CHAPTER 9

LIBS application to liquid samples

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1 Introduction

Liquid samples are usually classified as aqueous, nonaqueous, and mixtures. Examples of aqueous liquids are most often surface water, groundwater, drinking water, and wastewater, whereas nonaqueous liquids include organic solvents, oils, and many other hydrophobic liquids. Mixtures may be referred to as the combination of aqueous and nonaqueous liquids. Although most laser-induced breakdown spectroscopy (LIBS) research has been focused on the characterization of solid samples, the analysis of liquid samples by LIBS offers a huge potential in a number of applications such as surface and groundwater monitoring, oceanography, carbon dioxide (CO_2) leak detection in geologic carbon storage, quality control in pharmaceutical and food industries, medical diagnostics, and industrial process monitoring [1–4]. Traditionally, the analysis of liquid samples has been performed by well-established laboratory-based analytical techniques such as inductively coupled plasma atomic emission spectroscopy and inductively coupled plasma mass spectrometry. However, LIBS offers numerous advantages over the aforementioned techniques, including in situ and online measurements. Indeed, LIBS analysis is relatively fast, the instrumentation can be miniaturized to make the system portable, and the coupling of fiber optics allows LIBS measurements in harsh environments and places that are inaccessible by traditional lab-based techniques. In addition, only optical access to the sample is needed to perform a LIBS measurement to allow a standoff analysis.

LIBS analysis can be performed in a bulk liquid, in static or laminar flow of the liquid surface, in jets, and in a stream of aerosols or droplets [5–10]. Although bulk liquid analysis is relatively simple to set up, it is only usable for transparent liquids. The sensitivity of analysis in bulk liquid remains the main issue since most of the plasma energy is lost in vaporization of the surrounding liquid and in generation of a shockwave and cavitation bubble accompanying breakdown. Only a small fraction of

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the plasma energy is converted into radiative energy. Furthermore, plasma formation in bulk water generally suffers from short lifetimes as the emission intensity falls steeply after approximately 1 μs. On the other hand, liquid surface analysis is typically more sensitive than bulk analysis because of plasma expansion in air. However, strong mechanical effects arising from the laser-liquid surface interaction cause several experimental difficulties (i.e., splashing, generation of bubbles and aerosol, and ripples on the liquid surface), which greatly affect the accuracy, repeatability, and reproducibility of the measurement. Interestingly, most of these difficulties can be minimized by using various experimental configurations to convert liquid into jets, aerosols, or droplets. However, LIBS setup complexity increases due to the use of additional instrumentation (e.g., peristaltic pump or various types of nebulizers) to transform the liquid sample and to ensure that there is a continuous exchange of the sample in the flow channel. The limits of detection (LODs) obtained using the aforementioned configurations are mostly in the parts per million (ppm) or high parts per billion (ppb) level. Even though the sensitivity of these configurations can be satisfactory for a number of applications, research is under way to improve the detection limits and to expand LIBS applicability to a higher number of applications that require detection at trace level. To this end, many researchers have investigated various alternative approaches involving sample preparation or pretreatment [11–15] or the use of two successive laser pulses (double-pulse LIBS [DP-LIBS]) [16–19], including the use of hyphenated approaches (e.g., LIBS-laser-induced fluorescence [LIF]) [20–23]. Another approach proposed to enhance LIBS sensitivity is the use of an ArF laser at 193 nm as an excitation source instead of the commonly used 1064-nm YAG laser [24–26]. This chapter presents some general aspects and research trends on liquid sample analysis using LIBS. General procedures for preparing and analyzing liquid samples are described.

2 Experimental details

2.1 Samples

The main goal of LIBS study is to characterize a sample for its elemental composition qualitatively and quantitatively. LIBS has extensively been used for the analysis of liquids, particularly aqueous samples. In principle, sample preparation is not required for test samples; however, for quantifying the elemental concentrations a reliable calibration of the instrument is required. The calibration is generally achieved by using analyte solutions of known concentrations. These solutions are known as calibration standards and are prepared by mixing pure analyte liquid standards or dissolving analyte salts in desired concentrations. For construction of the calibration curves in their study of metal ions, Goueguel et al. [27] prepared stock solutions by dissolving pure powders of $CaCl_2{\cdot}2H_2O$, $MnCl_2{\cdot}4H_2O$, $SrCl_2{\cdot}6H_2O$, $MgCl_2{\cdot}6H_2O$, and $BaCl_2{\cdot}2H_2O$ in ultrapure water. The stock solutions were then used to prepare sets of calibration standards for quantification of Ca, Mn, Sr, and Mg. Ba solution served as an internal standard in this study. Bhatt et al. [28, 29] used solutions of Eu (10,017 ± 29 μg/mL Eu, 7% HNO_3) and Yb (9978 ± 27 μg/mL Yb, 7% HNO_3), which were diluted with deionized water containing 2% HNO_3 to obtain the desired concentrations of solutions for generating the calibration curves for Eu and Yb. In a separate study, Bhatt et al. [30] utilized calibration standards of Ca, Mg, Mn, and Sr for investigating the leaching of these metals from their carbonate pellets under rising CO_2 pressure. The released amount of Ca, Mg, Mn, and Sr from their corresponding metal carbonates was measured by LIBS and quantified by developing calibration curves using the calibration standards. A similar study by Goueguel et al. with $CaCO_3$ is reported in [31].

