APPLICATION OF LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR ELEMENTAL ANALYSIS

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Abstract

The article reviews some fundamental studies and analytical applications of Laser-Induced Breakdown Spectroscopy with an emphasis on environmental monitoring. This emission-type technique is based upon the spectral and time-resolved analysis of the atomic emission lines generated at the optical breakdown close to the sample surface and is suitable for sensitive, multi-elemental, and real time chemical composition analysis.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a laser-based technique that can provide nonintrusive, qualitative and quantitative measurement of elements in various test environments. LIBS is an emission-type technology that has been successfully applied to gas, liquid, and solid samples. The major advantage of LIBS compared to other analytical techniques is that no time-consuming sample preparation is necessary. LIBS involves the plasma generated by a high-energy laser beam to prepare and excite the sample in one step. It has the ability to perform multi-element real-time analysis. The LIBS technology allows analyzing a sample in less than one minute without any preparation and is specific to elements contained in the chemical structure of a sample. The versatility and ease of use of LIBS result in many practical applications.

In this work, some details of LIBS are described; the main characteristic and physical parameters which are important for quantitative analysis of LIBS are discussed; some analytical applications are reviewed.

The analytical abilities of LIBS are compared with some spectroscopic techniques commonly used in the laboratory, such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission (ICPAES), and X-ray fluorescence spectroscopy (XFS).

Laser-induced breakdown phenomena were observed just after the invention of the ruby laser by Theodore Maiman in 1960. Initial works were focused on understanding the various mechanisms involved in the process. As the material is atomized and excited at the high temperature of laser spark plasma, the potential for using LIBS for elemental analysis of gaseous, liquid, and solid samples was soon recognized by many researchers. Compared to other analytical techniques, LIBS uses very small amounts of samples, in the range of nanograms to picograms, and no sample preparation is necessary that helps to avoid the risk of contamination. It also permits analysis of extremely hard materials, such as ceramics, superconductors, which are difficult to dissolve. It has the ability to perform real-time analysis because it prepares and excites the sample in one step.

LIBS, like all other analytical techniques, is not without limitations. LIBS is subject to the matrix effect which can be minimized by good specimen preparation and the use of accu-

rate calibration standards, it is also subject to variation in the laser spark and resultant plasma which often limits reproducibility. The accuracy of LIBS measurements is typically better than 10% and precision is often better than 5%. The detection limits for LIBS vary from one element to the next depending on the specimen type and the experimental apparatus used. Even so, detection limits of 1 to 30 ppm by mass are not uncommon, but can range from >100 ppm to <1 ppm.

The physical process of LIBS begins with focusing a high-energy laser pulse on a sample of interest. The laser pulse causes photochemical and photothermal breakdown of the sample, generating plasma. The energy of the laser-created plasma excites target elements in the sample causing the emission of their characteristic light. Light emitted by these excited target elements is then transferred via fiber optic to a spectrometer equipped with a photoelectric detector. Emission line intensities for the target elements are then recorded providing quantitative and qualitative information about the sample of interest. Because all elements emit light when excited to sufficiently high temperatures, LIBS can detect all elements limited only by the power of the laser as well as the sensitivity and wavelength range of the spectrograph and detector. Nearly all components of the periodic system from hydrogen to plutonium have been measured and identified by LIBS, with the exception of artificially prepared short-lived radioactive elements [1].

Studies of LIBS characteristics for quantitative measurements and development of techniques for improvement of sensitivity and precision of LIBS have resulted in numerous applications, such as control of industrial processes, remote sensing of biological agents in defense or anti-terrorism applications, remote characterization of high-level radioactive metals and wastes preventing risk to the operator, detection of hazardous and toxic pollutants in environmental monitoring, analysis of explosive and energetic materials for military use, waste management, medical diagnostics, space research, etc.

2. Fundamental studies

The minimum optical power density required to form plasma is referred to as the breakdown threshold. Different types of laser, sample, and ambient conditions will have different breakdown thresholds. A laser power density greater than 10^{10} W cm^{-2} is generally required to generate a breakdown in air using a Q-switched Nd: YAG laser of 10-15 ns duration. Breakdown thresholds of solids and liquids are usually much lower than for gases. The two mechanisms responsible for electron generation and for growth in laser-induced breakdown are multiphoton absorption and collision-induced ionization. Multiphoton absorption involves simultaneous absorption of several photons by an atom or molecule, to cause its ionization. This mechanism produces a few initial free electrons in the focal volume. The electron density grows linearly with time. Generally, this mechanism is not the major process in the growth of electrons in laser plasma. In the collision-induced ionization process, free electrons in the focal volume are accelerated by the electric field of the laser beam. After the electrons have gained sufficient energy, they can ionize atoms by collision; thereby, the electron density grows exponentially with time. The evolution of laser plasma can be divided into several transient phases. The initial plasma (0-100 ns) is characterized by high electron and ion densities (10^{17}-10^{20} cm^{-3}) and $T \approx 20\,000$ K.

The emission spectrum from the early stage of the plasma is characterized by a continuum background emission due to deceleration emission as a result of strong collisions between the free electrons and the excited atoms and ions and processes of recombination of electrons with ions in the plasma.

Emission lines from ions and atoms can be found after about 300 ns delay. These lines are superimposed on the strong continuum background. Owing to the high electron density, the emission lines are broadened by the Stark effect. As the plasma expands and cools, the electrons and ions recombine, and a characteristic loud sound can be heard due to the shock wave emitted from the plasma. The continuum background decays rapidly and the atomic emission lines become narrower and weaker. After the initial plasma (>10 μs), the atomic emission decays slowly, and emission from the simple molecule appears. Figure 1 shows LIBS spectra recorded at delay times of 2, 16, and 50 μs [2].

