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Industrial Applications of Laser-Induced Breakdown Spectroscopy

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is an analytical detection technique based on atomic emission spectroscopy to measure elemental composition. With the development of lasers and detection systems, applications of LIBS encompass a broad range, including physics, engineering, space missions, environment, etc. due to the unique features of little or no sample preparation, noncontact, fast response, and multielemental analysis. The fundamental and application have been extensively studied to improve LIBS technique. This chapter largely targets the engineering fields, especially practical applications. Laser-induced breakdown spectroscopy will be discussed in this chapter including its fundamentals, industrial applications, and challenges.

Keywords: Laser-induced breakdown spectroscopy (LIBS), Industrial applications, Challenge

1. Introduction

Laser-induced plasma was introduced as a spectroscopic emission source only two years after the invention of laser. LIBS is the acronym of “laser-induced breakdown spectroscopy”, and it is also called LIPS (laser-induced plasma spectroscopy), laser spark spectroscopy (LSS), and other related names [1]. LIBS is an analytical detection technique based on atomic emission spectroscopy to measure elemental composition. A laser pulse focuses in or on a sample, which can be gas, liquid, aerosol, or solid, to form the micro-plasma. The spectra emitted are used to determine the elemental constituents of measured samples.

1.1. Theory

The initiation, formation, and decay of the plasma are complex physical and chemical processes. In the LIBS process, a laser beam is focused on a small area of the sample. When the laser energy exceeds the breakdown threshold, the plasma with high temperature and high density is produced in the portion. The core of plasma is firstly produced by the absorption of the incident laser energy, such as multiphoton ionization. The creation of the plasma core induces the rapid growth of plasma through the absorption of the laser light by electrons and the electron impact ionization process in it. After the termination of the laser pulse, the plasma continues expanding because of its high temperature and pressure gradients compared with the ambient conditions. At the same time, the recombination of electrons and ions proceeds due to the collision process and the temperature decreases gradually compared with that in the plasma generation process. Emission signals arise in the plasma cooling period [2]. In the plasma, the ions, atoms, and molecules distributed in the different levels transit from the high energy level to the low energy level, emitting the strong emission spectra. The emission intensity from the atomized species provides the elemental compositions of the materials. The light corresponding to a unique wavelength of each element is emitted from excited atoms in plasma, as shown in Figure 1.

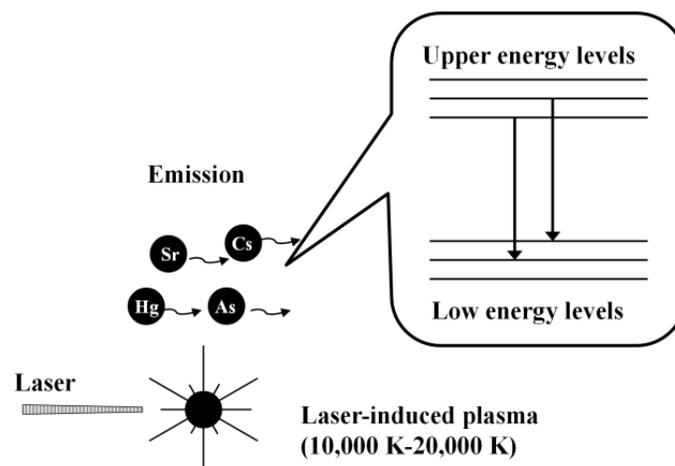


Figure 1. Laser-induced plasma processes

A calibration of the LIBS signal is necessary for quantitative analysis. Despite the fact that the LIBS processes involved are complex, the emission intensity from the atomized species can be described by the following equation with the assumption of uniform plasma temperature [2]:

$$I_i = n_i K_{i,j} g_{i,j} \exp\left(-\frac{E_{i,j}}{kT}\right) \quad (1)$$

where I_i is the emission intensity of species i , n_i is the concentration of species i , $K_{i,j}$ is a variable that includes the Einstein A coefficient from the upper energy level j , $g_{i,j}$ is the statistical weight

of species i at the upper energy level j , E_{ij} is the upper-level energy of species i , k is the Boltzmann constant, and T is the plasma temperature. Equation (1) is applicable under the conditions of local thermodynamic equilibrium (LTE). In Eq. (1), there are several factors that affect the emission intensity I_i , including plasma temperature, plasma nonuniformity, matrix effects, etc. It is very difficult to solve the LIBS process theoretically because it contains laser-material interactions, rapid temperature changes over 10,000 K in a nanosecond or picosecond timescale, and plasma cooling phenomena including the recombination process of ions, electrons, and neutrals. Therefore, the appropriate correction factors must be contained in K_{ij} to obtain the quantitative results.

The factors that affect the target signal in LIBS process generally include the background noise, stability of plasma, nonuniformity of plasma, matrix effects, dirt on measurement windows, etc. The main background noise of LIBS is the continuum emission from plasma itself. Atomic emissions appear after a certain time delay, which means that LIBS signals appear during the plasma cooling process. Therefore, it is important to choose the appropriate delay time and gate width to reduce the effect of the background noise. The fluctuation of plasma signal is an intrinsic characteristic in LIBS. Use of the intensity ratio and plasma temperature correction can reduce the fluctuation to some extent. The laser-induced plasma has its structure in it. In the plasma generation process, the plasma structure depends largely on the laser density pattern and measured material conditions. The LIBS signal depends on the measurement area across the plasma. In this sense, the correction method also includes the effects of plasma nonuniformity. Matrix effects are the combined effects of all components other than the measured species. The changes of these components may cause the alteration of LIBS signal intensity even if the number density of the measured species is the same in the measurement period. Matrix effects are usually corrected by the experimental calibrations. The attenuation of LIBS signals by the contamination of measurement windows is automatically neglected because the signal intensity ratio is usually used for the elemental composition analyses. Considering the measurement stability and soundness of windows, however, the cleanliness of measurement windows should be maintained, especially in the practical applications.

1.2. Geometric arrangement and measurement species

The LIBS apparatus fundamentally consists of laser, measured materials, lens, spectrometer, ICCD camera, and related devices. A typical geometric arrangement of LIBS is shown in Figure 2. Lasers such as a pulsed Nd:YAG laser are used as a light source. The output laser beam is focused onto the measurement area using the focal lens to induce the plasma. The plasma emission is focused onto the optical fiber. Emission signals are finally detected by the combination of a spectrometer, an ICCD camera, and auxiliary equipment. According to the measured materials of solid, liquid, and gas phases, different measurement chamber or platform can be employed. It is worth noting that the reflection of a laser light from the windows must be considered carefully. Its reflection often results in the damages of optics due to the high-energy laser light. The reflection from plasma is sometimes tricky and malicious for LIBS systems. Damages of optics by the reflection from plasma cause troubles in some cases, especially in the analyses of liquids.

