Laser-induced breakdown spectroscopy application in environmental monitoring of water quality: a review

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Abstract Water quality monitoring is a critical part of environmental management and protection, and to be able to qualitatively and quantitatively determine contamination and impurity levels in water is especially important. Compared to the currently available water quality monitoring methods and techniques, laser-induced breakdown spectroscopy (LIBS) has several advantages, including no need for sample pre-preparation, fast and easy operation, and chemical free during the process. Therefore, it is of great importance to understand the fundamentals of aqueous LIBS analysis and effectively apply this technique to environmental monitoring. This article reviews the research conducted on LIBS analysis for liquid samples, and the article content includes LIBS theory, history and applications, quantitative analysis of metallic species in liquids, LIBS signal enhancement methods and data processing, characteristics of plasma generated by laser in water, and the factors affecting accuracy of analysis results. Although there have been many research works focusing on aqueous LIBS analysis, detection limit and stability of this technique still need to be improved to satisfy the requirements of environmental monitoring standard. In addition, determination of nonmetallic species in liquid by LIBS is equally important and needs immediate attention from the community. This comprehensive review will assist the readers to better understand the aqueous LIBS technique and help to identify current research needs for environmental monitoring of water quality.

Abbreviations
LIBS   Laser-induced breakdown spectroscopy
LOD   Limit of determination
DP   Double pulse

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Introduction

Environmental monitoring of water quality is an important part of pollution warning, pollutant control, and effect evaluation. It has been widely used in managing and protecting natural water and also for wastewater treatment evaluation. Accordingly, we generally categorize water monitoring systems into the surface water monitoring and sewage outfall monitoring based on these two types of water source.

For water quality evaluation, the general focus is on the detection of the levels of total phosphorus, total nitrogen, heavy metals, chemical oxygen demand, total organic carbon, and permanganate salt presented in a water sample. Most of the current detection techniques are based on optical and mass spectroscopy measurements such as the atomic fluorescence spectrometry (Yuan et al. 2010), liquid chromatography (Zhao et al. 2011), UV-Vis spectrophotometry (Hosseini-Bandegharaei et al. 2013), infrared spectrophotometry (Qiu and Luo 2012), inductively coupled plasma mass spectrometry (Profrock and Prange 2012), graphite furnace atomic absorption spectrometry (Sun et al. 2012), and flame atomic absorption spectrometry (Gurkan and Yilmaz 2013). However, these methods require long detection cycle, and some of the methods need the use of specific chemicals which may cause secondary pollutions. In comparison, laser-induced breakdown spectroscopy (LIBS) can provide more versatile detection options, noncontact measurement mode, and in situ monitoring capability and is environmentally benign. Since LIBS requires no sample preparation, it can be used for all forms of samples: liquid, solid, or gas; the detection speed can be fast. LIBS has the potential to become an ideal analytic tool for monitoring water quality in real time. Yet, further understanding of laser interaction with liquid, plasma formation and sustainability, radiation emission, and signal quantification is needed. Also, operation conditions need to be optimized to improve and balance the detection sensitivity for different species. In the following text, we will review the existing research studies on LIBS for liquid samples.

LIBS technique

Principles of LIBS

LIBS is a spectral technique based on the detection and analysis of atomic emission. Once an aqueous sample is illuminated by high-power pulsed laser, local liquid will be ionized instantly upon absorbing the photon energy from the laser beam. A high-temperature and high-density plasma containing all elements presented in the solution will form. Upon plasma cooling, atomic emission spectra will be generated. By analyzing the wavelength and intensity of atomic emission, both qualitative and quantitative information of the species in the sample can be obtained. A typical LIBS system includes five

major components. These are the sample holder, laser source, optical path, spectrometer, and data analysis unit. As shown in Fig. 1, a high-power nanosecond or femtosecond pulse laser is often used as the excitation light source. The optical path controls the laser focusing on samples and also collects and guides the atomic emission to the spectrometer. The resolution and detection range of the spectrometer then directly determine the quantification capability of the entire system.