As shown in the figure, a properly selected detection window can improve significantly the signal-to-background ratio (S/B) of the data, which is very important for quantitative measurement. In this study, the average plasma emission intensity decays by more than a factor of 10 between the 2/2 and the 16/8 ms windows as well as between the 16/8 and 50/150 ms windows. The reduced atomic emission intensity at relatively long delay times is compensated by the use of long detector gate widths.

The excitation characteristics of the laser plasma are determined by the plasma properties, which can be described by the temperature and electron density of the plasma. The analytical measurements are generally performed after the initial plasma, when a state of local thermal equilibrium (LTE) is achieved. At the LTE condition, the emission intensity is proportional to the relative population of the level and follows the Boltzmann distribution.

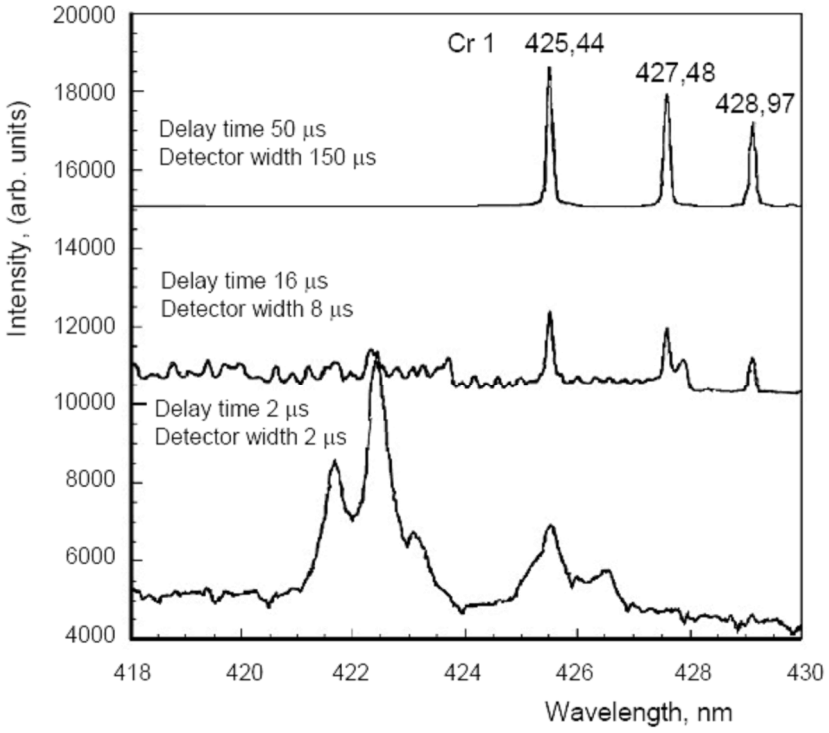

Fig. 1. LIBS spectra of Cr atomic emission lines recorded at different delay times. All spectra have the same scale and have been shifted vertically for clarity.

The Griem criterion [3] is usually used to check the existence of LTE in laser plasma. This formulation places a lower limit on the electron density

$$n_e \geq 9 \times 10^{11} \left(\frac{\Delta E}{E_H} \right)^3 \sqrt{\frac{T_e}{E_H}}, \qquad (1)$$

where n_e is the electron density in cm^{-3}, ΔE is the energy level difference between the ground state and the first ionization state, E_H = 13.6 eV is the ionization potential for hydrogen, and T_e is the electron temperature in eV. Equation 1 holds true only for optically thin plasma that transmits optical wavelengths. The Griem criterion necessitates the experimental determination of the electron density n_e and electron temperature T_e from plasma discharge.

2.1. Effect of physical variable parameters

Variables that can influence LIBS measurements are the laser properties (i.e. wavelength, energy, pulse duration and shot-to-shot power fluctuation), the focusing spot size, ambient conditions, the physical properties of a sample, and the detection window (delay time, gate width), Below, we describe how these parameters affect the precision and accuracy of LIBS.

2.1.1. Laser parameters. As the laser plasma is the excitation source of the LIBS measurement, the properties of the laser can influence the analytical qualities of the LIBS measurement. Regardless of type of the laser used, a power density on the order of 10^{10} $W \cdot cm^{-2}$ is required. If the laser energy is very close to the breakdown threshold, the pulse-to-pulse fluctuation can cause the plasma condition to be irreproducible, which results in poor measurement precision. The LIBS signal is proportional to the laser energy while the laser plasma is in the narrow optical region. When the laser energy increases further, it produces very dense and hot plasma that can absorb laser energy and cause self-absorption. This will lead to an increase in the continuum emission and a decrease in the signal intensity.

Laser wavelength can also affect the plasma-formation process. Collision-induced ionization is the dominant process for optical breakdown with a long-wavelength laser. As the laser wavelength decreases, the collision-induced ionization rate decreases and the multiphoton process increases. A maximum breakdown threshold is found in the intermediate laser wavelength. Laser wavelength can also affect energy coupling between the laser and the sample. Studies showed that the use of an ultraviolet (UV) wavelength can improve the energy coupling efficiency due to its low reflectivity for most metals.

In addition to laser wavelength and laser energy, the laser pulse duration and laser shot-to-shot fluctuation can also affect the signal reproducibility and, hence, LIBS precision. When the laser duration is short and compared to electron energy loss time, multiphoton absorption dominates over collision-induced ionization. It was shown that the threshold intensity increases with decreasing laser pulse duration for laser pulses shorter than 10^{-7} s at atmospheric pressure [4]. A 1000-fold breakdown threshold was found with an Nd:glass laser of about 10 ps than for a nanosecond width pulse in atmospheric air.

