as compared with a traditional short, single pulse. This improvement most likely is due to an interaction of a later portion of the laser pulse with the plasma plume [58]. Generally, well-resolved emission signals can be obtained by using the long-pulse ablation source in a high-pressure liquid environment [51]. Guirado et al. [59] applied underwater LIBS to study archaeological materials submerged in sea water. Organic and nonorganic materials collected from real oceanic environments were submerged into a tank filled with seawater and the LIBS spectra were recorded. While, Ca, Sr, and Fe emission lines were observed in the spectra obtained from the bone samples, the archaeological pottery was found to contain constituent analytes of quartz (SiO_2), clay (alumina-silicate of Ca and Mg), TiO_2, and iron oxides. The authors pointed out that the oxidation of sedimentary layers of samples could be characterized by identifying the Fe lines in the LIBS spectra. In a separate study, a handheld probe

(AQUALAS2.0) designed by Guirado et al. [7] was used to collect LIBS spectra from the bronze materials situated near the seafloor at approximately 30 m depth, and the Cu, Pb, and Zn emission lines were recorded in the spectra. However, the authors pointed out that the effect of immersion depth on the emission line intensity of Pb and Cu was different. While Cu signal intensity remained almost unaffected, the Pb signal decreased gradually with increasing depth. The variation can be attributed to the different volatilization rate of Pb and Cu and the depth effect is attributed to the pressure that increases with the increase in depth. AQUALAS2.0 was equipped with a multi-pulse excitation system and the use of the probe in the multi-pulse mode resulted in a 15-fold intensity enhancement over the single-pulse mode with the same laser irradiance. The probe was also applied by the authors to determine Ca, Mg, Sr, and Fe in submerged ancient pottery samples and to perform underwater LIBS measurements on the wreck of Bucentaure, a flagship of the French–Spanish alliance during the Battle of Trafalgar. In fact, the Bucentaure sank in the Bay of Cadiz, Atlantic Ocean in 1805, and its parts were discovered in 1949. Fortes et al. [6] examined the standoff LIBS (sensor) for the analysis of submerged solids where the distance between the laser source and the test sample varied up to 80 cm. An obvious decrease in ablation efficiency and hence a decrease in signal intensity was reported with increasing distance of the test sample from the sensor. While the ablation rate of about 20 μm/pulse was observed at 10 cm, the rate was less than 6 μm/pulse when the distance was increased to 80 cm. The authors concluded that the absorption and scattering of light by water and its constituents may primarily be responsible for the attenuation of the laser beam and hence for the weaker signal strength.

Double-pulse LIBS has been used by many researchers for the analysis of submerged solids under atmospheric and high-pressure conditions [43, 60, 61]. De Giacomo et al. discussed the effect of the cavitation bubble produced by the first pulse: (i) to optimize the double-pulse LIBS efficiency [62] and (ii) investigate the effect of liquid pressure and double laser pulses on the ablation of graphite submerged in water [43]. The same research group has also analyzed Ti, Cu, Pb, Sn, and Zn in submerged materials using the double-pulse LIBS technique [63, 64]. In addition to a decrease in plasma persistence and cavitation bubble size, the optimum inter-pulse delay also decreased with increasing pressure in double-pulse collinear LIBS when solid aluminum submerged in liquid was used as a test sample by López-Claros et al. [65].

26.3.3 Surface Measurements

As mentioned in the previous section, there is a significant loss of sensitivity due to fast quenching effects when LIBS measurements are performed inside a liquid environment. If the solutions are turbid, the laser pulse can be prevented from reaching the submerged target and the plasma emission coming back to collection optics can also be blocked. These problems can be minimized by creating a plasma from the test liquid in which the plasma has minimum interaction with the liquid and expands in the air. One of the simple methods used by many researchers is the creation of a plasma on the surface of the liquid sample [66–70]. Other approaches such as nebulization of the liquid into aerosols, forming micro droplets similar to the input of the ICP-MS, and hydride generation have also been found to be useful for enhancing the LIBS sensitivity during liquid measurements [71–73].