Development and application of LIBS

LIBS technique was first proposed (Brech and Cross 1962) at the 10th International Symposium on Spectroscopy. But, in the early years of LIBS development, its accuracy and reliability were no better than other conventional optical and mass spectroscopy technologies because of the limitation on lasers. Thus, people's interest did not re-emerge until 1980s, when laser performance was greatly improved and became readily available. In 1990s, commercialization of LIBS for engineering applications became common, and the number of LIBS-based instrumentations grew rapidly. LIBS now has become an irreplaceable analysis method and has been used extensively in many fields including online monitoring of industrial process (Gurell et al. 2012; Legnaioli et al. 2012; Werheit et al. 2011), archeological identification (Staicu et al. 2012; Kasem et al. 2011; Colao et al. 2010), environmental monitoring (Ayyalasomayajula et al. 2012; Dell'Aglio et al. 2011; Awan et al. 2013), geological exploration (Rakovsky et al. 2012; Pace et al. 2011; Lui and Koujelev 2011), national defense (Wang et al. 2012; Moros et al. 2012), and space exploration (McCanta et al. 2013; Wiens et al. 2013; Fabre et al. 2011).

LIBS for water quality monitoring

LIBS analysis in liquid

Liquid by its nature has significant amount of molecular and ion motions. When a liquid sample is illuminated by a beam of focused laser and absorbs light energy, there will be a local expansion. Unlike solid samples, liquid motions, shaking and splashing will result in change of laser focusing and instability in generated plasma. These effects will lead to unstable atomic emission and greatly affect LIBS detection capability. Actually, the

Fig. 1 The working process for LIBS
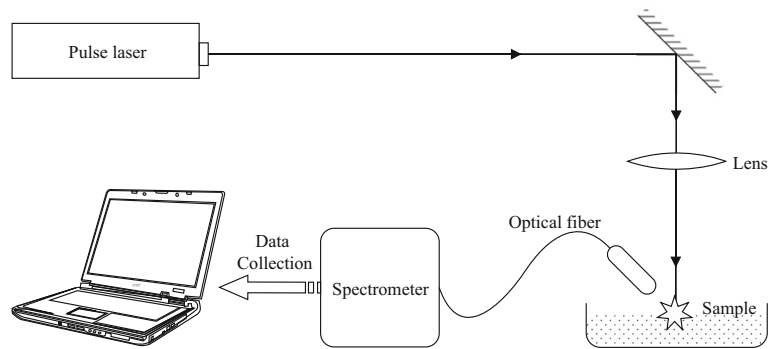
generation of sparks in liquid has been observed as early as 1909 (Konen and Finger 1909), but the use of such atomic emission for composition analysis has not been explored for a long time, and research on liquid LIBS started many years after LIBS technique was invented. The first application of LIBS on aqueous samples was for analyzing metallic elements in solution (Cremers et al. 1984). They used a 1,064-nm Nd:YAG laser as the exciting light source and were able to detect ten elements including Li, Na, K, Rb, Cs, Be, Mg, Ca, B, and Al in a water sample. In addition, a double-pulse LIBS (DP-LIBS) approach was introduced into liquid analysis in their work.

Compared to soil and air samples, quantitative determination of impurities in water samples is still challenging today. Most of the LIBS analyses and research in determining pollutant concentration in the water samples are still remained in laboratories. There is a great need of understanding and improving LIBS sensitivity and stability to apply it to real-time water quality monitoring.

LIBS analysis for metal elements in liquid

In recent liquid LIBS studies, most of the researchers focused on using this technique to detect metallic trace elements. A comprehensive list of journal publications and corresponding species studied in these research works are shown in Table 1. Generally, the metallic ions in water are grouped as the heavy metals and the alkali metals, with heavy metal concentration being one of the major indicators for water quality.