2.1.2. Focal properties. High laser power densities can produce laser-induced plasma (LIP), which has higher excitation temperatures with minimum matrix interferences due to more complete atomization. It is a condition preferable to quantitative measurement. The laser power density at the focal plane is inversely proportional to the focused spot size.

A collimated laser beam can be focused by an ideal lens down to a beam waist width (diameter of the focus) of

$$d_{\sigma 0} = \frac{4 f \lambda}{\pi D} M^2, \tag{2}$$

where f is the focal length of the lens, λ is the wavelength of the laser radiation, D is the diameter of the illuminated aperture of the focusing lens or diameter of the unfocused beam, M^2 is the laser beam propagation ratio or the laser beam quality factor [5]

$$M^2 = \frac{\pi}{\lambda}\frac{d_{\sigma 0}\theta_\sigma}{4}, \tag{3}$$

where θ_σ, the beam divergence angle, is a measure of the beam width or beam diameter with increasing distance from the beam waist location. For an ideal Gaussian beam, M^2 attains the minimum value 1. The average irradiance of a pulsed laser beam or radiant power per unit area in the units of Wm^{-2} at the beam waist is

$$I_f = \frac{\pi E_L D^2}{4\tau_L f^2 \lambda^2 M^4}, \tag{4}$$

where E_L is the energy of laser pulse, and τ_L is the pulse duration (FWHM).

The last equation shows that the beam propagation ratio has a strong influence on the achievable irradiance. A higher laser power density at the focal point can be achieved by reducing the focused beam waist using a shorter focal length lens or larger unfocused beam. The ablation rate increases with decreasing spot diameter; however, if the size of the spark is very small and the distribution of material within it is inhomogeneous, the precision and accuracy of the measurement is degraded. A short focal length lens is preferred to produce a highly localized spark for a spatially resolved measurement. A long focal length lens provides a larger focal volume and is usually used when the focal lens cannot be kept close to the sample. This situation requires higher laser energy to produce the laser spark, and the larger focal volume associated with the long focal length can cause particle induced sparks - formed at different locations along the focal axis - and this introduces noise into measurements.

The lens-to-surface distance (LTSD) is a critical parameter for the LIBS measurement of a solid sample. If the laser beam is tightly focused on the surface, a change of the LTSD of a few millimeters can affect the absolute light intensity. By defocusing the laser beam on the sample surface, a more reproducible LIBS signal can be obtained. Therefore, this technique can be used to improve LIBS precision.

2.1.3. Physical properties of the sample. All types of material can be sampled using LIBS. However, the physical properties (such as reflectivity of the sample surface, density, specific heat, and boiling point of the target) can have a considerable influence on the result. The surface reflectivity determines the fraction of the laser energy that can be absorbed by a sample, and hence can affect the material ablation rate. If the laser energy is high enough, the laser impulse can still effectively couple to a sample with high reflectivity. This is because during a laser pulse, the laser energy causes rapid heating of the sample and results in a sample phase change, which significantly reduces the reflectivity.

The laser plasma heats the sample to cause the vaporization and atomization of the sample material. The amount of material vaporized depends on thermal properties of the sample (i.e., conductivity, specific heat, and boiling point). At a low laser power densities thermal conductivity is the most important parameter for material vaporization. If the material has a high thermal conductivity, the absorbed heat is conducted away quickly and results in a lower amount of material being vaporized. At higher laser power densities, the heat is provided too quickly to be conducted away. Therefore, the latent heat of vaporization of a sample becomes a more important factor in determining the amount of material vaporized during a laser pulse.

2.1.4. Detection time window. In LIBS, the desired atomic emission signal is always accompanied by a strong continuum background. As the continuum background and analyzed signal decay with different rates, it is possible to use the time-resolved technique to discriminate against the strong continuum radiation and also avoid spectral interference between spe-

cies that emit at different times during the plasma decay (see Fig. 1). The detection window is selected to obtain an optimum S/B value. As the background signal decays at a faster rate than the emission signal, the best S/B can be achieved at a long delay time. The long delay time also ensures that LTE is achieved. Generally, signal-to-noise ratio (S/N) and S/B values follow the same trend as the delay time changes. However, a low S/B can sometimes give a good S/N. Therefore, the selection of the best detection window should depend on both S/B and S/N.

2.1.5. Ambient conditions. The hot plasma interacts with the surrounding gas by expanding the high-pressure vapor, driving a shock wave into the atmosphere, and transferring the energy to the atmosphere via heat transfer and heating by the shock wave. The size and shape of the LIP are largely dependent on the ambient conditions such as pressure, gas composition, and mass density of the gas.

The spatial confinement of the plasma becomes stronger with increasing gas pressure. The confining effect produces denser and hotter plasma which could cause an increase in both the emission period and the emission intensity. At low pressures, owing to the weak confining effect of the plasma by the surrounding gas, the laser-produced plasma expands rapidly and becomes thin, resulting in a increase in the emission intensity. At moderately high pressures, high temperature and high-density plasma is generated, and the intensity of the continuous emission spectrum is very high. Also, the self-absorption effect takes place due to the increase in concentration of the absorbing species surrounding the hot plasma. It results in lower precision and sensitivity. To obtain intense emission spectra free from self-absorption, LIBS measurements should be performed at a moderate pressure range of 50-500 Torr in the air.