2.2 Experimental apparatus

In general, the LIBS apparatus consists of three units: excitation source (laser), optics (lens, optical fiber), and detection system coupled with a computer (camera, spectrometer) for analysis. For the LIBS study of liquids, the laser pulse is focused either on the surface or into the liquid. The generation of a laser spark on the liquid surface sometimes results in splashing and surface agitation. The excitation capacity, on the other hand, may be compromised due to lower temperature spark in the liquid. The experimental setup used by Goueguel et al. [31] for liquid LIBS analysis is shown in Fig. 1. Laser radiation at 1064 nm was produced in pulses of 6-ns duration by a solid-state Nd:YAG laser (Q-smart 850, Quantel). The laser beam was focused 2 cm inside the liquid using two ultraviolet-grade fused-silica planoconvex lenses of 180 and 70 mm focal length, and 25.4 cm diameter. The lenses were separated by 1 mm, resulting in a focal length of approximately 50 mm. In these experiments, the laser repetition rate was held at 5 Hz. Pulse energy levels were attenuated by means of two pairs of half-wave plates and polarizing beam splitter cubes. The monitoring of the pulse-to-pulse energy was carried out using a high-energy pyroelectric head detector (70,273, Oriel Instruments) connected to a computer through an Ophir compact Juno USB interface. The liquid samples were kept in a 0.5-L stainless-steel high-pressure vessel to perform measurements under pressurized conditions. Similar LIBS setups have been reported by other research groups with some changes in laser sources, optics, and detection systems depending on the nature of the study and availability of the equipment [32, 33]. Joseph and David created laser sparks on the surface of the solution to determine uranium [34]. If DP-LIBS is to be used, a second source of excitation can be added to the system in various geometrical configurations, such as collinear, orthogonal, and oblique [16, 18, 35, 36]. Rai et al. [18, 37] focused the laser pulse on the jet orthogonally.

3 Optimization of experimental parameters

Major experimental parameters that come into play in a single-pulse LIBS (SP-LIBS) study of liquid samples are laser energy, gate time delay,

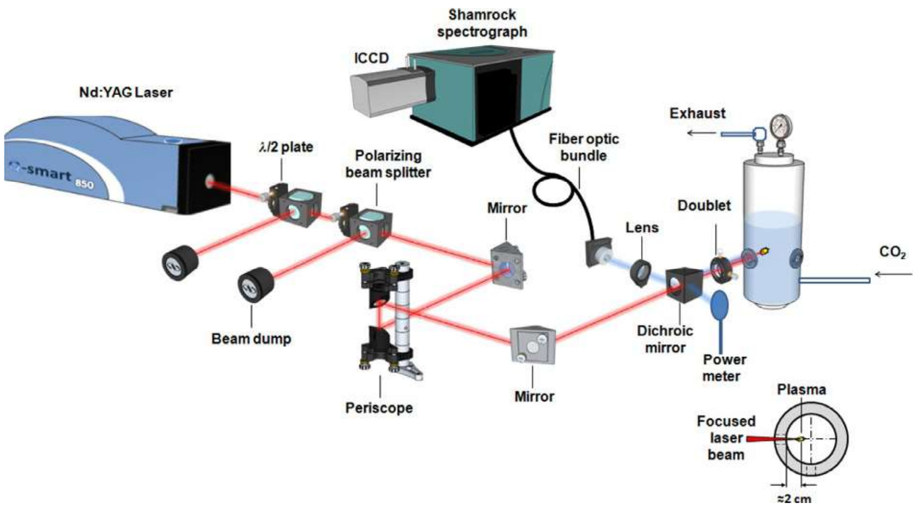


FIG. 1 Experimental setup for laser-induced breakdown spectroscopy.

gate width, and sample-to-the-focusing lens distance. Interpulse delay adds up when two lasers are used for sample excitation in DP-LIBS. For generating accurate and precise results, all these parameters need to be optimized. LIBS study primarily depends on emission lines of analyte elements. The intensity profile of spectral lines provides hints as to whether there are any detrimental effects, like self-absorption, phase reversals, and unequal temperature in the center and edges of the plasma. For quantitative analysis, emission lines should be free from these effects. Moreover, for better sensitivity, emission intensity of analyte lines should be maximum with minimum background effects. Considering favorable signal-to-noise ratio (SNR) values is one of the more widely followed practices for optimization of experimental parameters.

Generally, signal intensity is higher in the beginning and decreases as time delay increases. Since the background emission is higher at early times, the SNR consideration would be better for the determination of optimum time delay. Gougeuel et al. [38] optimized gate time delay and laser energy by using SNR as shown in Fig. 2 to study the matrix effect of sodium compounds on metal ions in aqueous solutions. Optimum values of experimental parameters are not always those producing the largest SNR; some adverse effects may be associated with them. For instance, higher laser energy may produce larger SNR, but it sometimes causes plasma shielding and moving the breakdown along the laser beam pathway. Therefore moderate energy is preferred rather than the energy values producing the largest SNR [39].