Heavy metals

In environmental monitoring, heavy metals are also referred as the toxic elements since they often cause

serious harms to human and other organisms. Heavy metals often presented in water include chromium (Cr), arsenic (As), mercury (Hg), cadmium (Cd), lead (Pb), and zinc (Zn). Rai et al. (2008a, b) evaluated the performance of LIBS on detecting Cr in water. The pulsed laser they used could provide a maximum energy of 425 mJ at 532 nm, with a pulse width of 4 ns. Limit of determination (LOD) for Cr was determined to be 1.1, 1.5, and 2.0 ppm in unitary, binary, and tertiary matrix, respectively. Using the same LIBS system, authors also detected the Cr concentrations in tannery wastewater from different industrial areas of Kanpur, India, where measured Cr concentrations were found to be higher than the safe drinking water limit of 0.05 ppm. Shi et al. (2012a) conducted both qualitative and quantitative analyses on trace metal Zn in water. A 1,064-nm Nd:YAG laser was used as the excitation source, and the laser energy and pulse width used were 165 mJ and 10 ns, respectively. Using the Zn 481.1-nm line for analysis, they determined that the optimum laser pulse delay is 1,100 ns in achieving the lowest LOD of 4.108 mg/L.

A large percentage of LIBS research investigated more than one element presented in a water sample (Ilyin and Golik 2013; Sobral et al. 2012; Golik et al. 2012; Wu et al. 2008; Charfi and Harith 2002; Fichet et al. 2001; Samek et al. 2000), and there are studies comparing the same sample in both liquid and solid ice states. Using the respective Hg, Cd, Pb lines located at 253.65, 214.44, and 405.78 nm, Sobral et al. (2012) compared the detection sensitivity of these elements in water and ice using LIBS. LODs of the three elements in water were determined to be 21.4, 7.1, and 12.5 mg/L; in comparison, LODs in ice were 3.7, 1.4, and 1.3 mg/L, respectively. This provides direct evidence that LIBS detection for liquid is more difficult than that for solid samples.

Table 1 LIBS analysis for metallic elements in liquid

LOD of analysis elements	References
Ca 0.01 mg/L, Mg 1 mg/L, Na 0.0009 mg/L, Al 0.19 mg/L, Zn 2.5 mg/L, K 0.006 mg/L	Ilyin and Golik (2013)
Cu 7.37 mg/L	Li et al. (2013)
Cu 9.6 mg/L, Mg 0.9 mg/L, Pb 12.5 mg/L, Hg 21.4 mg/L, Cd 7.1 mg/L, Cr 10.5 mg/L, Fe 10.5 mg/L	Sobral et al. (2012)
Al 0.19 mg/L, Ba 0.08 mg/L, Ca 0.01 mg/L, Cu 0.78 mg/L, Fe 3.4 mg/L, K0.006 mg/L, Mg 1 mg/L, Na 0.0009 mg/L, Zn 2.5 mg/L	Golik et al. (2012)
Zn 4.108 mg/L	Shi et al. (2012a)
Cu 23 ppm	Fu et al. (2008)
Cr 1.1–2.0 ppm	Rai et al. (2008a)
Cu 31 ppm, Pb 50 ppm	Wu et al. (2008)
Na 2 μg/mL, Mg 1 μg/mL	Charfi and Harith (2002)
Pb 100 μg/mL, Si 25 μg/mL, Ca 0.3 μg/mL, Na 0.5 μg/mL, Zn 120 μg/mL, Sn 100 μg/mL, Al 10 μg/mL, Cu 7 μg/mL, Ni 20 μg/mL, Fe 30 μg/mL, Mg 1 μg/mL, Cr 0.4 μg/mL	Fichet et al. (2001)
Al 18 mg/L, Cr 200 mg/L, Cu 5 mg/L, Pb 40 mg/L, Tc 25 mg/L, U 450 mg/L, Na 0.08 mg/L, Mn 10 mg/L, Mg 3 mg/L, Li 0.009 mg/L, K 4 mg/L, Ca 0.6 mg/L	Samek et al. (2000)

Alkali metal

Alkali metals have much smaller atomic weight than the typical heavy metals and require much lower atomic excitation energy. For Na and K, they are 2.1 and 1.62 eV, respectively. In other words, electrons in alkali atoms can be more easily excited and will have stronger atomic emissions. Indeed, Na and K LIBS signal can be detected at very low ion concentration. This phenomenon has been reported by Golik et al. (2012).