The effects of various atmospheres including Ar, air, O_2, N_2, and He on LIBS spectra have been studied with the use of a Q-switched Nd:YAG laser over a laser energy range of 20 to 95 mJ [6]. Argon, helium, and air were used as surrounding atmospheres, and the pressures were changed from atmospheric pressure to 1 Torr. The experimental results showed that the maximum spectral intensity was obtained in argon at around 200 Torr at a high laser energy of 95 mJ, whereas the signal-to-background ratio was maximized in helium at around 40 Torr at a low energy of 20 mJ.

The inert gas acts like a buffer gas to prevent rapid oxidation of the free atom in the plasma. Argon breakdown occurred in the plasma at a relatively high pressure. The argon atmosphere can enhance the analytical signal by re-excitation of atoms, resulting from collision with photon-excited argon. LIP in the Ar atmosphere has a higher plasma temperature and longer emission period due to the low thermal conductivity of Ar. The higher plasma temperature in the Ar atmosphere also produces the highest continuum background. The emission characteristics of LIP from the air atmosphere are similar to that from the Ar atmosphere. However, the continuum background is only 50% of that in the Ar atmosphere. Helium has higher thermal conductivity and higher ionization potential than nitrogen or argon. Hence, it has a high-efficient energy coupling. Therefore, background from a He atmosphere is lower and less sensitive to changes in laser energy and pressure.

2.2. Analytical characteristics

In LIBS, the material due to the high plasma temperature is immediately reduced to elemental form and the resulting atoms are electronically excited. Interaction of the laser pulse with the sample strongly influences plasma properties. In a gas, most laser energy is used to excite the sample. But in liquids and solids, a lot of laser energy goes into material vaporization and less energy is left for excitation. Therefore, the optimum experimental conditions for different phases of samples will be different.

2.2.1. Solid samples. The variable parameters considered important factors to improve LIBS precision of solids analysis are laser pulse energy, degree of focusing, sample translation speed, buffer gas, surface contamination, and surface smoothness. As the laser beam is focused on the sample surface, the sample material absorbs the laser energy to melt and vaporize the target material. The vapor absorbs more energy and forms high temperature plasma near the surface. The plasma expands and transfers its energy to the surrounding atmosphere. Highly ionized emission lines can be found close to the target surface, whereas single ionized and neutral emissions appear further away from the surface. As the laser breakdown threshold is lower in solids than in gas, generally less laser energy is needed for solid-sample measurements. The analyzed signal is proportional to the laser energy. Increasing the laser energy could cause ambient gas breakdown prior to the formation of metal vapor plasma. This will influence the laser energy coupling to the target and result in a weak signal. A lower plasma temperature is expected for solid-sample measurement. The relatively colder plasma can result in incomplete atomization and, hence, a poorer analytical result.

Interaction of the laser spark with the sample surface causes nanograms of material to be ablated from the surface and form a small crater on the sample surface. As the laser continuously samples at the same location, the crater size changes and results in a time-varied LIBS signal. To obtain reproducible results, LIBS measurements should be taken after a certain ablation time when the signal is at a more stable level. If possible, the sample should also be slowly translated to ensure that the measurement is performed at a new spot each time.

Surface properties can affect the material ablated from the sample and therefore can affect LIBS precision and accuracy. As the laser spark only interacts with the sample surface, a clean surface that has representative elements of the bulk sample is necessary. Surface contamination can greatly distort LIBS analysis. However, this problem can be solved by applying a few laser shots at the same spot to clean the sample surface, so that reliable LIBS signal can then be obtained.

Sample homogeneity is very important for bulk analysis. For an inhomogeneous sample, averaging the data taken at various locations of the sample can improve the accuracy of the measurement. The sample roughness can change the lens-to-sample distance from shot to shot and, therefore, influence the plasma characteristics and also affect the LIBS precision. Therefore, choosing a smooth surface for LIBS analysis can also improve LIBS precision.

The presence of a buffer gas also affects the energy coupling to the target and, hence, the LIBS signal. Some spectral interference can also be deduced with the selected buffer gas. For example, the interference of C emission due to the dissociation of CO or CO_2 in air can affect the accuracy of carbon measurement in molten steel. Use of an He atmosphere can improve the C detection and minimize the interference from air atmosphere.

At high pressure of the surrounding atmosphere, a high density and high temperature plasma is generated, emitting a strong continuum emission, and self-absorption takes place. This reduces the system sensitivity and the linearity of the calibration curve. One way to improve the detection sensitivity is to use gated detection with variable delay. Another method is to reduce the pressure of the buffer gas.

2.2.2. Liquid samples. LIBS for liquid-phase analysis can be performed by focusing the laser beam in the bulk liquid or at the surface. The bulk focusing requires a liquid that is transparent at the wavelength of the laser and the emission lines. When plasma forms inside a liquid, the atomic and ionic emissions from the constituent elements have relatively short lifetimes compared to a spark in the air. Also, emissions from the background continuum, neutral and ionized atoms, and simple molecules appear simultaneously. Therefore, the time-resolved

measurement cannot effectively eliminate spectral interferences for liquid analysis. However, a significant improvement of S/B for liquid analysis has been demonstrated with a shorter laser wavelength [7].

Studies revealed that a 532-nm laser beam produced a very strong continuum background interfering with signal emission, whereas a 193-nm laser beam produced signal several orders of magnitude higher with relatively dimmed plasma. The improvement of S/B with a short-wavelength laser is because the LIP process became less thermal, and the optical energy is effectively coupled into the target rather than heating up the plasma shield. This avoids violent ablation while the liquid is absorbing the laser energy, and makes single-shot measurement in liquids possible.