Although the surface measurement provides a better sensitivity, splashing can be a major issue that may compromise data reproducibility. When a high-power laser pulse is focused on the liquid surface, splashing occurs in the direction perpendicular to the surface because the laser-induced plasma expands in that direction. This splashing may create liquid droplets, which can contaminate the optics. Interaction of the laser pulse with the surface may also create a wave on the liquid surface that will ultimately affect the measurement precision. The splashing effects can be avoided to some extent by using the optics in a tilted configuration and keeping the laser frequency settings low. Fichet et al. [67] applied the above concepts in their experiments to measure 12 elements (Pb, Si, Ca, Na, Zn, Sn, Al, Cu, Ni, Fe, Mg, Cr) in water and oil solutions separately. Another widely used method for reducing splashing effects is the focusing of laser pulse on the surface of a narrow laminar jet produced from the test samples [74–79]. Ito et al. [74] used this approach of laminar flow in 1995 for the first time to detect the colloidal iron in water.

Subsequently, Yueh et al. [77] examined the liquid jet system for detecting the trace elements in liquids and claimed a better limit of detection (LOD) and improved signal stability as compared with bulk liquid measurements. When Yaroshchyk et al. [80] compared LIBS sensitivity between measurements utilizing laminar liquid jets and surface of static liquid, the liquid jets yielded a fourfold improvement in LODs of examined analytes over surface analysis. This can primarily be attributed to reduced splashing in laminar liquid jets and a larger plasma plume. Further improvement in LIBS measurements was reported by using the liquid capillary method as it limits the disturbance on the liquid surface induced by the laser pulse [76]. Ho et al. [78] and Ng et al. [79] compared the effect of laser wavelengths on the liquid plasma generation and analyte emission. While using the liquid jet for LIBS measurements, two different research groups indicated that the particle size may affect the analyte signal in suspensions [81, 82]. Rosado et al. [81] observed a significant decrease in the slope of a linear regression (from a plot of Al 396.1 nm signal intensity and Al concentration) with increasing particle size. Compared with the solution, the authors reported a 39% reduction in the slope from the suspension containing 2 μm particles and the slope was reduced by 99% when the particle size was increased to 87 μm. This reduction in slope can primarily be attributed to a partial ablation/vaporization of particles. Incomplete vaporization of particles can also result in analyte signal saturation as reported by Faye et al. [82].

In addition to experimental parameters (i.e. gate time delay and laser energy), the liquid flow rate generally plays a significant role in signal optimization and reproducibility in liquid jet analysis. While analyte signals may not be visible at low flow rates due to unstable flow, the high flow rates could cause a splashing and weaker signal reproducibility during measurement [83]. Wall et al. [84] used microwave-assisted LIBS for the detection of indium in aqueous solutions. A near-field applicator was used to couple external microwave radiation in this study. Bhatt et al. [3] employed single and double-pulse LIBS for the analysis of As, Hg, S, and Se in aqueous solutions. While no spectral signatures of these elements were detected using traditional underwater LIBS, the laser ablation on the surface of a laminar jet produced easily detectable emission signals of the analytes. In this experiment, a laminar jet of approximately 0.5 mm diameter and 1 cm long was produced at the nozzle of a pipette and a laser was focused on the jet to produce the plasma. For double-pulse LIBS, the second laser was used in collinear mode. Strong spectral lines As I 228.8 nm, Hg I 546.07 nm, S I 921.2 nm, Se I 196.09 nm, Se I 203.98 nm, and Se I 206.27 nm were identified in both