As will be discussed later, laser characteristic is a critical factor affecting LIBS results since it determines the light and matter interaction and excitation. Improvement in the LIBS method is directly related to the advancement in laser technology. Ilyin and Golik (2013) reported the LIBS study on seawater using a femtosecond laser. The excitation source is a Ti:sapphire laser system with a 800-nm wavelength and a 42-fs pulse width. They identified characteristic spectrum lines of Ca, Mg, Na, Al, Zn and further confirmed that the LODs of Na and K were at least 1–2 order of magnitude lower than other elements.

Methods to enhance LIBS signal in liquid

LIBS signal of liquid samples is relatively weak and unstable. This will affect the sensitivity, accuracy, and stability of quantitative measurements of sample chemical composition. Also, the concentration of pollutants in water samples is usually low, and we want to achieve as low as possible LOD. How to enhance LIBS signal from liquid has been a hot topic among researchers. At the moment, there are two types of commonly adopted approaches. One type of methods is to pretreat the aqueous sample before measurement, and the other is using a double-pulse excitation scheme. Sometimes, these two methods are combined for further enhancement.

Pretreatment of aqueous samples

There are several ways to pretreat liquid samples to improve LIBS signal strength and stability. First is to concentrate the impurities from original sample; adsorption is the most common approach. Materials such as filter paper, graphite, metal electrode, ion exchange membrane, bamboo, and wood chip have been explored to not only increase impurity concentration but also transform liquid samples to solid. Second approach is to change the bulk liquid sample into mist using a nebulizer or create a fluid jet stream. Both treatments can reduce the instability of the laser illumination region to generate more stable signal. The third treatment approach is to directly turn liquid into solid. Table 2 summarizes the LIBS study using pretreatment for liquid samples.

Table 2 LIBS analysis for aqueous samples with pretreatment

Pretreatment of samples	LOD of analysis elements	References
Filter paper	Cu 1.5 μg/mL	Zheng et al. (2013)
	Pb 75 ppb, Cr 18 ppb	Lee et al. (2012)
	Cr 230 mg/L, Cd 46 mg/L	Bukhari et al. (2012)
	Ca 1.9 μg/mL, Mg 3.2 μg/mL	Zhu et al. (2011)
	Sm 1.3 ppmw, Eu 1.9 ppmw, Gd 2.3 ppmw	Alamelu et al. (2008)
	Th 0.72 ppmw, U 18.5 ppmw	Sarkar et al. (2008)
Graphite	Cr 0.520 mg/L	Wang et al. (2013b)
	Ni 0.28 mg/L	Shi et al. (2012b)
	Pb 0.0665 mg/L	Wang et al. (2011)
	B 0.01 μg/g	Sarkar et al. (2010)
Electrode	Cr 0.317 μg/L, Mn 0.176 μg/L, Cu 0.162 μg/L, Zn1.35 μg/L, Cd 0.787 μg/L, Pb 0.57 μg/L	Zhao et al. (2010)
	Cr 0.25 μg/L	Xiong et al. (2010)
Ion membrane	Cu LOD can reach mg/L level.	Kim et al. (2010)
	Ba 0.13 μg/mL, Cd 0.21 μg/mL, Cr 0.13 μg/mL, Co 0.0042 μg/mL, Cu 0.0095 μg/mL, Ag 0.43 μg/mL, Pb 1.1 μg/mL, Hg 2 μg/mL, Ni 0.31 μg/mL, Zn 0.85 μg/mL	Schmidt and Goode (2002)
Wood and bamboo	Pb 8.5 mg/mL	Zhu et al. (2012)
	Cd 55 μg/L	Jiang et al. (2011)
	Pb 30 ppb	Chen et al. (2010)
Ultrasonic nebulization	Na 0.45 mg/L, K 6.01 mg/L, Mg 1.85 mg/L, Ca 1.83 mg/L, Cu 1.99 mg/L, Al 6.47 mg/L, Cr 6.49 mg/L, Cd 43.99 mg/L, Pb 13.6 mg/L, Zn 41.64 mg/L	Aras et al. (2012)
	Mg 0.242 ppm	Zhong et al. (2011)
Jet flowing	B 0.8 ppm, Li 0.8 ppb	Lee et al. (2011)
	Pb 4 ppm, Cd 68 ppm	Cheri and Tavassoli (2011)
	Pb 60 ppm	Feng et al. (2010)
	Mg 0.1 ppm, Cr 0.4 ppm, Mn 0.7 ppm, Re 8 ppm	Yueh et al. (2002)
Freezing	LOD can reach ppm level.	Al-Adel et al. (2013)
	Na 2 ppm, Al 1 ppm	Caceres et al. (2001)