The detection limits of some elements were improved by forming the laser spark on the surface of the liquid, which produced a higher-temperature spark than the spark formed in the bulk liquid. Uranium could be detected in the bulk liquid at $300\,gL^{-1}$, whereas a detection limit of $0{,}1\,gL^{-1}$ can be achieved with the surface excitation technique [8]. For LIBS measurements in liquids, it is also useful to send the laser beam through the side or the bottom of the mixture, to avoid optical interference from liquid splashing and the gas bubbles liberated as the liquid-gas surface [9].

2.2.3. Gas samples. The breakdown in the atmospheric pressure gases for a nanosecond laser pulse width is governed by the cascade ionization mechanism where the threshold is proportional to the ionization potential of the gas and inversely proportional to the collision frequency. The laser breakdown threshold depends on laser wavelength, laser pulse energy, and gas pressure. The experimentally obtained breakdown threshold is much less than that predicted by theory, because the presence of aerosol particles causes aerosol-induced breakdown. Aerosols, acting as seeds, can significantly lower the breakdown threshold of clean gas. Typically, laser-induced air breakdown has a plasma temperature of 20000 K and an electron density of 10^{17}-10^{18} cm^{-3} after the plasma is formed. Under such conditions, new compounds can be formed of components of the gas atmosphere.

For example, emission from CN can be observed from LIP in air. The CN is produced from the reaction between C and N, produced in the spark. The intensity of the CN bands depends on the concentration of a C-containing compound in the gas stream. The elements in the spectral region covered by the CN bond have less sensitivity due to this spectral interference.

LIBS can directly measure a gas sample, eliminating the need of sample preparation. The presence of Cl and F in the air was detected with detection limits of 80 and 2000 ng, respectively [10]. It was found that the absolute detection limit for Cl and F can be improved to 3ng in He atmosphere. LIBS was used to detect Be, Na, P, As, and Hg in the air [11]. Owing to the small sample volume and possible sample inhomogeneity, the measurement precision in a gas sample is generally poor. Variously sized participates in the gas can cause breakdown to occur at different locations along the axis of the laser beam, and this leads to significant signal variation. The variables affecting the characteristics of LIBS spectra in a gas include particle size, gas pressure, temperature, and laser energy. For quantitative measurements, the calibration procedure should keep these variables as close to the measurement conditions as possible.

2.3. Interference

Three types of interferences - self-absorption, spectral overlap (spectral line interference, band interference), and matrix effect (chemical interferences) - are generally encountered in LIBS. Self-absorption occurs when the emission from the hotter region is absorbed by cool

atoms surrounding the high-temperature core of the laser plasma. To avoid the problems with self-absorption, resonance lines should only be used for the measurement of trace elements.

Spectral interference due to line overlap is very common, because the resolution depends upon the monochromator used. Care should be taken to avoid spectral interference lines in the analysis. Emission lines are often superimposed on bands emitted by oxides and other molecular species from air or samples. A background correction for band emission is necessary. The absolute intensity of an analyzed line can be obtained by subtracting the peak height from the background signal near the emission line.

The physical and chemical properties of the sample can affect the plasma composition, a phenomenon known as the matrix effect. The matrix effect can result in the sample being ablated differently from the target sample. This was found in measurements of Zn-Cu alloy foil, for which the Zn/Cu weight ratio was found to be as much as 30% greater than that of the sample composition [12]. The matrix effect may be due to the incomplete vaporization (atomization) in LIP.

Sometimes interferences from the same element, dissociated from the molecular species in the atmosphere, can cause a higher measured concentration. In carbon measurement in the air, atmospheric CO_2 near the laser spark is dissociated, and the resulting carbon atoms are added to those arising from the sample. This leads to a higher carbon concentration. To improve the carbon measurement, LIBS must be performed in a CO_2-free environment.

Other types of interference include signal fluctuations due to particles and detector saturation by a very intense signal. In addition to experimental precaution, certain data selection schematics are sometimes needed to exclude some distorted data. Often, the resonances lines are not the most suitable lines for quantitative analysis, because they are susceptible to self-absorption. Reducing the pressure of the surrounding atmosphere can minimize the occurrence of self-reversed emission.

As the plasma conditions fluctuate from pulse to pulse, and it is difficult to control the variables associated with the excitation condition, an internal standard is generally employed to compensate the effects of laser plasma variation. An internal standard is the major element in the sample. The concentration of the internal standard is known from independent measurements and always is the same. An emission line of the internal standard is selected for measuring the relative concentration of the other elements in the samples using the intensity ratio of the analyzed line to the standard line. The excitation energies for the complete atomization of a sample in LTE microplasma volume for the analyzed and internal standard lines should similarly match to compensate the changes in plasma. To minimize the effects of the spectral response of the detection system at different spectral regions, the analyzed lines and the standard line should be chosen from the same spectral region.

2.4. Calibration methods

For practical applications, the measured emission intensities need to be related to the relative or absolute elemental concentration. The system response must be calibrated for a certain measurement. Calibration is the most difficult issue in the development of LIBS, especially for field measurements. LIBS is an atomic emission spectroscopy. In addition to variables related to emission spectra, several other variables greatly affect the intensity of the LIBS signal:

- fluctuation of incident laser energy;
- size and density of particles and associated matrix effects in the gas flow;
- location of the focus point for solid and liquid samples;
- surface features;

- history of ablation by laser shots for solid samples.