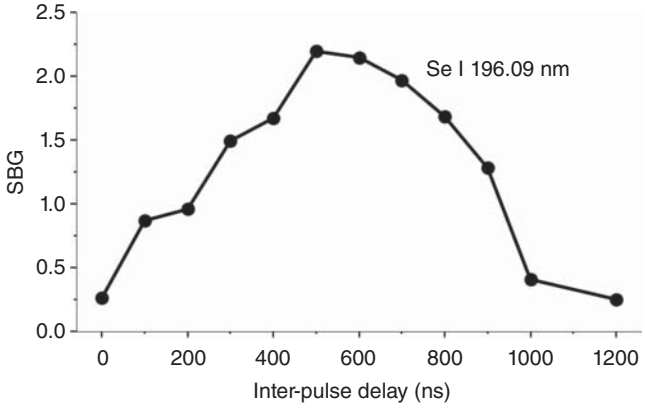

Figure 26.4 The dependence of signal-to-background ratio (SBG) on inter-pulse delay for line Se I 196.09 nm.

single- and double-pulse LIBS measurements. Inter-pulse delay between two laser pulses was found critical to obtain optimum signal-to-background ratio (Figure 26.4). Significant improvement in signal intensity and two- to fivefold improvement in the LOD was observed with double-pulse as compared with single-pulse LIBS.

26.3.4 Measurements on Pretreated Samples (Concentrated Liquids)

When real-time measurements are not necessary, the liquid samples can be preconcentrated prior to LIBS measurement to enhance the analyte sensitivity. The sample treatment methods used to achieve preconcentration are generally time-consuming, could contaminate the sample, and alter the physical and chemical properties of the sample from its original state. In spite of these demerits, sample pretreatment is highly advantageous to improve the analyte signal intensity and LOD significantly. Various sample preparation methods to enhance analyte sensitivity are discussed by Harun et al. [85] and Jantzi et al. [86].

Preferably, the liquid samples are converted into solids either by freezing or by other physical and chemical treatments of the sample to improve the LIBS detection limits. Some of these methods result in preconcentration and a significant increase in the analyte concentrations. Once aqueous samples are converted into solids, a simple LIBS experimental setup for solids can be used to ablate the samples and required information can be gathered from the LIBS spectra. However, the experimental parameters like gate time delay and laser energy need to be optimized to obtain the best qualitative and quantitative results. Since solids have a lower breakdown threshold energy and a better data acquisition rate, it generally contributes to a higher plasma emission efficiency. Freezing is one of the simplest sample treatment methods as it does not require pre-enrichment of a solution [87, 88]. Ablation on ice also helps to mitigate the splashing issues and hence the analytical performance is improved. Sobral et al. [89] froze aqueous solutions containing trace amounts of Mg, Cu, Fe, Cd, Cr, Hg, and Pb by immersing the container in liquid nitrogen. They observed better signal-to-noise ratio in ice than in the liquid samples at all of the gate time delays used in this study for data collection. The LOD was improved by three- to nine fold depending on the analyte measured. When dealing with frozen samples, control of sample temperature is

very important as it could significantly affect the ablation rate and emission intensity. Also, the sample composition and the melting of frozen samples during the warm up phase could result in changing the sample properties [85].