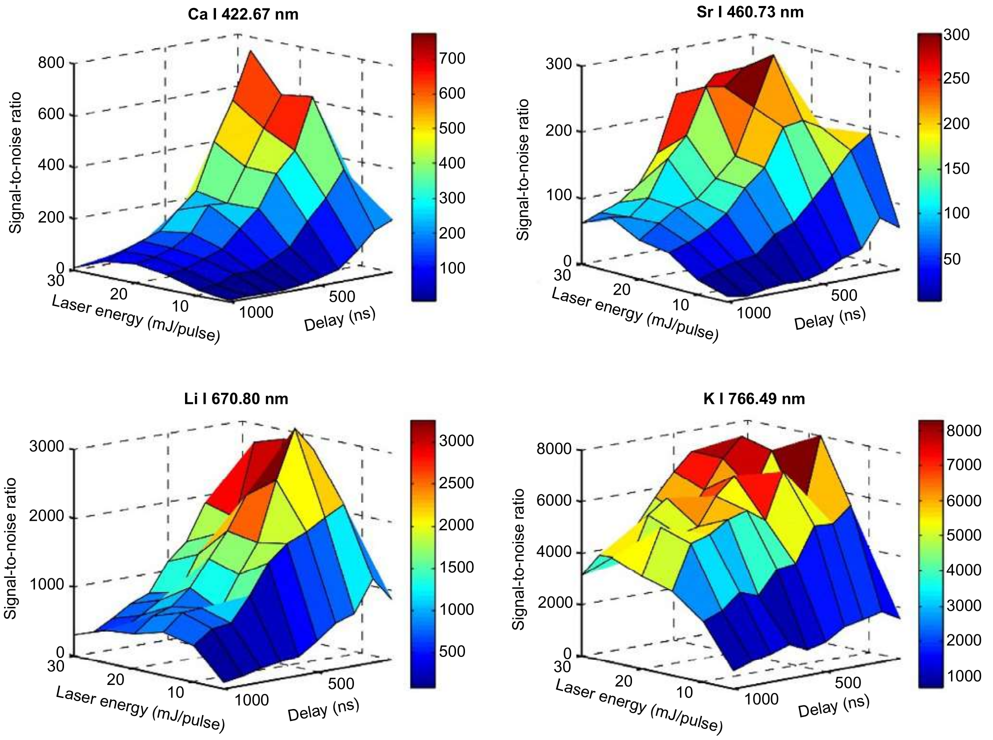


FIG. 2 3D display of the signal-to-noise ratio for the Ca I 422.67-nm, Sr I 460.73-nm, Li I 670.80-nm, and K I 766.49-nm emission lines versus laser energy versus gate delay [38].

In DP-LIBS, an appropriate interpulse delay is required to maximize sample ablation and plasma production. With larger plasmas, both plasma temperature and electron density will be increased producing stronger emission signals in the LIBS spectra. Optimum interpulse delay for underwater LIBS measurements is generally analyte and pressure dependent. Michel et al. [40] reported the importance of shorter interpulse delay at high pressures.

4 LIBS signal enhancement techniques

Laser-induced plasma formation and its emission mechanism are different in an aqueous media than in gas. This is due primarily to the difference in compressibility of liquids compared to gases. The formation and evolution of plasma and emission spectra from a plasma created in liquids generally suffer from matrix, pressure, plasma shielding, line broadening due to increased collisions, and Stark-broadening effects [38, 39, 41–46]. Moreover, the plasma loses its energy more rapidly to the surrounding liquid, resulting in reduction of persistence time and lower temperature. All these effects in the liquid environment contribute to weakening of the emission signals and compromising the sensitivity, accuracy, reproducibility, and stability of analysis. Although these effects are inevitable while using LIBS in real field applications, it is important to explore ways of enhancing the emission signals. To enhance the emission signals, several enhancement techniques have been reported by various research groups. Some of the common enhancement techniques are briefly described in the following sections.

4.1 Substrate technique

In this pretreatment technique, liquid samples are transformed into solid samples by using different solid substrates. Chen et al. [47] used a wood slice as the solid substrate in their experiment for fast and sensitive trace heavy metal analysis and claimed two- to threefold improvement in LODs for Cr, Mn, Cu, Cd, and Pb. Likewise, carbon planchet, paper, $Ca(OH)_2$, and ion exchange polymer membrane have also been used as solid substrates [48–53]. When calcium oxide (CaO) is added to aqueous solution, calcium hydroxide ($Ca(OH)_2$) is formed and the resulting precipitate in the form of solid can be used for LIBS analysis. The ion exchange polymer containing an iminodiacetic acid functional group has also been used for preconcentrating liquid samples for LIBS analysis. As carboxylate groups are negatively charged, the membrane exchanges cations at a $pH > 5$ [49].

In their recent study, He et al. [54] reported LOD in low ppb (18.4 ppb) for Li detection in a liquid sample by using filter paper as the adsorption substrate. To analyze Mn in aqueous solution and seawater, the use of a paper substrate as an absorber is demonstrated in [55]. Alamelu et al. and Sarkar et al. were able to detect low levels of some lanthanides and actinides in aqueous solutions by LIBS using the substrate techniques [56, 57].

4.2 Dual-pulse technique

Another useful and widely used technique for enhancing emission signals is DP-LIBS. In DP-LIBS, two laser pulses either from two different sources or from the same source in various geometrical configurations are employed to induce sample ablation and subsequent plasma expansion and emission. Various research groups have used different geometrical configurations, like collinear, orthogonal, prespark, orthogonal preheating, and dual-pulse crossed-beam modes for signal enhancement. In double-pulse mode, the first pulse induces the plasma, which starts cooling down and decaying. Depending on the interpulse delay, the second pulse will reheat the plasma produced by the first laser pulse or a certain portion will be absorbed by the plasma and the rest will be used for further ablation of the sample. The second pulse could also ablate the sample again to create a plasma. Therefore interpulse delay has a significant role in signal enhancement in the double-pulse regime.