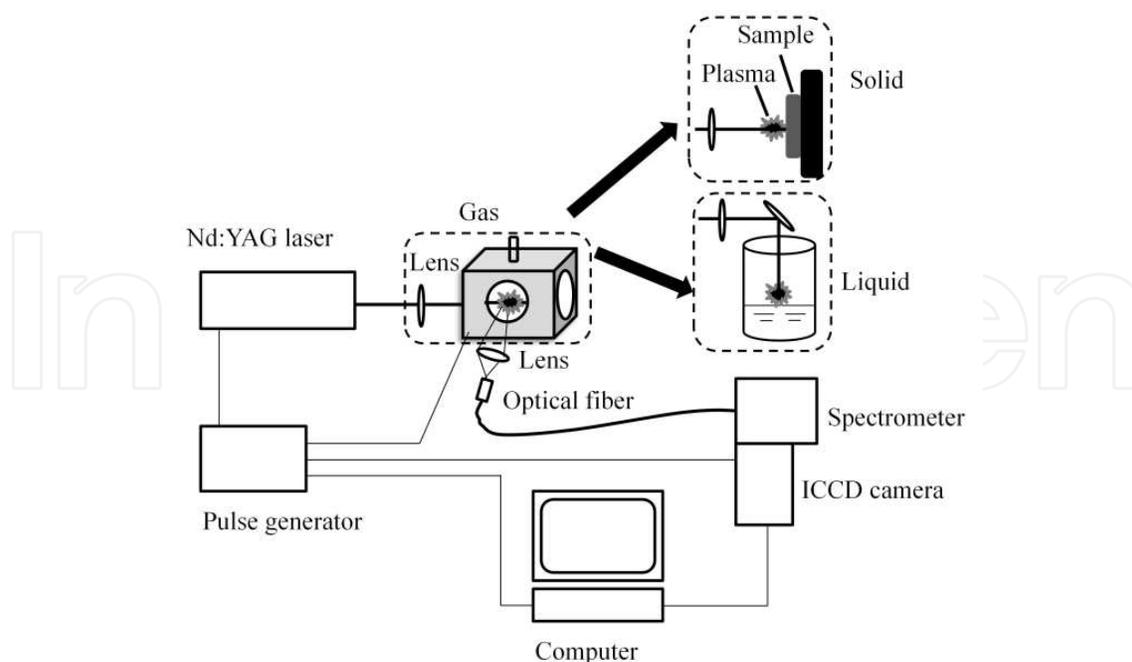


Figure 2. Typical geometric arrangement of LIBS

The basic components of LIBS system are similar but the component specifications are tailored to the particular applications. These specifications include the equipment types, physical parameters, and the technical specifications belonging to operational performance.

2. Fundamentals

Since it is the basis of successful application of LIBS technology, the fundamental study is of great importance. With the development of LIBS, the mechanism of laser–material interaction, plasma generation, plasma–environment interaction, self-absorption effect, signal enhancement, and some other fundamental research have been studied extensively to promote LIBS technique [3-7]. Various quantitative analytical methods have also been studied and improved, such as traditional calibration method, internal calibration method, calibration-free method, partial least squares (PLS) method, etc.

2.1. Plasma and its models

Plasma is a local assembly of atoms, ions, and free electrons, overall electrically neutral. Plasma is characterized by a variety of parameters. The degree of ionization is the most basic parameter. The ratio of electrons to other species is less than 10% in the plasma, called weakly ionized plasma. On the other hand, highly ionized plasma may have atoms stripped of many of their electrons, resulting in very high electron to atom or ion ratios. The plasma produced in LIBS typically belongs to the category of weakly ionized plasma. The goal of LIBS technique is to

create the optically thin plasma, which is in local thermodynamic equilibrium and whose elemental composition is the same as that of the sample.

The LIBS plasma features inhomogeneities that can lead to spatial differentiation. This fact is important in choosing the temporal window in order to accumulate spectroscopic data. The spatial and temporal evolution of LIBS plasma from a steel target was monitored using time of flight and shadowgraph techniques [8]. Two regions in the plume were observed, one characterized by air and continuum emissions produced by shock wave ionization, and the other one by emissions from ablated material. The sufficiently high laser fluence and acquisition delay time are necessary to assure the homogeneity for the analytical applications. The homogeneity of LIBS plasma was investigated using the curve of growth method employing five Fe(I) lines [9]. In that formalism, the line shapes as a function of temperature and concentration were modeled. The agreement between modeled and experimental line shapes implied that the Stark effect was the dominant broadening mechanism in the plasma. The temperatures obtained from neutral and ion spectral lines were studied [10]. The different temperatures studied can be obtained from Boltzmann and Saha plots. The difference was explained by the spatial variation of the plasma temperature and densities leading to a difference in spatial locus for populations in the upper levels of transitions for neutrals and ions.

Plasma models are becoming more comprehensive and detailed. A radiative model of LIBS plasma expanding into a vacuum was validated by the experiments [11]. The inverse problem was specifically addressed, which means finding the initial conditions by the comparison of the calculated synthetic spectra and the experimentally measured ones. The composition of the material was effectively deduced from the calculated spectra. The plasma was considered to be characterized by a single temperature and electron density. The combination of the original modeling work on laser-evaporated plasma plume expansion into a vacuum and ablation leading to vaporization and particle formation was studied [12]. The interaction of a nanosecond pulse with a copper target was modeled in vacuum. Some of the parameters were studied including the melting and evaporation of the target, the plume expansion and plasma formation, the ionization degree and density profiles of neutral; once-ionized; and doubly ionized copper and electrons, and the resultant plasma shielding.

2.2. LIBS detection ability

Most fundamental studies focused on signal enhancement to improve the detection limit. The measured results showed that the spatial confinement and fast discharge would be able to enhance the signal from several times to dozens of times, while dual pulse is able to enhance signal 100–1000 times [13–15]. Besides signal enhancement, there were also some other studies worth mentioning. The self-absorption in laser-induced plasma was studied. The results suggested that the self-absorption effect could be alleviated by the selection of suitable atomic line, operating at higher pulse energy and detecting with longer delay [16]. The pressure effect on the plasma emission from fundamental 0.1 to 40 MPa in bulk seawater was investigated [17]. The time-resolved LIBS emission results demonstrated that plasma emission is weakly dependent on the ambient pressure during the early stage of plasma and the pressure has a significant influence on the plasma form during plasma evaluation at a later stage of plasma.