Use of adsorbents (substrates) has proved to be a useful technique to transfer liquids onto solids to increase the trace elements concentration and hence LIBS sensitivity [90–92]. Haider et al. [90] used ZnO and zeolite as adsorbents to detect Pb in four adsorbates $PbSO_4$, $Pb(NO_3)_2$, $Pb(CH_3COO)_2{\cdot}Pb(OH)_2$, and $PbCl_2$. They claimed 0.5 ppm LOD for Pb when used analyte lines Pb I 363.958 and 368.319 nm and ZnO as an adsorbent. Zhu et al. [91] used bamboo charcoal as a solid-phase extraction adsorbent to detect trace metals in aqueous solutions. Porous electrospun ultra-fine fibers have also been found to be very good solid support material to lower the LODs for Cr and Cu in aqueous solutions [92]. Likewise, the use of a wood slice substrate improved LODs for Cr, Mn, Cu, Cd, and Pb by two to three orders of magnitude as compared with those obtained by measurements on the liquid surface [93]. Alamelu et al. [94] used filter paper as a substrate to study three lanthanides, Sm, Eu, and Gd. Analyte solutions were transferred to the filter paper and the samples were dried prior to analysis. In this study, the authors were able to achieve LODs of 1.3, 1.9, and 2.3 ppm for Sm, Eu, and Gd, respectively. Single-pulse and double-pulse LIBS was employed by Yaroshchyk et al. [95] to analyze engine oils using paper substrates and the results were compared with those obtained from laminar liquid jets and static liquid surfaces. Paper substrates yielded better results and the improvement in LODs was two- and fourfold over liquid jets with single-pulse and double-pulse LIBS, respectively. To convert liquid samples into a solid matrix, simply drying the sample or adding chemical reagents followed by drying is also in practice. For analyzing four heavy metals (Cr, Pb, Cd, and Zn) in liquids, Pace et al. [96] added calcium oxide to the samples and the resulting precipitate was dried to make pellets. In this study, the detection limits obtained for Cr, Pb, Cd, and Zn were in the range of 1–120 ppm. Double distillation of crude oil followed by heating was applied to make pellets that were subsequently used to estimate the trace metals concentration in the crude oil [97]. While Lin et al. [98] employed the hydrogel-based solidification technique to study Al, Cu, and Cr in solutions, Moncayo et al. [99] used a collagen gel to solidify red wine samples to classify them by LIBS. For the liquid samples containing suspended solids, distillation, filtration, and drying of the residue were also found useful for LIBS studies [100, 101]. Viscous liquids can be spread on metallic plates and then interacted with a laser pulse to obtain LIBS spectra and the desired results [102–105].

26.4 Field-Deployable LIBS Sensor

Traditional lab-based LIBS instrumentation requires samples to be retrieved and transported to the laboratory for analysis. That is not only a time-consuming process but could potentially alter the sample chemistry and compromise sample integrity. Use of a portable, field-deployable LIBS system can be advantageous for in situ analysis of liquid samples to provide rapid, real-time results in their original state and environment. Although the LIBS sensor developed in our laboratory for water-quality monitoring is capable of performing both surface and subsurface measurements, the device suitable for subsurface analysis is described in this section [106, 107]. The sensor head is built using a low-cost, passively

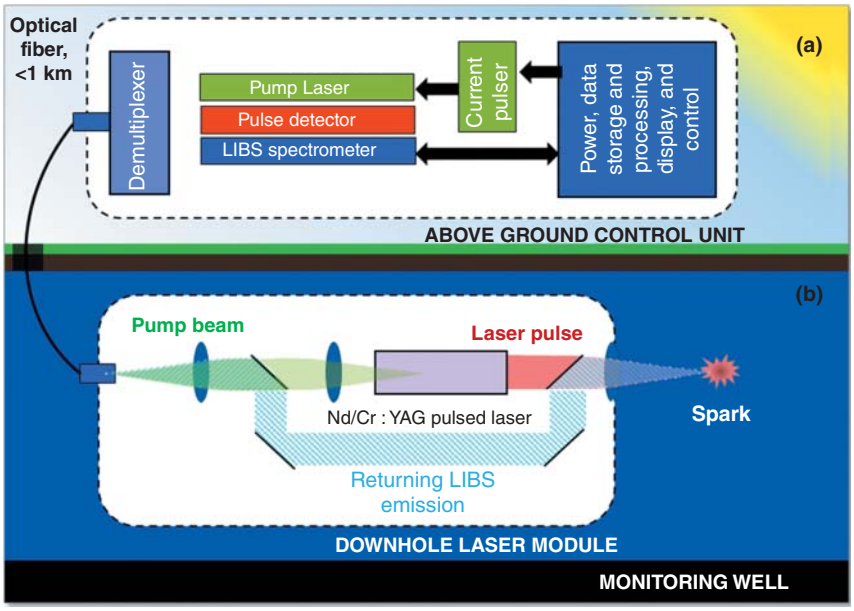

Figure 26.5 Field-deployable LIBS sensor design concept – (a) surface control unit and (b) subsurface sensor head.