Cremers et al. [58] were the first to demonstrate bulk liquid analysis by using multiple laser sparks. They studied the emission lines of Be, Mg, Ca, B, Al, and five alkali metals (Li, Na, K, Rb, Cs) without taking pressure effects into account. Nakamura et al. [59] reported detection of a 20-ppb concentration of Fe in FeO(OH) colloidal suspensions by using two laser pulses at optimum interpulse delay and gate delay time. Laser pulses were focused perpendicularly onto the laminar jet of aqueous Cr solution to study the temporal enhancement of Cr emission by Rai et al. [37]. These authors observed that the material ablation in DP-LIBS was ≥3–5 times that of SP-LIBS. Their experimental results were found to qualitatively match with theoretical calculation of the enhancement. By combining DP- and crossed-beam LIBS, the detection limit of Na was brought down to 0.1 ppb by Kuwako et al. [60]. DP-LIBS has also been used for the study of submerged materials in water and the analytical performances were evaluated for sensitivity enhancement [35, 61, 62].

4.3 Hyphenated techniques

In hyphenated techniques, two different analytical techniques are combined or coupled to form a more powerful integrated system for material analysis. Hyphenated techniques may include separation-separation, separation-identification, and identification-identification techniques. Nakane et al. [20] reported the detection of trace metal atoms in water by combining LIBS and laser-excited atomic fluorescence spectroscopy and claimed LODs as low as10 ppb for Fe in water. Loudyi et al. [21] detected traces of metallic impurities in acid solutions using LIBS combined with LIF; the LODs obtained were 39 and 65 ppb for Pb and Fe, respectively. The authors claimed that the use of a flow cell improved the reproducibility of analysis. Similarly, other groups have also combined LIF with LIBS for improvement in sensitivity and analytical performance [22, 23].

5 Underwater LIBS measurements

Underwater LIBS has been demonstrated as a powerful tool for the analysis of both dissolved materials and submerged materials. This is becoming a very useful technique for a number of applications, including environmental and industrial waste monitoring, and geological and marine research activities [63–65]. Although problems related to splashing of a sample by a liquid surface are eliminated in underwater LIBS, the liquid pressure comes into play when the plasma is created at depths below the surface. This becomes more prominent when LIBS analysis is performed in oceanic and hydrothermal vent fluids [33, 39]. In the complex natural aqueous samples, matrix effects also affect the LIBS analysis. It is therefore important to analyze and quantify matrix and pressure effects on the LIBS signal to assist in designing appropriate instrumentation for underwater LIBS measurements.

5.1 Matrix effects

Matrix effects are simply an influence of constituents other than analyte of interest on the analyte signal. In LIBS, major matrix effects can be explained as spectral, chemical, and physical effects [66]. When weak emission lines of an element of interest and strong emission lines of matrix elements overlap, spectral interference takes place. If emission characteristics of analyte are altered due to the presence of matrix elements, it is known as the chemical matrix effect. Lastly, because of differences in physical properties of elements present in the sample the plasma behavior can be affected resulting in a physical matrix effect. The matrix effect could bring increased false-positive or false-negative LIBS response to compromise analytical precision. For quantitative measurements in complex matrix samples, multivariate analysis is generally preferred to achieve better accuracy. In oceanic environments, deep saline waters contain Na as the most abundant element constituting approximately 70%–90% of the total cation mass [67, 68]. Other major constituents of saline brines include Ca, Mg, and K; however, brine composition varies by location. Therefore understanding the matrix effect of NaCl on LIBS measurements becomes crucial. In general, matrix effects cause suppression of analyte emission signals; however, in the case of an NaCl matrix, the outcome is different. While atomic emission signals are enhanced the suppression of ionic spectral lines was observed in the presence of a sodium chloride (NaCl) matrix. This effect on spectral lines may be because of the higher plasma temperature and electron number density caused by NaCl. Significant increase in the intensity of atomic emission (Ca I 422.67 nm) and no notable change in ionic emission (Ca II 393.366 nm and Ca II 396.847 nm) were observed by Michel et al. [32] with NaCl addition. Likewise, Thornton et al. [69] also observed more intense Ca signals in an Na matrix when they compared the spectra recorded from solutions with and without NaCl. While decrease in intensity ratio of Ca(II)/Ca (I) was reported by Cremers et al. [58], Michel et al. [32] did not observe any change in Mn I 403 and K I (766.491-nm and 769.897-nm) intensities by NaCl. Goueguel et al. [38, 41] carried out a detailed study of the effect of NaCl concentration and other Na compounds on underwater LIBS measurements of common metal ions. For determining the effect of NaCl on Ca and K the authors used three concentrations (0.5 M, 2 M, and 3 M) of NaCl. Although NaCl enhanced both Ca and K signals the magnitude of enhancement varied. Intensity of a Ca I 422.67-nm line increased two-, four-, and eightfold in the presence of 0.5 M, 2 M, and 3 M NaCl, respectively (Fig. 3A). In the case of a K I 766.49-nm line the magnitude of enhancement was fivefold with 0.5 M NaCl and 10-fold with 3 M NaCl added to the solution (Fig. 3B). Signal enhancement by NaCl in this study was attributed to the increase in plasma temperature and electron density.