For on-site measurement, LIBS is considered as a no sampling technique. However, this implies an extra difficulty for calibration. For solid sampling, a standard sample can usually be pressed from well-mixed powders. In [13], the radiation embrittlement in steel nuclear reactor pressure vessels was investigated by means of LIBS. The concentration of copper, a key impurity contributing to radiation embrittlement, was quantified in A553b steel. Cylindrical calibration samples were prepared using a hot isostatic press process. Eleven samples with flat polished surface containing from 0.01% to 5.00% copper were used to obtain calibration curve. To reduce the effect of some variables, the intensity ratio of Cu/Fe was used, instead of Cu intensity, to receive the calibration curve against the Cu concentration. For some solid samples, instead of pressing, well-mixed powders can be melted in a furnace and then frozen.

For gas-phase sampling, a sprayer inserted into the optical path when the calibration is required, is widely used to produce a dry aerosol from a solution of standard reference materials.

In some cases, if the absolute concentration calibration is too difficult to obtain, the relative concentration may be considered. Relative concentration can be obtained by the comparison of the intensities of two or more different elements in one LIBS spectrum [14].

3. Experimental techniques

3.1. Experimental methods

Since the first observation of a laser-induced spark with a ruby laser, a variety of experimental methods have been developed to perform basic research and practical applications. The development of LIBS is closely related to the development of laser techniques. From the early ruby and CO_2 lasers to the more recent widely used Nd: YAG and excimer lasers, more powerful, reliable, and compact laser systems have been used to perform LIBS. LIBS development is also based on the development of detectors and fiber optics. New detectors, the so-called intensified charge coupled device (ICCD), that is, a CCD with fiber-optically connection to a micro-channel plate to increase the sensitivity, has replaced the old photomultiplier tube (PMT) and photodiode array, and have achieved much faster time responses and higher S/N values. Due to this technique, the detection limits of LIBS are in the low hundreds to tens of ppm range for most common elements. In addition to the gain in sensitivity, the possibility of gating the micro-channel plate also offers the possibility to gate ICCD cameras very rapidly. Therefore, ICCD cameras are also used for range-gated detection. A digital delay and pulse generator are used to control the delay and the duration of the ICCD's gating signal. Advanced computer technologies enable LIBS to perform real-time operations, which have enhanced its capability as a method for process monitoring and control.

3.1.1. Experimental setup. A schematic diagram of the typical experimental setup for time-resolved laser-induced breakdown spectroscopy is shown in Fig. 2 [11]. It includes a Q-switched Nd-YAG laser, which is most frequently used in LIBS, with 10-20 ns pulse duration, 50-500 mJ energy, 10-20 Hz pulse repetition rate, a sample chamber with regulated atmosphere and rotating device for mounted samples, a collecting optics of plasma emission, high-resolution monochromator (0.1 nm FWHM) with ICCD photon detector and data acquisition system based on a PC and a gate controller.

A pulse from Nd-YAG laser is focused by a convex lens onto a sample. A bundle of seven 600-μm diameter optical fibers collects the light generated by the plasma spark on the sample surface and delivers this light to a high-resolution spectrometer with 200 to 1100 nm spectral range using several linear silicon charge-coupled diode array detectors.

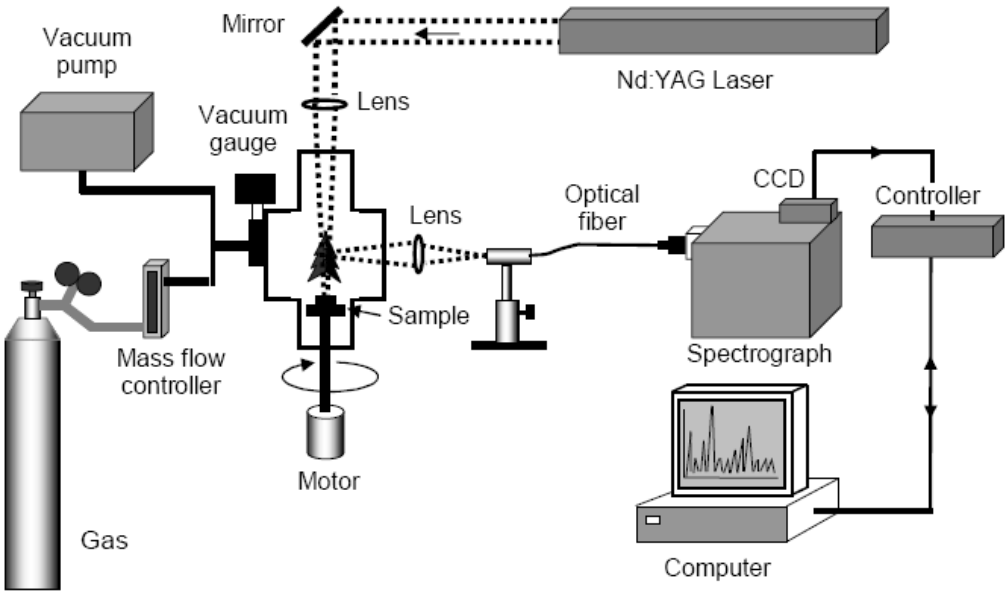

Fig. 2. Schematic diagram of the typical experimental setup for time-resolved LIBS.

As the emission characteristics of the induced spark vary with time, the time-resolved measurement can temporally separate the emissions from different species in the induced plasma. For the first time, the new time-resolved technique was introduced to record the LIBS signal in [11]. This technique has been successfully used to maximize the S/B tie and to minimize the spectral interferences between atoms of different ionization stages as well as between atoms and molecules. In the time-resolved detection, the detector was only exposed to light during a specified gate time, which is controlled by a time gate pulse generator.