Q-switched (PQSW) laser, which is fiber-coupled to a pump laser and a gated spectrometer. While most LIBS systems utilize an actively Q-switched laser, use of a PQSW laser simplifies the design of down hole components and increases sensor robustness. In order to apply LIBS to a down hole environment, the design concept (Figure 26.5) splits the instrument into two sub systems: (i) a surface control unit containing the spectrometer, pump laser, and computer and (ii) a rugged, all-optical LIBS-based sensor head is built around a PQSW laser. These subsystems are then connected by a fiber-optic umbilical, allowing the large, fragile, and expensive components to remain on the surface while only the relatively low-cost sensor head needs to enter the hostile, subsurface environment.

26.4.1 Prototype Design

A prototype sensor head was built around a Nd/Cr : YAG doped PQSW laser, producing 3 ns, 4 mJ, and 1064 nm pulses [107]. Pump light is delivered to the sensor head from the surface via a 30 m fiber-optic umbilical where it is coupled into the PQSW laser producing a high peak power laser pulse (Figure 26.6a). This pulse is focused into the surrounding water to create a plasma. The plasma emission is then collected by a focusing lens and transmitted to the surface via another fiber-optic umbilical (return fiber). The use of two fibers in the design make the sensor head more efficient because the optics for the pump and return fibers could be optimized separately for transmission of pump energy and plasma emission, respectively. Detector triggering was accomplished by detecting a small amount of the 1064 nm laser pulse scattering throughout the sensor head that is picked up by the return optics and transmitted to the surface. In this process, a dichroic mirror separates

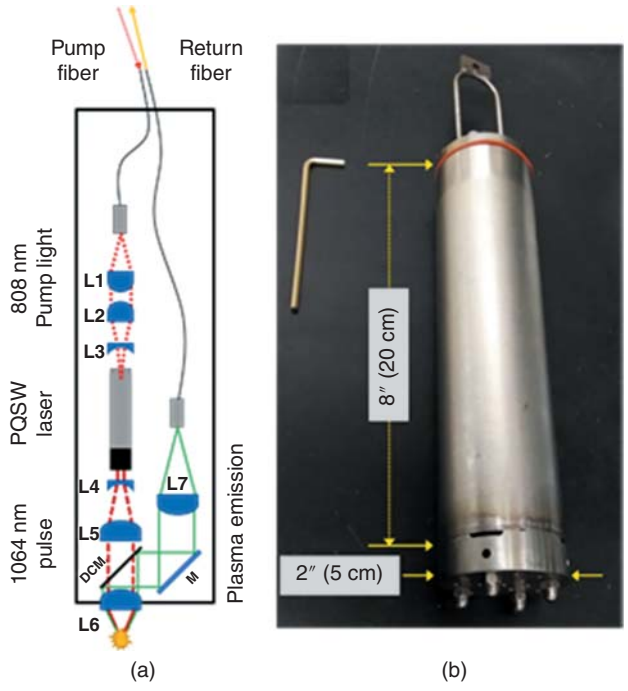

Figure 26.6 (a) Optical schematic of the prototype sensor head; (b) finished prototype sensor head.

the weak 1064 nm pulse from the plasma emission, which is subsequently detected by a photodiode and used to trigger the gated spectrometer in the surface control unit. The entire optical system is placed into a pressure resistant 2″ (diameter) by 8″ (length) enclosure that makes it rugged for the down hole environment (Figure 26.6b).