Reports on using the filter paper enrichment method can be traced back to 2008. Alamelu et al. (2008) and Sarkar et al. (2008) used the method to detect lanthanide series and actinium series metal elements in liquid. Then, similar approaches were used to analyze heavy metals, alkali metals, and other metals by other groups (Zheng et al. 2013; Lee et al. 2012; Bukhari et al. 2012; Zhu et al. 2011). In the graphite enrichment method (Wang et al. 2011, 2013a, b; Shi et al. 2012b; Sarkar et al. 2010), sampling liquid was dropped onto the surface of a high-purity graphite (99.99 %) substrate, and after solvent (normally water) evaporation, impurity salts precipitated out on the graphite surface as solids for

LIBS analysis. Impurity enrichment can also be realized electrochemically (Zhao et al. 2010; Xiong et al. 2010) for certain species; the normal practice is to use a high-purity inert electrode and apply a DC voltage to reduce or oxidize the ionic species in water to form a solid layer. Other impurity enrichment methods include using ion exchange membranes as reported by Schmidt and Goode (2002) and by Kim et al. (2010) for Cu detection. Wood and bamboo have also been used as substrates; Zhu et al. (2012), Jiang et al. (2011), and Chen et al. (2010) pretreated the aqueous samples by immersing wood or bamboo chips in liquids followed by drying. In these enrichment approaches, researchers seek to

overcome the low sensitivity and poor stability challenges of liquid samples by increasing chemical concentration and in most of the cases also eliminate the solvent to obtain solid phase sample.

Another route to enhance LIBS signal is not to change the impurity concentration but to generate a more stable samples and thus more stable signals. Zhong et al. (2011) demonstrated the use of an ultrasonic nebulizer to disperse liquid into small droplets in the air and then detected LIBS of the liquid mist. The measured LOD for Mg can be as low as 0.242 ppm. The same technology was used by Aras et al. (2012) to detect Na, K, Mg, Ca, Cu, Al, Cr, Cd, Pb, and Zn. Jet flowing method (Lee et al. 2011; Cheri and Tavassoli 2011; Feng et al. 2010; Yueh et al. 2002) is another simple but effective method; instead of directly focusing the laser inside a bulk liquid sample, the liquid is allowed to flow as a continuous thin jet stream, and the laser can be focused on the water column to generate more effective and stable plasma. The liquid jet stream can be controlled by using a water pump.

As been mentioned earlier, Sobral et al. (2012) showed that ice sample could provide better LIBS signals due to the formation of solids. Freezing is another commonly used liquid pretreatment technique in LIBS. Caceres et al. (2001) reported on a fast freezing method for quantitative LIBS analysis of trace metals in liquid. Al-Adel et al. (2013) used the same approach to detect metal elements with LODs reaching ppm level in water. It is shown that liquid nitrogen is an effect media for rapid water freezing and LIBS analysis should be completed before ice melted.

Double-pulse LIBS

In addition to pretreat the liquid samples, we can manipulate the excitation laser light to enhance LIBS signal. An effective approach is to use the so-called double-pulse (DP) method. Instead of using single pulse generated from one laser, we can use well-timed two laser pulses to improve LIBS signal intensity. This DP-LIBS approach was firstly applied to bulk liquid analysis by Cremers et al. (1984). This work is the first to show detection sensitivity enhancement of metallic elements in a solution by using DP excitation. It was demonstrated that optical dielectric breakdown in liquid caused by the first laser pulse generated a gaseous cavity containing molecules and atoms from the solution. This gaseous cavity could maintain for several hundred

microseconds with high temperature. During this process, if a second pulsed laser light arrived, the existed cavity would be further excited to generate much enhanced emission. This study has since stimulated many other researchers to study aqueous systems using DP-LIBS. Table 3 lists the related published in recent years.