In an another study, Gouguel et al. [38] investigated the effect of Na compounds (NaCl, Na_2CO_3, and Na_2SO_4) on the LIBS measurements of Li. The analyte emission intensity was found to increase in the presence of NaCl and Na_2SO_4 and decreased with addition of Na_2CO_3 as shown in Fig. 4. This behavior appears to be related to a change in Bremsstrahlung process efficiency with increasing amount of impurities and difference in the thermal properties (boiling point and thermal conductivity) of the impurities.

Gouguel et al. [38] also generated calibration curves of Li and K in the presence of three different concentrations (0.1, 1, and 10 wt%) of NaCl, Na_2SO_4, and Na_2CO_3 (Fig. 5). The authors pointed out that it is feasible to perform quantitative analysis by LIBS in complex matrix samples such as groundwater.

5.2 Pressure effects

The laser-induced plasma formation process is basically the same in gaseous and liquid media; however, there are some differences in plasma expansion and emission processes. Plasmas formed in liquid are more confined than those in air and are relatively smaller in size. As surrounding pressure increases, both plasma evolution and emission process are affected significantly [70]. It should be noted that the extent of pressure effect on emission line intensity and width depends on several factors, including emission lines, elemental concentration, sample matrix, and experimental conditions (temperature, laser energy, gate delay). Effect of pressure

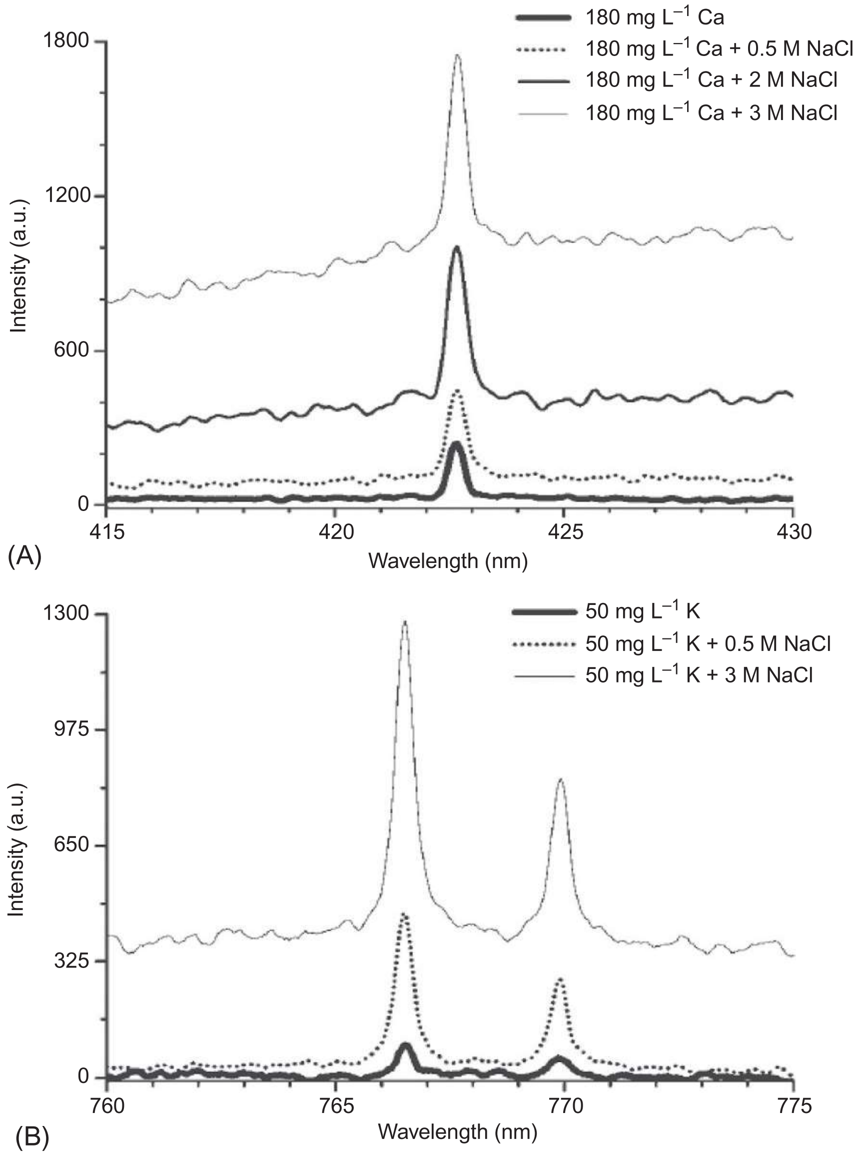


FIG. 3 Effect of NaCl concentration on emission spectra recorded using samples containing 180 mg L^{-1} Ca and 50 mg L^{-1} - K. (A) Ca I 422.67 nm, (B) K I doublet (766.49 and 769.90 nm) [41].

in underwater LIBS measurements was first taken into account by Lawrence-Snyder et al. [46]. The authors reported larger pressure effects on the emission line width and minor effects on the intensity of the Li I 670-nm line, mostly during late-stage plasma evolution. In 2014, Hou et al. [71] observed the pressure effects on the peak width, intensity, and integrated intensity of Ca, K, and Mg in seawater. The intensity of three atomic lines, Ca I 422 nm, K I 766 nm, and Mg I 518 nm, increased with increasing pressure until 15 MPa and then