The gate pulse signal was delayed with respect to the laser pulse. With a different gate time, the ionic and neutral lines of nitrogen were successfully observed. This time-resolved technique was later adopted by many researchers due to its ability to obtain a better S/B.

3.1.2. Double pulses and fiber technique for enhancement of the LIBS sensitivity. In its original version, the LIBS analysis used a single laser pulse; that is, the plasma on the target was produced by a single laser shot directed onto the sample surface. Even in this relatively simple configuration, the interaction of laser radiation with a solid target is a complex phenomenon still under intensive investigation. In addition, it is difficult to obtain suitable standards, because of interference effects (the matrix effect). Conventional single-pulse LIBS has a poorer sensitivity than competing atomic spectroscopic techniques, such as Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES).

In recent years, one way to overcome these difficulties was proposed through the use of double-pulse LIBS, when two pulses from one laser or two different lasers separated by a delay time on the order of microseconds are used. Significant improvements to the analytical performance of LIBS were achieved by the use of laser double-pulse technique. Double-pulse LIBS was first applied to the analysis of liquid samples and then to solids immersed in liquids [11]. Double-pulse LIBS has also been extensively applied to the analysis of solid samples in a gaseous or ambient air environment [15]. The laser is fired twice with a pulse separation on the order of one to a few tens of microseconds. Depending on pulse separation, the second pulse is more or less absorbed by the plasma plume caused by the previous pulse, resulting in a reheating of the laser plasma.

Different geometrical configurations are used in double-pulse LIBS. In the so-called "collinear" configuration, the two laser pulses have the same axis of propagation and are both directed orthogonally to the sample surface. Studies of collinear double pulses were performed in [16, 17] using a single Nd:YAG laser capable of emitting multiple or two sequential pulses.

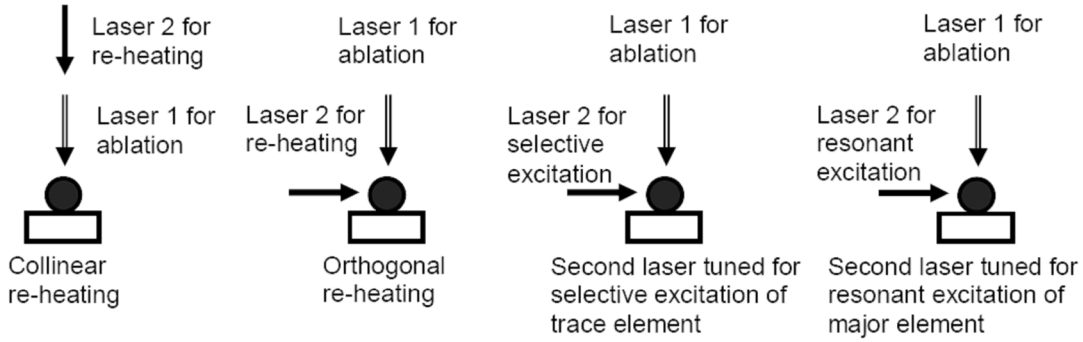

Fig. 3. Double-pulse configurations for LIBS. The arrows depict the laser pulses and their direction of propagation; numbers 1 and 2, their temporal sequence.

Material ablation is found to increase with multiple pulses compared to single pulses of fixed total energy as well as electron temperatures and densities. After the interaction with the double pulse of the same total energy, electron densities amount to about 3×10^{18} cm^{-3} at the center of the hemispheric plasma geometry at a delay time of 2 μs and the volume of the plasma is greater by more than a factor of 3. Line intensities can be increased by a factor of 2-3 using double pulses.

In the "orthogonal" configuration [18], the first laser impulse (output 13 mJ) was focused on the sample surface perpendicularly to vaporize the sample. In order to increase the intensities of analyzed lines the microplasmas were reheated by the second Nd:YAG laser after the process of atomization had been completed. The second laser beam (output of 77 mJ per pulse) was directed parallel to the sample surface and 1.5 mm above the surface. It was focused 2 mm behind the middle of the first plasma. The samples were placed in a sample chamber filled with argon. There was a time delay between two laser shots. The detection system was a gatable optical multichannel analyzer. The intensity of the Zn line at 468.014 nm was observed to be more than 10 times stronger than the intensity with the vaporizing laser only. Similarly, an eightfold analyte signal enhancement was observed for Si I atomic emission line at 288.16 nm and Mg I at 285.21 nm using dual-pulse orthogonal configurations with 20 μs delay as compared with traditional single-pulse LIBS [19].

The double-pulse LIBS also significantly reduces the matrix effects. Double-pulsed systems are also useful in conducting analysis in liquids, as the initial laser pulse forms a cavity bubble in which the second pulse acts on the evaporated material. Even greater increase in sensitivity of the method has been achieved using tunable lasers for selective or resonance ionization of the atoms of a detected element.

Due to progress in fiber optic material science, the high breakdown threshold for the modern optical fibers is possible. Silica-silica-clad multimode fiber with 1-mm core diameter was used to deliver the Q-switched Nd:YAG laser beam (1.064 um) for LIBS excitation [20]. The new fiber-optic probe, which is developed to deliver the laser beam to the sample and atomic emission to the recording system in LIBS applications, makes remote laser-induced breakdown spectroscopy possible. Because of the large acceptance angle of fiber optics, light from a wide angle range is collected by the fiber and is not changed significantly at the output

end. This fiber collection technique is suitable for “in situ” field measurements because it is insensitive to the spark position changes.