The detection ability of trace species using LIBS has been improved with the development of LIBS devices. The utilization of short pulse laser for plasma generation has been extensively studied [18,19]. Short pulse irradiation allowed for a specificity of excitation that could yield LIBS signals more tightly correlated to particular chemical species and showed significantly lower background emission. A new method to control the LIBS plasma generation process is necessary for the enhancement of detection limit, i.e., low pressure and short pulse LIBS [20-22]. Because of the pressure, volatility, and quenching effects of liquid, the plasma lifetime of liquid sample is shorter compared with that of solid and gas phases. Meanwhile, sputtering of liquid sample by LIBS plasma often raises the problem of the measurement windows. The sensitivity, stability, and repeatability of LIBS signal are much lower, leading to the increasing difficulty of its analyses. Numerous papers have reported LIBS measurement of different forms of liquid phase materials including the solidification, liquid bulk, liquid surface, and others [23-28], which shows different detection features and detection limit.

2.3. Quantitative analysis

The ultimate goal of LIBS technique is to provide a quantitative analysis with high precision and accuracy. Usually, a quantitative analysis begins with determining the response of a system for a given concentration or mass of the analyte of interest, which usually takes the form of a calibration curve. The calibration is usually strongly dependent on the analysis conditions, such as the stability of the laser pulse energy, the sample and sampling procedure, the physical and chemical properties of the sample, etc. The dependence of elemental signals of LIBS on the plasma temperature attributes to a very complex process in plasma. Several studies have reported the LTE condition of plasma in several types of plasmas [29]. The plasma temperature is a very important factor for the quantification of the LIBS measurement. There are several calibration methods to analyze the measured species quantitatively, including the traditional calibration method, internal calibration method, calibration-free method, etc. [30,31].

As for the simple samples, the emission intensity of the measured species is linear with the species content under the ideal condition. The traditional calibration model is relatively simple and convenient. However, the influences of matrix effect and element interference are not considered in the model. The accuracy becomes worse when the complex samples are measured or the experimental parameters fluctuate. The internal calibration method is a commonly used spectral analysis model with strict conditions. The elements with the features of high content, low detection limit, and good stability are mainly selected as the internal calibration elements. Usually, the compositions of the calibration sample and measured sample are not entirely consistent. When the measured samples contain various elements, the accuracy will be affected due to the matrix effect.

A new procedure is proposed for calibration-free quantitative elemental analysis of materials using LIBS technique. The method based on an algorithm developed and patented overcomes the matrix effects. The precise and accurate quantitative results on elemental composition of materials can be acquired without the use of calibration curves. Some applications of the method have been illustrated, e.g., the quantitative analysis of the composition of metallic

alloys [32]. This model of CF-LIBS is applicable under the conditions of LTE and optically thin, as well as the assumed conditions without the element interference and self-absorption. Research recently focused on the correction for self-absorption. Multivariate analysis (MVA) is an effective mathematical and statistical approach for LIBS data analysis, since it can utilize much quantitative information from the complex LIBS spectra. Partial least squares (PLS) is such an MVA method and has shown great potential for LIBS quantitative measurement. The model utilizes the multiline spectral information of the measured element and characterizes the signal fluctuations due to the variation of plasma characteristic parameters, such as plasma temperature, electron number density, and total number density, for signal uncertainty reduction [33,34]. LIBS can be used to provide the quantitative analysis of a variety of samples in the laboratory and in the field. However, each application has some unique characteristics that must be dealt with in order to optimize performance. In the real applications of LIBS, the procedures for obtaining quantitative results reproducibly will be developed.

A much deeper understanding of LIBS fundamental physics is the key to overcome the bottlenecks for wide applications of LIBS, such as the relatively low measurement repeatability due to the plasma property and morphology fluctuations, the relatively low accuracy suffered from matrix effects, etc. The plasma generation and evolution processes are complicated processes. Much more work is still required to improve the qualitative and quantitative analyses, as well as the applications of LIBS technique.

3. Applications

LIBS has attracted great attention in various industries as a qualitative and quantitative analytical detection technique due to its noncontact, fast-response, and multidimensional features. With the development of laser and detection systems, LIBS has been applied in various fields, including combustion, metallurgy, food, human, the Mars project, and so on. Especially, the advantages of this method are more significant in the areas of combustion, metallurgy, and harsh environments. Many applications have successfully demonstrated the monitoring of plant control factors using LIBS. LIBS has been actively applied to commercial plants such as iron and steel making, thermal power, waste disposal, and so on. Environmental monitoring and safety applications are also the growing fields for LIBS. Applications of LIBS have covered all industry fields, including analyses from food, plant to space missions, which will be discussed in detail in the next section. In these cases, ruggedness and reliability become important requirements.

3.1. Applications for plants

LIBS, with the features of excellent temporal and spatial resolutions, appears to be a very promising analysis method in steel industry where element distribution measurements of materials at all stages of production provide the information of material quality and production process. By the continuous monitoring of element distribution, the raw materials with narrow composition tolerances can be available ahead of further processing. LIBS measurement of

geological materials on the conveyor belts was studied and discussed preliminarily [35,36]. A multispectral line calibration method was proposed for the quantitative analysis of elemental compositions. Its feasibility and superiority over a single-wavelength determination have been confirmed by comparison with the traditional chemical analysis of the copper content in the ore. Two iron ore samples were employed to complete the mineralogical classification using a combination of LIBS and principal components analysis (PCA)/principal components regression (PCR) [37,38]. The combined method of LIBS and PCR was applied to determine the elemental compositions of a series of run-of-mine iron ore samples, which exhibited the potential for in situ determination of ore composition. The calibration models of LIBS have also been studied and discussed in the measurement of ores. The different data-driven multivariate statistical predictive algorithms, such as Principal Components Regression (PCR), Partial Least Squares Regression (PLSR), Multi-Block Partial Least Squares (MB-PLS), and Serial Partial Least Squares Regression (S-PLSR), were compared for the quantitative analysis in iron ore measured using LIBS to improve the performance of the quantitative measurements [39,40]. The on-line measurement system of LIBS has been discussed for the real applications. Figure 3 shows a LIBS system for on-line measurement using extractive sampling. For example, an analytical instrument based on LIBS technique was developed to operate on-line in the harsh environment of iron-ore pelletizing plants. The detection system was successful for the measurements of Si, Ca, Mg, Al, and graphitic C contents in different iron ore slurries prior to filtration and pelletizing [41]. A method for automated quantitative analysis of ores was developed using a commercial LIBS instrument fitted with a developed computer-controlled auto-sampler [42]. The preparation and analysis time for each sample was less than 5 min. The similar method was suitable for a range of ores and minerals.