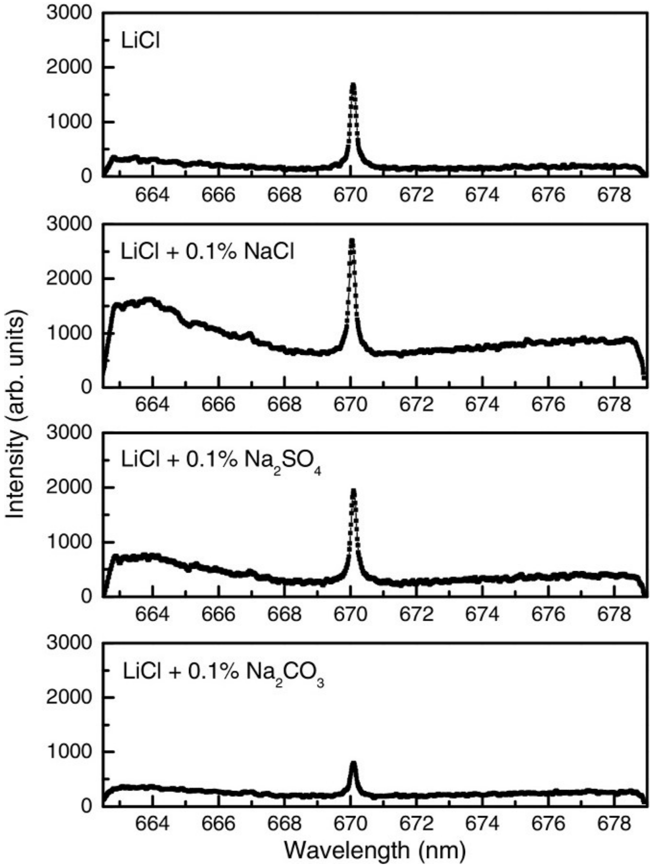
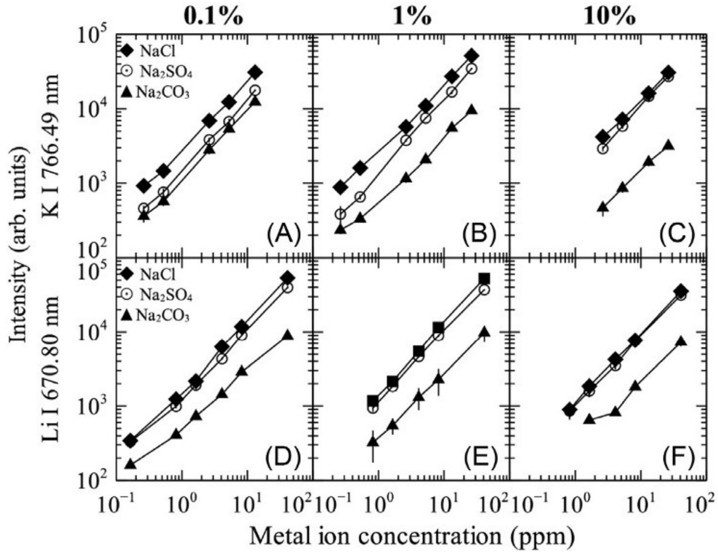


FIG. 4 Li emission spectra acquired using (*from top to bottom*) LiCl, LiCl-NaCl, LiCl-Na_2SO_4, and LiCl-Na_2CO_3 aqueous samples [38].

decreased. It was, however, noticed that the atomic and ionic lines of Ca behaved differently and followed a different trend in variation of their intensity as the pressure was increased. While the intensity of the atomic line (Ca I 422 nm) increased until 15 MPa and then decreased, the intensity of the ionic line (Ca II 393 nm) increased steadily with increasing pressure up to 40 MPa except a marginal decrease observed in the pressure range of 15–20 MPa. In contrast, the integrated intensity and the line width of both the Ca lines increased gradually with the increasing pressure. The integrated intensity of the Mg I 518-nm line also gradually increased with increasing pressure; however, in the case of the K I 766-nm line, the intensity increased sharply up to 15 MPa and then decreased steadily.

In separate studies, Thornton et al. [9, 69, 72] reported no significant effect of pressure on Zn and Cu spectra recorded from metal plates immersed in water. However, decrease in emission intensity of Zn I lines and broadening of Cu lines in DP-LIBS with rising pressure are reported in [73, 74], respectively. LIBS has also been demonstrated for the study of sediments in aqueous medium. Lazic et al. [75] used DP excitation from a single laser source to study natural and certified sediments by underwater LIBS.

FIG. 5 Comparison of the effect of NaCl, Na_2CO_3, and Na_2SO_4 on the calibration curves of Li and K in aqueous solutions [38].