DP-LIBS can be realized by using either one (Lazic et al. 2007; De Giacomo et al. 2005; Koch et al. 2005) or two (Rifai et al. 2012; Rai et al. 2008b; Kumar et al. 2003; Pearman et al. 2003; Pu and Cheung 2003) laser sources. Using one laser source has the advantages of low cost, simple beam path, and more convenient beam steering and focusing, but the pulses cannot be tuned separately as the wavelength and pulse energy are fixed. In comparison, if the two pulses are generated by two separate lasers, then the pulse energy and wavelength can be tuned independently. For example, Rifai et al. (2012) and Pu and Cheung (2003) used a UV-IR laser combination to increase the signal intensity of LIBS. It is found that the UV light is more suitable for initial liquid sample excitation due to its higher absorption coefficient from water, but longer wavelength light is more efficient in the further excitation of plasma because the plasma heating rate goes up as square of wavelength. Using a two-laser setup, the optical paths of the two laser beams can have one of the following three configurations, namely, the coaxial DP lasers (Rai et al. 2008b; Kumar et al. 2003), orthogonal DP lasers (Pearman et al. 2003), and oblique crossing DP lasers (Rifai et al. 2012; Pu and Cheung 2003), as shown in Fig. 2. In the coaxial DP laser configuration (a), two beams propagate along the same path. In the orthogonal configuration (b), the two pulse laser beams are perpendicular to each other. And, for the oblique crossing configuration (c), the two pulse laser beams form a certain angle.

In the case of DP-LIBS, interval time between two pulses is a key parameter, which strongly affects the signal-noise ratio and intensity of the spectra lines. As is known, the initial plasma plume produced by the first pulse has a lifetime for expansion and cooling. In order to obtain maximum enhancement, the second pulse should be triggered at an appropriate time to re-excite the plasma, and the interval time between two pulses should be controlled and optimized by using a delay generator. For instance, Rai et al. (2008) found that the maximum enhancement in emission occurred by a 2–3-μs time delay between lasers in their work. This indicated that during that time, plasma plume induced

Table 3 Study of liquid samples with DP-LIBS

Configuration of Lasers	LOD of analysis elements	References
1st pulse: Nd:YAG laser@266 nm, 7 ns, 32 mJ 2nd pulse: Nd:YAG laser@1, 064 nm, 7 ns, 140–250 mJ	Fe 8 ppm Pb 6 ppm Au 13.5 ppm	Rifai et al. (2012)
1st pulse: Nd:YAG laser@532 nm, 5 ns, 300 mJ, p-polarized 2nd pulse: Nd:YAG laser@532 nm, 5 ns, 300 mJ, s-polarized	Cr 120 ppb	Rai et al. (2008b)
1st pulse and 2nd pulse were generated by a single Nd:YAG laser@1, 064 nm, 10 Hz, 300 mJ	Mg 0.034 ppm Mn 0.38 ppm Cr 0.92 ppm	Lazic et al. (2007)
1st pulse and 2nd pulse were generated by a single Nd:YAG laser@1, 064 nm, 10 Hz, 100 mJ	Mg 1.4 ppm Na 0.4 ppm	De Giacomo et al. (2005)
1st pulse and 2nd pulse were generated by a single Nd:YAG laser@532 nm, 6 ns, 5 Hz	Mg 80 µg/L	Koch et al. (2005)
1st pulse: Nd:YAG laser@532 nm, 8 ns, 10 Hz, 130 mJ 2nd pulse: Nd:YAG laser Surelite III, 160 mJ	Mg 0.06 ppm	Kumar et al. (2003)
1st pulse: Nd:YAG lasers Continuum Surelite III@1,064 nm, 5Hz 2nd pulse: Nd:YAG lasers Quantel Nd 580@1,064 nm, 5Hz	Ca 41.7 ppb Cr 1.04 ppm Zn 17 ppm	Pearman et al. (2003)
1st pulse: ArF laser@193 nm, 15 ns, 5 Hz, 18 mJ 2nd pulse: Nd : YAG laser@1,064 nm, 6 ns, 56 mJ	Pb 136 ppb	Pu and Cheung (2003)

by the first laser pulse reached the best conditions for absorption of the second laser pulse. Rifai et al. (2012) observed that the SNR reached a maximum value for a time delay in the 2–4-ms range.