26.4.2 Performance

The fabricated sensor was evaluated for its performance in the laboratory settings by analyzing Ca, K, Li, Mn, and Na solutions. An aqueous stock solution of these elements was prepared, and the stock solutions were diluted to generate a set of calibration standards for these elements. The concentration range of calibration standards used for each element is provided in Figure 26.7. All of the calibration curves showed a high degree of linearity with $R^2 > 0.99$ for all elements with measured LODs similar to or better than those obtained from actively Q-switched high-power benchtop LIBS systems. This indicates that the developed sensor has excellent optical performance and sufficient energy to generate a laser-induced plasma in both air and deionized (DI) water at atmospheric pressure.

26.4.3 Subsurface Testing

The prototype system was deployed to perform subsurface measurements in a monitoring well, which is 30 ft. deep and has a diameter of 4 in. The analysis of well water performed over a 14-day period included three spectral ranges: 330–470 nm (encompassing Mn and

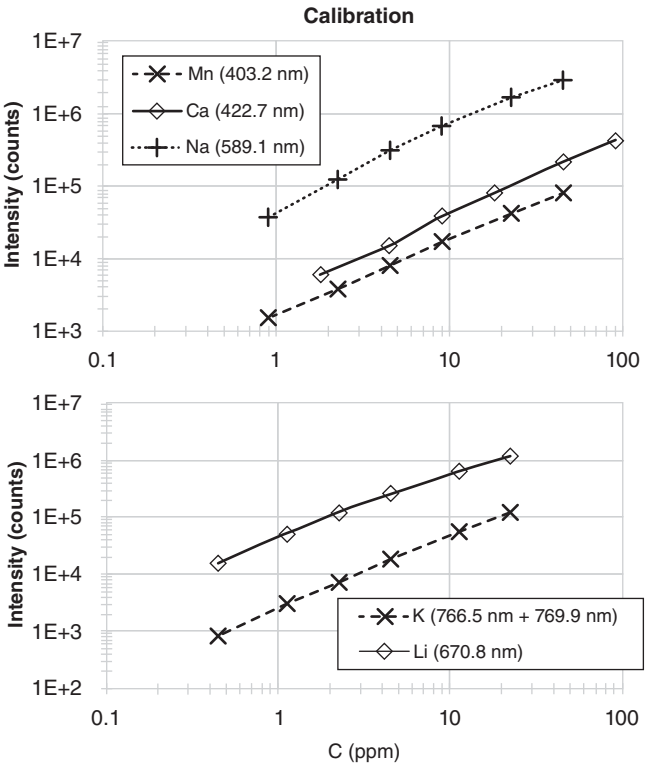

Figure 26.7 Calibration curves for Ca, Mn, Na, Li, and K.

Ca), 570–700 nm (Na and Li), and 665–800 nm (Li and K). The data (not presented here) indicate that the performance of the sensor in the downhole environment is very satisfactory, easily detecting Ca, K, Mn, and Na within the 0.3–3 ppm concentration range (Li was not detected). A more detailed account of this testing will be published elsewhere.

26.5 Conclusions

A brief overview presented in this chapter indicates that LIBS is an outstanding technique for real-time measurements of liquids and suspended solids inside liquids. Depending on the nature and location of a sample and environmental conditions, both laboratory and field-based LIBS methodologies can be developed. For measurements in hard-to-reach places and/or in harsh environments, both standoff and in situ LIBS techniques can be useful. If analyte concentrations are sufficient enough, the underwater LIBS can be used for their detection; otherwise sample treatments or alternative ways of laser–matter interaction mechanisms can be employed to improve analyte sensitivity and detection limits. Measurements on the surface of a laminar liquid jets appears to provide a significant improvement in LIBS detection capability. Similarly, preconcentration methods improve LIBS sensitivity further for the liquid samples, which do not require real-time measurement or analysis

in their original environment/state. A field-deployable LIBS instrument/prototype was developed and employed for well-water monitoring and the preliminary test results are very promising for downhole applications. Since LIBS application for liquids and suspended solids is quite diverse, more advanced LIBS systems incorporating modern technologies and data acquisition and analysis tools need to be developed and optimized.

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