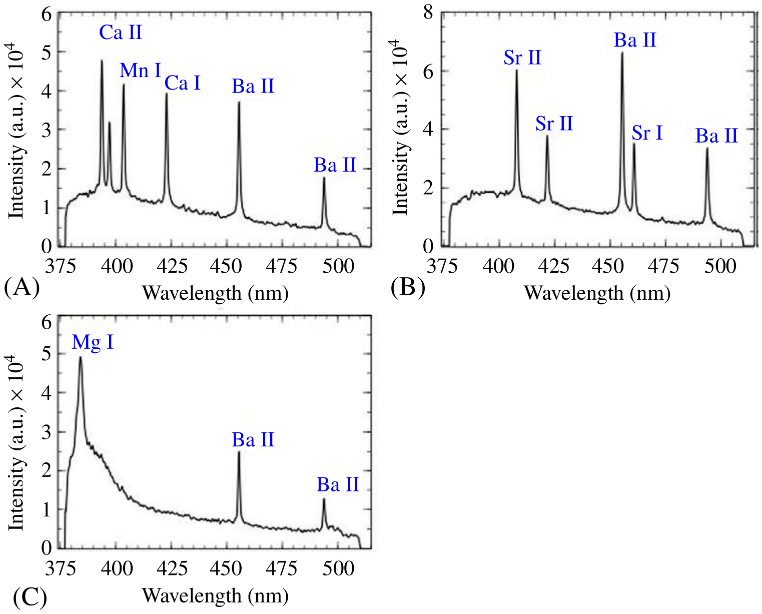


FIG. 6 Underwater laser-induced breakdown spectroscopy spectra of Ca, Mn, Ba, Sr, and Mg obtained in CO_2–water solutions. The spectra were acquired at a CO_2 pressure of 400 bar using (A) $CaCl_2$–$MnCl_2$–$BaCl_2$, (B) $SrCl_2$–$BaCl_2$, and (C) $MgCl_2$–$BaCl_2$ aqueous samples [27].

5.3 LIBS study in a compressed gas-water mixture

Pressure conditions in oceanic and downhole environments generally change due to increasing depth and hydrothermal activities. It is therefore important to evaluate the effect of increasing pressure on the LIBS measurement in compressed gas-water mixtures. Goueguel et al. [76] performed underwater LIBS measurements to detect Ca under rising CO_2 and N_2 pressures. Their study demonstrated that Ca emission line (Ca I 422.67 nm) intensity decreased with increasing CO_2 and N_2 pressures. However, the gas-dependent differences were evident as the Ca line intensity in CO_2 was found to be higher at 120 bar but lower at 10 bar than that in N_2. LIBS measurements of common metal ions (Ba, Ca, Mg, Mn, Sr) in a compressed CO_2-water mixture are also reported by Goueguel et al. [27]. In these experiments, the Ba emission line was used as an internal standard; LIBS spectra in the wavelength range of 375–510 nm are shown in Fig. 6.

Underwater LIBS study in a compressed CO_2–water mixture could be useful in geological carbon storage (GCS). In GCS, CO_2 is captured and injected deep underground for permanent storage. In case of leakage, upward migration of CO_2 could react with carbonate minerals of storage formations to release specific metals to shallow groundwater aquifers. These metals could be useful to provide early indication of CO_2 leakage. Goueguel et al. [31] demonstrated underwater LIBS for studying the dissolution of calcium carbonate under elevated CO_2 pressures up to 350 bar. In this study a $CaCO_3$ pellet was inserted into an aqueous $BaCl_2$ solution in a pressure vessel, and Ba was added to use it as an internal standard. CO_2 was injected into the liquid to raise the pressure to 50, 150, 250, and 350 bar and LIBS spectra were recorded at each pressure setting (Fig. 7). Ca emission lines

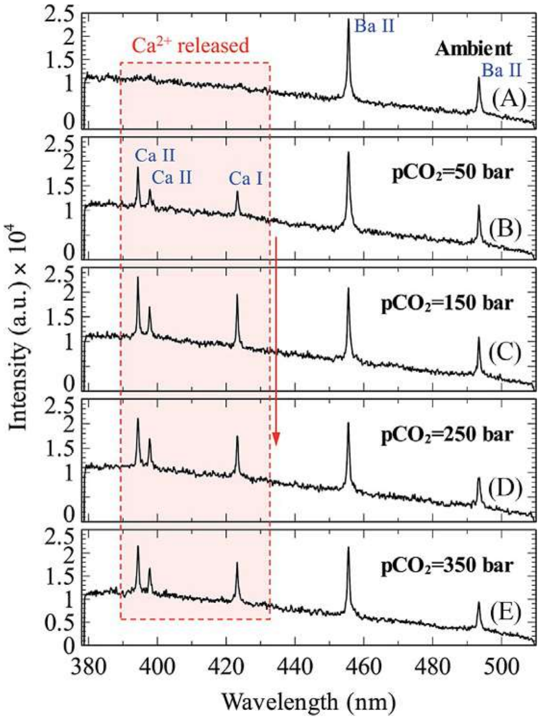


FIG. 7 Laser-induced breakdown spectroscopy spectra showing leaching of Ca^{2+} cation from $CaCO_3$ by CO_2-enriched water [31].

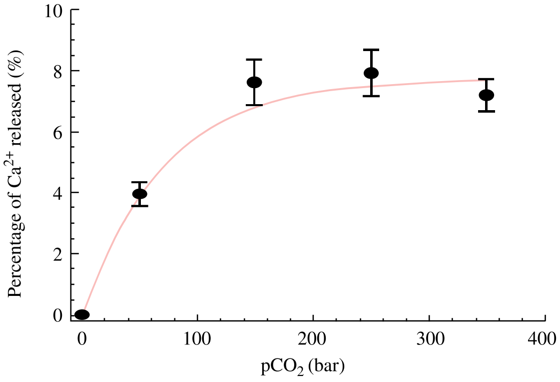


FIG. 8 Ca ion released to the water as a function of CO_2 pressure (pCO_2) [31].