Data processing and quantification

Data processing

A large number of data will be generated during the LIBS analysis, and the data are always accompanied by noises which affect the accuracy of analysis result. Therefore, using the appropriate data processing methods to reduce spectra noise is very desirable, especially for liquid samples. Recently, Schlenke et al. (2012) and Zhang et al. (2013a) carried out theoretical studies on LIBS data's de-noising using wavelet theory. They have shown significant improvements for LOD and signal-to-noise ratio after data processing.

In addition to data de-noising, automatic identification of spectral characteristics and distinguishing overlapped spectrum peaks are also useful in LIBS detection. Liu et al. (2011) studied the algorithm for automatic recognition of spectral characteristics of LIBS spectra, and they (Liu et al. 2012) also proposed a variable sliding window method. At the same time, Hu et al. (2012) have tried to develop Labview based program to realize automatic recognition of LIBS spectrum. Zhang et al. (2013b) proposed a method based on curve fitting to separate overlapping peaks. In that study, a Levenberg-Marquardt method was introduced. Both the simulation and LIBS experimental results showed that the mathematical methods used in their research could effectively solve the problem of peak overlap in LIBS data.

Quantitative methods

As all other scientific measurements, quantification is always important. Ideal LIBS analysis should provide

Fig. 2 Lasers path of DP-LIBS **a** coaxial double-pulse lasers, **b** orthogonal double-pulse lasers, and **c** oblique crossing double-pulse lasers
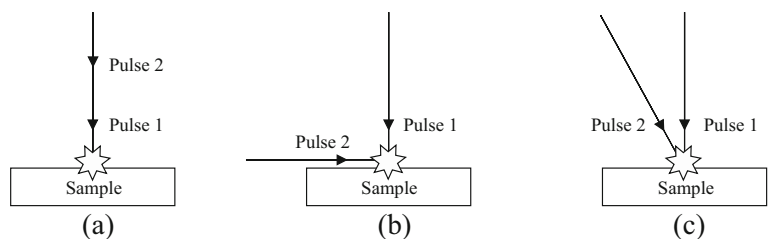
high sensitivity, accuracy, and reliability in determining all species concentration in water. Traditionally, there are two common methods for quantitative LIBS analysis. One is the standard calibration method (Huang et al. 2013) where a standard sample with known composition and corresponding spectral information is used to establish a reference function between sample concentration and measured signal strength. Then, the concentration of unknown samples can be calculated based on the calibrated reference model. The other calibration-free method (Pedarnig et al. 2013) is derived based on the analysis of all elements contained in samples. During the process, each element's information has to be collected for percentage derivation using normalized algorithm.

More recently, Wang et al. (2013a) proposed new quantitative methods by establishing inversion algorithm for LIBS. Three different approaches including the multiple linear regression, neural network regression, and support vector machine regression were used for correlation establishment and comparison. Ni in water was used as a reference in this research. It is found that the average relative standard deviation determined by using multiple linear regression, neural network regression, and support vector machine regression were 7.60, 4.86, and 2.35 %, respectively, with the maximum relative standard deviation of 23.35, 15.20, and 8.29 %. The average relative errors were 25.98, 10.58, and 2.72 %, and the maximum relative errors were 116.47, 47.38, and 9.89 %, respectively. This study has provided new data processing schemes and references for further implementation of rapid quantitative analysis using LIBS.

Research on characteristics of plasma in liquid

Formation mechanism and characteristics of laser-induced plasma have always caught researchers' attention. For the same reason mentioned previously, research on characteristics of laser-induced plasma generated in solid and gaseous samples started much earlier than the plasma in liquids. For the liquid phase plasma studies, people have been focused on two main areas: the time-dependent plasma evolution characteristics and plasma electron density and temperature characteristics.