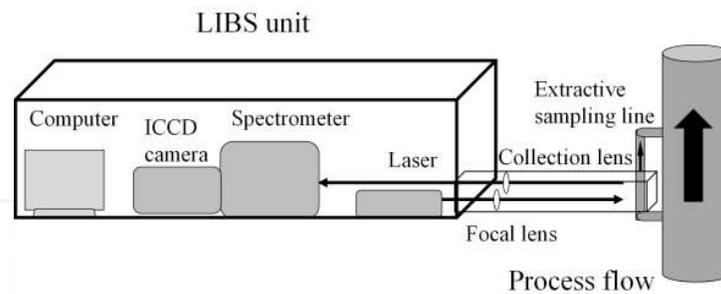


Figure 3. A LIBS system for on-line measurement using extractive sampling

Operating characteristics of coal-fired boilers are heavily influenced by factors such as the differences in fuel properties and combustion conditions. In order to achieve the optimal operation of multiple coal-fired boilers, it is necessary to accurately understand the coal quality and the state of combustion, and to adjust the control parameters. LIBS technique has been widely applied to analyze the compositional characterization of coal [43-45]. A nonlinearized multivariate dominant-factor-based partial least-squares (PLS) model was applied to coal elemental concentration measurement using LIBS [46]. Unburned carbon in fly ash is an important factor to estimate the combustion efficiency of boiler. Fly ash and bottom ash

resulting from the coal combustion in a coal-fired power plant were analyzed using binders. Once the experimental conditions and features are optimized, application of LIBS may be a promising technique for combustion process control even in on-line mode [47,48]. Software-controlled LIBS systems including LIBS apparatus and sampling equipment have been designed for possible application to power plants for on-line quality analysis of pulverized coal and unburned carbon in fly ash [49,50], which shows the capability of reliable and real-time measurement using LIBS. LIBS has been applied for detection of unburned carbon in fly ash, char, and pulverized coal without any sample preparation. Figure 4 presents the examples of LIBS spectral lines obtained from fly ash. The calibration difficulty of aerosol sample was surpassed by using the correction factors for quantitative measurement. This automated LIBS apparatus was applied in a boiler-control system of a power plant with the objective of achieving optimal and stable combustion [51,52], which enabled real-time measurement of unburned carbon in fly ash, as shown in Figure 5. The boiler control in the real power plant was demonstrated to achieve an optimized operation without time consumption.

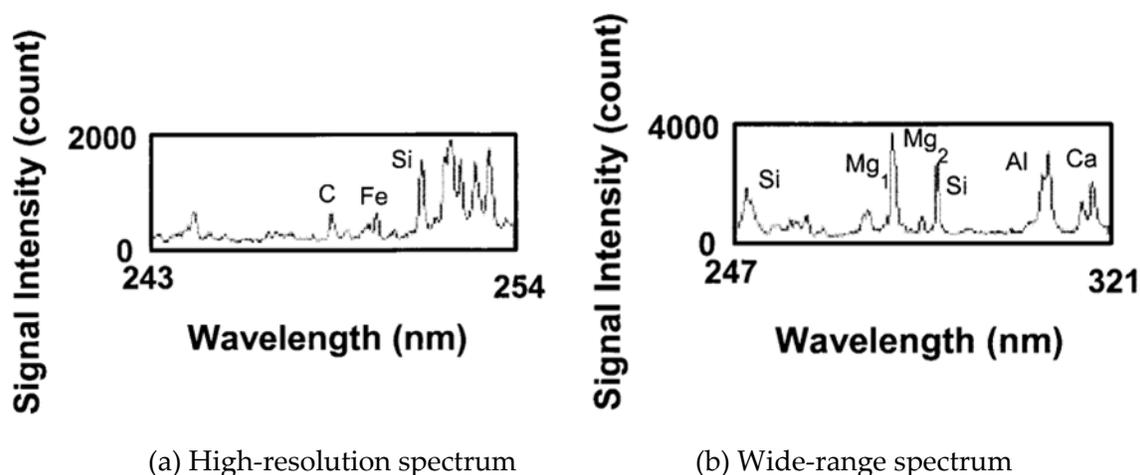


Figure 4. Fly ash LIBS spectra [52]

The safe and rational utilization is very important for nuclear power application. The radioactive contamination is a serious problem for the environment and human health. The radioactive materials released from the nuclear power plant are one of the main sources. Simultaneously, nuclear weapons testing fallout, some industry waste discharge, and radioactive substances employed for research also contribute to the issue [53,54]. The atmosphere, water and soil are polluted by these released radioactive materials. There are several serious pollutions to environment and human not only in the surrounding area of the nuclear power plant but also in the outlying regions [55-57]. LIBS has been investigated as a potential analytical tool to improve operations and safeguards for electrorefiners such as those used in processing spent nuclear fuel [58]. Detection of uranium and other nuclear materials is very important for nuclear safeguards and security. The spatial and temporal evolutions of uranium species in laser-produced plasmas were investigated. A set of optimal operating conditions was determined based on the experimental results, which is important for obtaining the