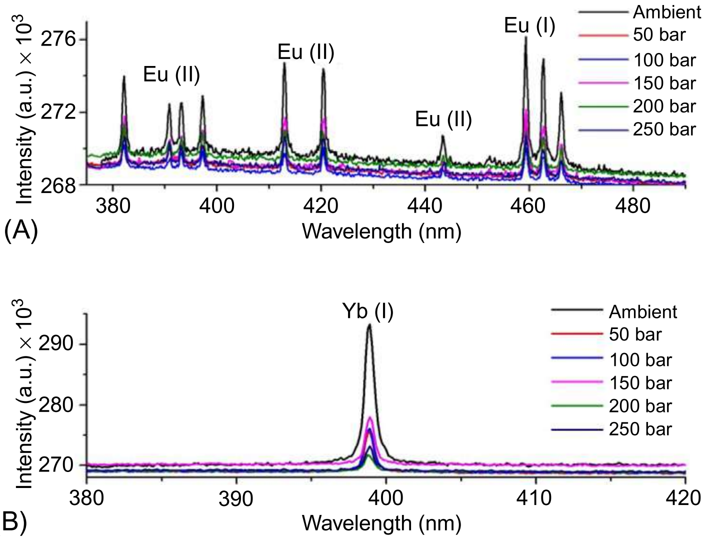


FIG. 9 Emission lines of Eu and Yb identified in the spectra obtained from (A) 4000-ppm Eu solution, (B) 4000-ppm Yb solution.

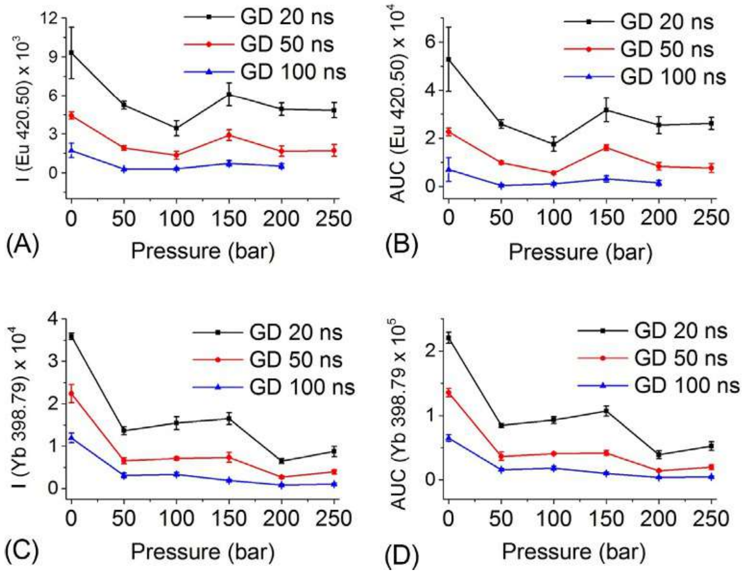


FIG. 10 Pressure effect on Eu and Yb emission. (A, C) Effect on intensity of emission lines and (B, D) effect on integrated intensity (AUC).

(which were not present at ambient conditions) were detected at higher pressures confirming the pressure-induced leaching of Ca ion from the carbonate by CO_2-enriched water. Increasing intensity of Ca emission lines with increase in pressure revealed the proportionate dissolution of $CaCO_3$ with applied CO_2 pressure. The amount of dissolved Ca at each pressure setting was quantified by generating calibration curves at the corresponding CO_2 pressure (Fig. 8). It is clear from Fig. 8 that the released amount of Ca increased up to 150 bar and then remained almost constant up to 350 bar.

Bhatt et al. [28] analyzed two rare earth elements (REEs), Eu and Yb, by underwater LIBS in a compressed gas–water mixture. LIBS spectra were recorded at six different pressure settings (ambient, 50, 100, 150, 200, 250 bar) from solutions of Eu and Yb and the detected emission lines are shown in Fig. 9. This study demonstrated the capability of LIBS to identify REE liquid sources present in high-pressure environments.

Effect of pressure and gate delays on the intensity and integrated intensity (area under curve) of Eu II 420.50-nm and Yb I 398.79-nm lines shown in Fig. 10. Intensity and integrated intensity of both elements declined with increase in gate delay. On the other hand, a steep decline in intensity and integrated intensity was observed in the beginning of CO_2 injection until the pressure reached 50 bar. No significant changes in both parameters were seen after 50 bar and the influence of pressure on the emission of Eu and Yb remained negligible up to 250 bar. The suppression of emission intensity in this study could be attributed to the confinement of laser-induced plasma by pressure in the beginning of CO_2 injection. Michel et al. [32] and Thornton et al. [9] also reported the weak effect of pressure on emission of Ca, Na, and Zn.

6 Conclusions

This chapter partially reviewed the applications of LIBS for the analysis of liquid samples. The technique could be used for in situ analysis and quantification of elements in both ambient and high-pressure conditions. Major challenges in underwater LIBS measurements and possible solutions to generate reliable data were discussed. Improvement in analytical performance could be achieved to some extent by using an appropriate experimental setup, proper gating parameters, excitation energy, and averaging the emission line intensity for several laser shots. LIBS signals in liquid media are generally weaker than in solids, therefore the signal enhancement techniques were briefly described. Lastly, matrix and pressure effects play a major role in underwater LIBS analysis that could bring challenges in quantitative analysis. Based on the recently published research, these effects were explained to improve the accuracy of analysis in liquids.

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