Time-dependent plasma evolution characteristics

Electromagnetic wave from the pulsed laser beam will have strong interactions with molecules, atoms, and ions in the sample. When the interaction is strong enough, plasma will form. Since pulsed laser is used, this excitation is not continuous, and plasma will attenuate in short period of time due to fast energy dissipation. In the initial plasma excitation process, continuous optical emission with strong background can be observed. As time goes on, the continuous background signal attenuates, and sharp atomic spectral lines become significant. Therefore, based on understanding of plasma time-dependent evolution, the signal-to-noise ratio of characteristic lines can be improved by adjusting the spectrum acquisition time. Sarpe-Tudoran et al. (2006) used instantaneous imaging technology and reflection spectra analysis to study the time evolution properties of plasma produced underwater by femtosecond laser in details. A 20-ps delay has been observed before plasma expansion. The initial plasma expansion speed was determined to be 5,900 m/s, and the plasma attenuation rate was $1.6 \times 10^{-9} \pm 0.3 \times 10^{-9}$ cm^3/s.

Electron density and temperature characteristics

Electron density and temperature characteristics are two of the most important physical parameters describing plasma properties. Through the analysis of plasma's electron density and temperature, evolution of plasma can be better understood. The electron density and plasma temperature in a $CuCl_2$ solution excited by LIBS process were investigated by Luo et al. (2012). An electron temperature of 1,850 K with an electron density of 5.8×10^{16} ea/cm^3 was measured. The experiment also indicated that the plasma induced by laser in liquid could satisfy the local thermodynamic equilibrium. Subsequently, Hu et al. (2013) used a combined liquid jet and DP-LIBS technique to study the plasma's electron density and temperature in calcium chloride solution and found that they were 10^{17} ea/cm^3 and 10^4 K, respectively. The variations of plasma temperature and electron density with delay time and the time between two pulses were discussed based on experimental results.

Factors affecting liquid LIBS analysis

LIBS signal is affected by the exciting laser properties, such as the source wavelength, energy density, and spot size. Li et al. (2012) reported on how the wavelength of the excitation light affected the measurement results on Ca concentration in solution. It was also found that the

lifetime of plasma was around 1,200 and 600 ns when the laser wavelength was 1,064 and 532 nm, respectively. In order to get the best analysis results, relationship between excitation laser energy and plasma to detector distance was established based on transmission characteristics of light in water. It was noted that when the detection distance was less than 5 cm, laser energy could be kept below 100 mJ for the 1,064-nm light source, and if the detection distance increased to 10 cm, the 532-nm laser at 30-mJ energy level will provide best results. Golik et al. (2013) studied the relationship between the spectral line intensity of Ca, Hα, and the laser spot size in solution. It was found that when the laser spot diameter was enlarged from 7 to 14 mm, the spectral line intensity of both elements increased, by 3 and 20 times, respectively. But, only these two laser beam spot size results were reported, and no correlations were established for other spot sizes.

Besides the properties of laser source, pressure generated in water also affects LIBS signal. Sukovich et al. (2011) studied the relationship between the underwater pressure and the plasma generation threshold energy for LIBS. They investigated it over a range of pressures from 0 to 1,380 bar underwater. Plasma was formed by using a 12-mJ Nd:YAG laser, with the wavelength of 532 nm. From the result, they found that the threshold energy value increased with pressure. This study provided useful information on the application of LIBS technique in the deep water.

Conclusions

In summary, there are a number of research works studying the application of LIBS for determining liquid composition, and this technique is very valuable for water quality monitoring. Yet, due to liquid intrinsic instability and complicated interactions with light, most of these studies are still limited at the laboratory stage. Liquid LIBS signal is affected by instrumentation properties, sample status, and also data collection and processing methods. Although the demonstration of LIBS capability of detecting various elements in water is well documented, detection limit, signal-concentration correlation is not well established. Furthermore, most of existing study investigated metal species in water, and there lacks studies on nonmetallic chemicals such as nitrogen and phosphorus, which are arguably the more important pollutants in water. Therefore, there is critical

need to further study the mechanism of liquid LIBS, improving instrumentation, optimizing data analysis process, and developing liquid LIBS system.

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