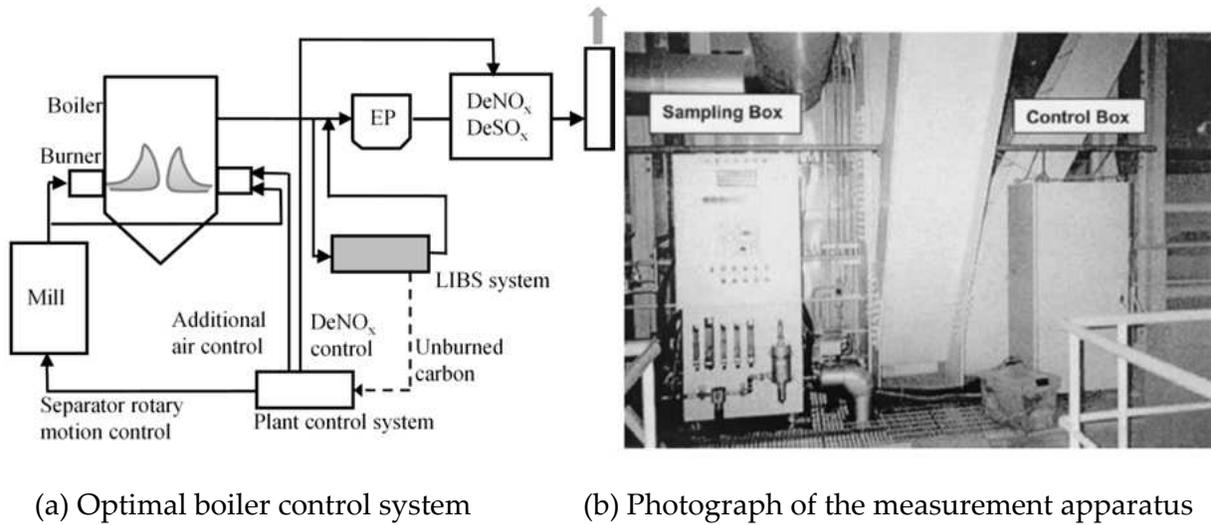


Figure 5. Unburned-carbon measurement in thermal power plant [52]

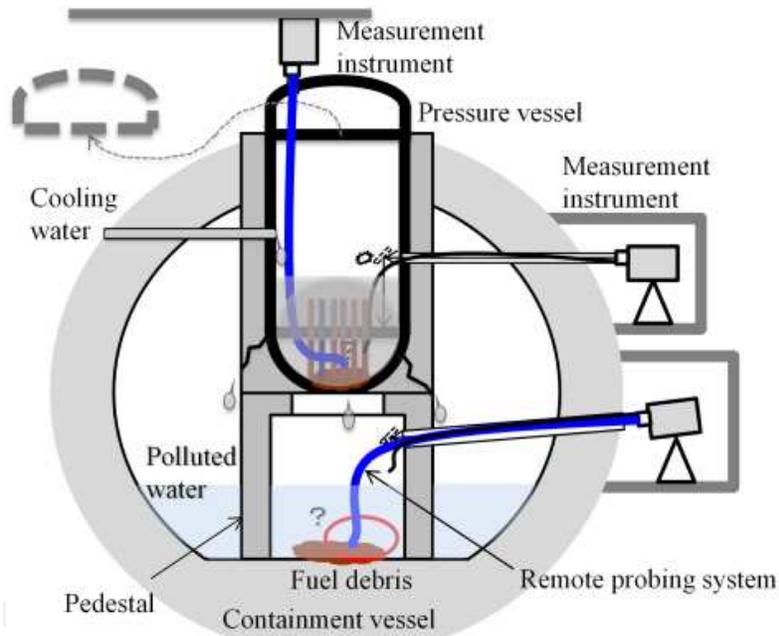


Figure 6. Image of the inside of the post-accident Fukushima Daiichi nuclear power plant and the inspection technique using optical fiber [60]

optimal spectral intensity from samples containing very small amounts of uranium [59]. LIBS can be applied to monitor radioactive elements, which is of utmost importance in case of leakage of radioactive materials from a nuclear power plant [60,61]. Figure 6 shows a schematic of the imaging observation using the imaging fiber, which was equipped for additional electric delivery. A transportable fiber coupled LIBS instrument was developed, which is feasible for the material analysis of underwater debris under a high-radiation field.

3.2. Applications for food, humans, and archaeology

As for LIBS applications to food, composition and contamination measurements of flours of wheat, barley, etc., have been demonstrated. The feasibility of quantifying trace elements in powdered food samples by spatially resolved LIBS has been demonstrated under a reduced argon atmosphere. The selection of the location in the plasma is crucial for obtaining the best signal-to-background ratio of analytical signal and to avoid background continuum and line broadening. The operating parameters affected the plasma property were optimized and used for further analysis of trace elements in starch-based food samples. Spatially resolved LIBS has been shown to be an accurate technique for determining trace elements of ppm level in starch-based food samples directly with an acceptable precision without any tedious digestion and dilution procedure [62]. A procedure for the analysis of K, P, Mg, and Ca in crop plant samples using a commercially available LIBS spectrometer was also developed. Real plant samples employed as the calibration standards were analyzed by ICP-OES or AAS after microwave digestion. A satisfactory agreement between LIBS and AAS/ICP-OES results was achieved [63]. The trace and ultra-trace element detection and qualitative analysis in fresh vegetables have been demonstrated using LIBS technique [64]. For a typical root vegetable such as potato, spectral analysis of the plasma emission reveals more than 400 lines emitted by 27 elements and 2 molecules, C₂ and CN. Many elements such as Mg, Al, Cu, Cr, K, Mn, Rb, Cd, and Pb have been measured by LIBS, as shown in Figure 7. These results demonstrate the potential of an interesting tool for botanical and agricultural studies as well for food quality/safety and environment pollution assessment and control.

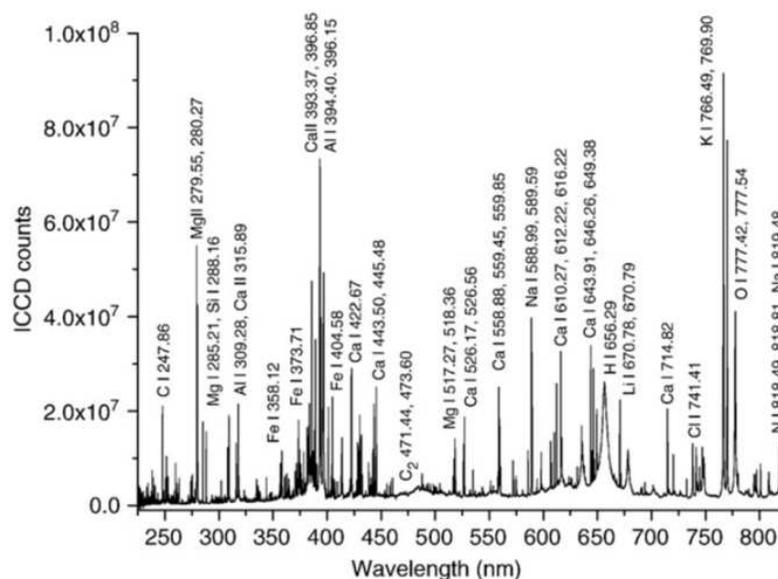


Figure 7. Typical LIBS spectrum of a fresh potato [64]

The application of LIBS to the analysis of important minerals and the accumulation of potentially toxic elements in calcified tissue has been reported [65], which exemplified for quantitative detection and mapping of Al, Pb, and Sr in representative samples, including teeth

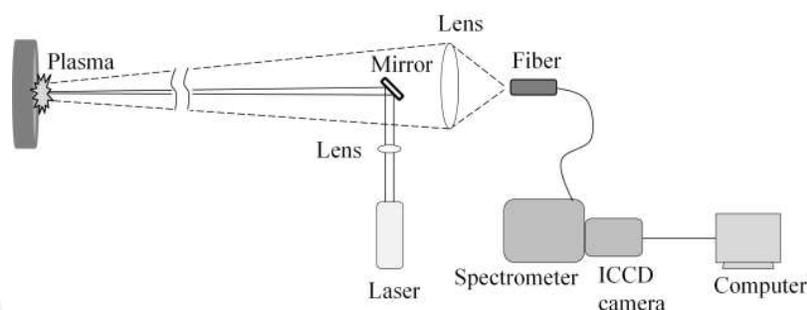


Figure 8. LIBS schematic diagram for measurements from a distance

and bones. In order to identify and quantify the major and trace elements in the tissues, one- and two-dimensional profiles and maps were generated. The state of the tooth has also been diagnosed using prominent constituent transitions in laser-excited tooth [66]. The spectroscopic observations in conjunction with discriminate analysis showed that calcium attached to the hydroxyapatite structure of the tooth was affected severely at the infected part of the tooth. It is possible to distinguish the healthy and caries infected tooth using emission spectroscopy and ICCD imaging of the expanding plasma.

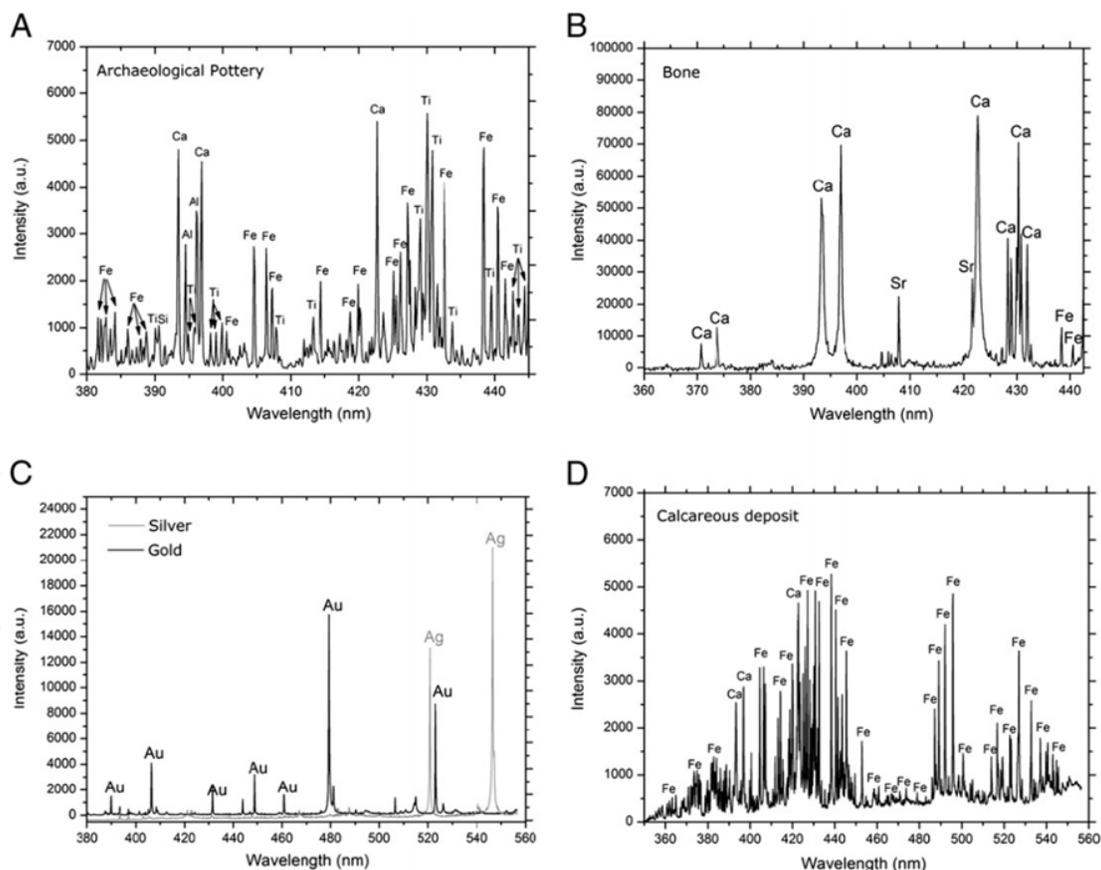
Advancement in LIBS technique has led to its increased use in the fields of conservation, art history, and archaeology [67,68]. A prototype LIBS system was used to determine the elemental composition of multilayer structures in a metal jug from the mid-twentieth century [69]. The piece was highly deteriorated due to environmental damage. The LIBS technique was used as part of a historical investigation that required the determination of the material employed. The jug was selectively sampled at different points on the surface using the stereoscope. By sampling at different points, the surface composition was determined. Furthermore, the presence of two layers of Pb and Cu and their thicknesses were determined through in-depth analysis.

3.3. Applications for space and underwater explorations

One of the more exotic and exciting applications of LIBS instrumentation is for space missions to planet surfaces. Current technological developments of lasers, spectrometers and detectors have made the use of LIBS for space exploration feasible. Figure 8 shows the LIBS schematic diagram for measurements from a distance. LIBS technique greatly increases the scientific return from new missions by providing extensive data relating to planetary geology, which is one of the main goals of space exploration. Meanwhile, the geologic analysis can provide some information of a planet's history, e.g., whether earlier conditions were favorable for life. Several studies have addressed the feasibility of LIBS for space exploration [70-72]. The feasibility of LIBS for stand-off analysis of geological samples under Martian atmospheric conditions has been demonstrated. Under Martian conditions, the analyzed signals appear to be somewhat enhanced compared to that recorded at atmospheric pressure due to the increased ablation.

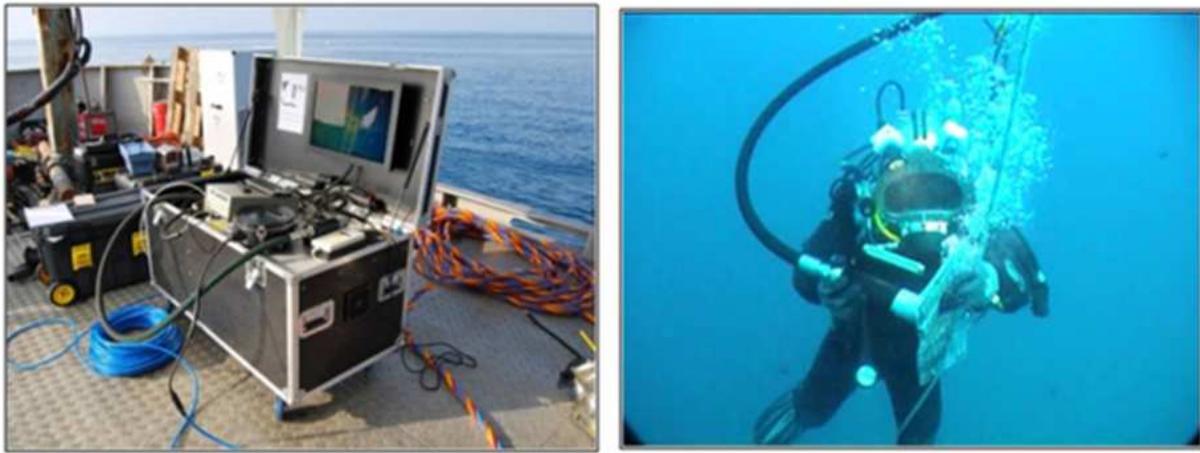
It is a big challenge to apply LIBS to ocean in situ detection, which has been studied with the development of LIBS. In order to apply LIBS to in situ elemental analysis in the deep ocean,

the multielemental analysis of high-pressure aqueous solutions has been studied. The affected factors, such as pressure, laser energy, and so on, have been discussed [73,74]. The potential of LIBS for the underwater chemical characterization of archaeological materials has been also demonstrated [75,76], which involves the delivery of a focused laser pulse toward the distant target through the aqueous media and then the transmission of the light emitted by the laser-induced plasma back to the detection system. Figure 9 shows the LIBS spectra corresponding to different submersed materials obtained in laboratory. The performance of the remote LIBS system was evaluated in a measurement campaign in the Mediterranean Sea. The pictures taken during the on-site trials using LIBS are illustrated in Figure 10. The seashell as the biomineralization product records the growth development and the ocean ecosystem evolution. Therefore, the seashell has been studied as a representative for marine research [77]. LIBS-Raman combination was introduced to obtain the compositional distribution of scallop shell on the surface and also in the shallow layers, which suggested that the micro-chemical diagnostics of LIBS-Raman was a potential way to construct a 3D analysis for the shell research. There are also other techniques that combine LIBS and other methods for the 3D surface analysis.



(a) Archaeological pottery (b) Bone sample (c) Precious metals (d) Calcareous deposit

Figure 9. Underwater LIBS spectra of different submersed materials [75]



(a) Remote LIBS instrument on the research vessel

(b) Diver working at a 30 m depth

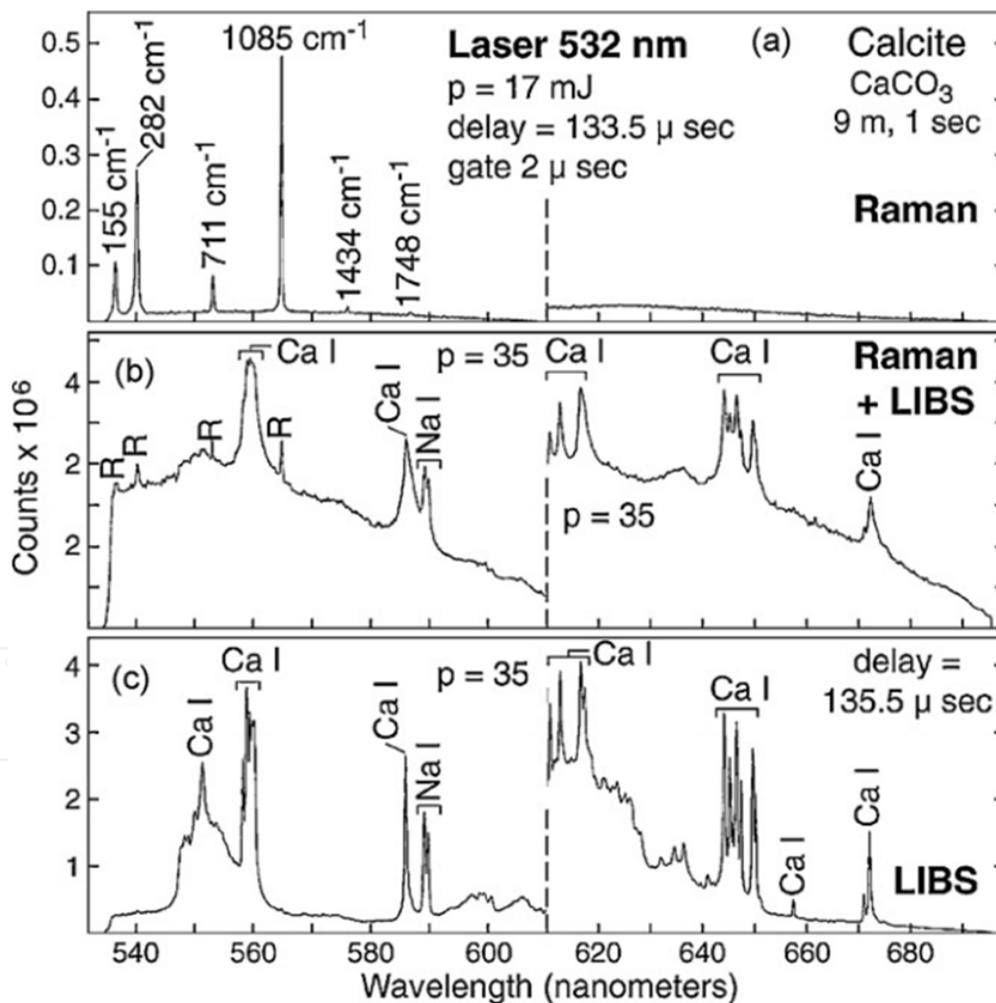
Figure 10. Pictures taken during the on-site trials on the Mediterranean Sea [75]

3.4. Other applications

Applications of LIBS have covered all industry fields, including analyses from food, plant, to space missions. Apart from the applications mentioned above, there are a variety of other applications of LIBS. In engine applications, LIBS has been used to measure the fuel–air ratios in combustion. If the fuel composition does not change, the fuel–air ratio can be inferred from the elemental analysis of unburned and burned gases. It is useful to know that the equivalence ratio can be inferred from burned gas measurement because the elemental composition does not change during reactions [78]. LIBS can be also used for the elemental analysis of particles, such as soot, which contain not only carbon but also metallic elements [79,80]. Tighter environmental regulations recently have focused on global limit of harmful substances released from industry, traffic, and domestic waste. Due to the sensitive and fast analysis features, LIBS has the capability to be used as a continuous-emission monitor for toxic metals, such as Be, Cd, Cr, Hg, and Pb. The sampling methodology and signal processing have been improved [81-83]. The utilization of LIBS technique has been extensively studied in different phase conditions, i.e., solid, liquid, and gas materials, which show different laser-induced plasma processes. The wide pressure dependence and various atmospheric compositions have been studied to understand the LIBS phenomena [84]. One of the challenging targets of LIBS is the enhancement of detection limit of gas phase materials. A new method to control the LIBS plasma generation process has been proposed for the enhancement of detection limit, i.e., low pressure and short pulse LIBS.

LIBS is a promising technique for in situ elemental analysis. The advancement of portable LIBS systems becomes a key technique. There have been a growing number of applications using LIBS in life science, medical fields, and so on. A new mobile instrument for LIBS analysis was developed, which is based on double-pulse LIBS and a calibration-free LIBS technique. Some

applications have been presented including the analysis of cultural heritage, environmental diagnostics, and metallurgy [85]. Laser-induced breakdown spectroscopy and Raman spectroscopy have several features that make a combined instrument for remote analysis. These two techniques are very useful and feasible as the combination of elemental compositions from LIBS and molecular vibrational information from Raman spectroscopy strongly complement each other. Remote LIBS and Raman spectroscopy spectra were taken together on a number of mineral samples [86,87]. Figure 11 shows the Raman spectra, the combined Raman and LIBS spectra, and the LIBS spectra of calcite (CaCO_3) in air in the 534–699 nm wavelength range. The Raman lines in Figure 11(b) are marked with the letter “R.” On the other hand, an approach to further increase the sensitivity of LIBS for the determination of traces is the combination of LIBS and laser-induced fluorescence, which has been studied. The combination of LIBS and LIF allows linking the multispecies capability of LIBS for a broad range of analytes with the high sensitivity of LIF for individual selected species [88].



(a) Raman spectra (b) Combined Raman and LIBS spectra (c) LIBS spectra

Figure 11. Combined remote Raman and LIBS spectra of calcite in the 534–699 nm range [86]

4. Challenges

LIBS features various merits of the noncontact, fast response, and multidimensional detection and has been widely studied and applied in different fields as the qualitative and quantitative analytical detection technique. However, one of the major drawbacks of LIBS is the difficulty of quantitative analysis. There are numerous correction methods for LIBS to achieve the quantitative information, which are usually application-dependent. On the other hand, it has become increasingly important to monitor factors in plant conditions in order to improve the operation of industrial plants. Furthermore the long-term continuous use of LIBS system is a considerable factor for industrial applications. As a consequence, the improvement of measurement accuracy, quantitative analysis, and real-time measurement is very necessary for the operation of the overall plants using LIBS system.

4.1. Accuracy and durability

The laser-induced plasma processes are different from the phase samples in various applications. The measurement methods and parameters should be determined according to the specific conditions. There are several important factors that need to be considered when obtaining quantitative information using LIBS. Choosing the appropriate experimental parameters, therefore, is important to make the theoretical treatment applicable for quantitative measurements. On the other hand, data processing and modeling play an important role in LIBS for the analytical results of the measured spectra. An ideal data processing method should be based on a deep understanding of plasma physics and should be capable of minimizing the noise effects, compensating for the signal fluctuations, and reducing the matrix effects. There have been several calibration methods such as the Boltzmann plot method using many emission lines to increase the correction precision. The calibration methods should be developed to realize the quantitative analyses with the precision and accuracy of a measurement. As for the on-line application in the industry, the system simplicity and real-time measurement capability are also significant factors to be considered. The methods for quantitative analyses should be workable and satisfactory for practical applications.

The real advantage of LIBS technique is that the results are delivered continuously and in real time compared with periodic sampling and standard analytical methods with the time consumption. Consequently, LIBS gives a more representative reading of the state of the process, particularly when rapid perturbations occur, and allows process optimization and quality improvement. Current research aims to develop the commercial equipment for continuous industrial applications. However, in these applications the long-term stability and durability of LIBS devices, especially lasers, is one of the challenges. LIBS employs pulsed lasers and their lifetime often limits the plant applications, especially the long-term continuous use for plant monitoring and control. In a harsh environment, actually, all the devices should be paid attention to, including lasers.

4.2. Instrument development

The applications of LIBS technique have recently been proposed in the fields of materials science, industrial process control, environmental protection, cultural heritage conservation, etc. All of these applications would benefit from a mobile instrument. Therefore, the availability of affordable commercial instrumentation, the standardization of measurement procedures, and the calibration standards are required for reproducible and reliable quantitative LIBS analysis in situ.

The focus of a laser beam of LIBS, for instance, is one of the most important factors to be considered when applying LIBS to industrial processes with the change of a target profile. 3D profile information of the object is required for the positioning of a focused laser beam. The noncontact-type profile measurement systems, in general, can be divided into three categories, including a measurement machine integrated with a triangulation laser probe [89], a measuring machine integrated with a laser line projector and one/two CCD cameras [90-92], and a measurement machine integrated with a structured fringes projector and two CCD cameras [93]. To digitize small complex objects with dimensions smaller than about 30 mm, using a measurement machine integrated with a triangulation laser probe is a good strategy due to its small spot size. In general, phase shifting algorithm is applied to calculate the phase map and the 3D profile of an object using the structured fringes projection system [94]. If a 3D profile measurement system can be integrated with a LIBS system, the measured 3D profile information of the object can be used for the real-time positioning of a focused laser beam in a LIBS system.

It has become increasingly important to monitor factors in plant conditions in order to improve the operation of industrial plants. As a consequence, improved on-line monitoring techniques for plant control factors are necessary to enhance the capability of maintaining the overall plant operation. The associated monitoring and control techniques are necessary for the continued operational improvement. Emphasis is placed mainly on instrument development for applications as well as fundamental scientific investigations.

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