3.1.3. Femtosecond time-resolved LIBS. The potential of femtosecond laser-induced breakdown spectroscopy (femto-LIBS) has been successively demonstrated for detection and analysis of inorganic matter and biological samples with a number of attractive features [21, 22]. These features of femto-LIBS are basically due to the specific ablation regime of femtosecond pulses. A pulse duration shorter than the thermal coupling time constant in matter (10^{-12} s) leads to a domination of multiphoton-induced ionization over thermal decomposition and to expansion of the ejected plasma without further interaction with the laser pulse. For analysis using LIBS, specific properties of the plasma induced by a femtosecond pulse, such as lower and faster decreasing temperature and explosive ejection of matter, allow expecting an improved sensibility for trace element detection.

In femto-LIBS, the emission from excited ambient air is almost negligible because of a lower temperature of the laser-induced plasma [22]. This contrasts with nano-LIBS, in which the air in the vicinity of the laser impact spot emits an intense spectrum of atomic nitrogen and oxygen in the near infrared. For the analysis of organic or biological materials, this air spectrum interferes with emission from the sample. Lower temperature of femtosecond laser-induced plasma reduces drastically the blackbody emission from the plasma according to the Stefan’s law of fourth power temperature dependence of the radiation power. That allows plasma lines to be detected with a higher contrast (analyzed line to continuum emission ratio), which is crucial for detecting trace elements.

3.1.4. Remote filament-induced breakdown spectroscopy. Applications in hostile environments, for example, the identification of highly radioactive nuclear waste and the monitoring of radioactive and chemically contaminated zones or high temperature molten alloys, require remote analysis. LIBS is particularly suitable for these purposes, since samples must only be directly visible from the operation site. A remote-sensing LIBS technique based on long-range high-power ultrashort laser pulses (3.56 TW, 80 fs) focusing and remote light collection, has recently been demonstrated to reach distances up to 90 and 180 m limited by the available free space in front of the laser [21-23]. Results of this experiment showed that this technique can be successfully extended to the kilometer range. Under the same conditions, laser pulses with 200-ps and 5-ns pulse duration yield neither ablation nor LIBS signal.

Propagation of intense short laser pulses in the atmosphere involves a variety of diverse linear and nonlinear optical processes. The nonlinear processes are the consequences of the high intensity of a laser pulse. Processes affecting the laser spot size include diffraction, nonlinear self-focusing, ionization, and plasma defocusing.

The intensity dependence of the refractive index, which is known as the optical Kerr effect, underlies the phenomenon of self-focusing. In addition to the familiar constant, the refractive index has a term that depends on the intensity of light:

$$n = n_0 + n_2 I ,$$

where n_0 is the linear refractive index of the medium and n_2 is the medium constant which gives strength of the Kerr nonlinearity in units of inverse light intensity.

The most prominent phenomenon observed when a high-power laser beam propagates in the air is the formation of self-guided laser filaments. When no external focusing is provided, the wave nature of the light emitted from a laser will naturally diffract, and the laser beam size will continuously diverge and increase in size. However, the refractive index of air varies with the intensity of the laser in such a way that the higher intensity portion of a laser pulse encoun-

ters a higher value of the refractive index. Since the refractive index is a measure of the ratio of the speed of light in vacuum to that in the medium under consideration, a higher index of refraction signifies a slower speed of propagation for that portion of the laser pulse, and the laser pulse will converge (focus) onto this lower velocity portion. This has a very close analog to the propagation of light inside an optical fiber where the core of the fiber has a higher index of refraction. A laser pulse will be guided just like the light traveling down an optical fiber.

The condition for which such self-focusing can occur is governed by the initial laser power in the pulse. When the laser power reaches a threshold value, the nonlinear self-focusing effect can overcome the diffractive divergence of the laser beam, and an ideal laser beam will remain at a constant size forever. Fused silica used for optical fibers with a nonlinear index $n_2 \approx 3 \cdot 10^{-16}$ cm^2/W has a critical power in the megawatt range. For air, n_2 is so tiny that the power must considerably exceed this value for self-focusing. The conventionally known value for this critical power is about 3 GW [23]. If the laser power is above this critical value, the laser beam will converge. Self-focusing increases the intensity, which leads to greater self-focusing, which further increases the intensity, and theoretically it will continue decreasing in size until a catastrophic collapse is reached. Ionization and plasma formation halt the filament propagation.

When self-focusing pushes light intensity above 10^{13} Wcm^{-2}, multiphoton ionization creates plasma whose refractive index, being less than that of the air, causes the beam to defocus. Without self-focusing to boost it, I drops below the ionization threshold. The Kerr effect switches back on, and self-focusing resumes. The propagation of the filaments depends, therefore, on a quasi-dynamic equilibrium between Kerr focusing and plasma defocusing.

Self-guided filaments generated by high-power ultrashort laser pulses can overcome the diffraction limit and deliver high laser intensities in a range of $10^{13} - 10^{14}$ W/cm^2 at remote locations over several kilometers without focusing, allowing a Remote Filament-Induced Breakdown Spectroscopy (R-FIBS) scheme. This intensity is above the threshold for laser ablation on metal samples without focusing.

4. Comparison with other spectroscopy techniques

The LIBS technique has several advantages compared to conventional emission methods. In LIBS, a high-energy pulsed laser beam is used to produce atomic emissions from the focal volume. Hence, it provides time and spatially resolved measurement. It requires only a small amount of sample and minimal sample preparation. Gated detection with an intensified detection system discriminates the background emission and also improves the detection limit. With properly selected atomic lines, multiple species can be simultaneously monitored in a spectral region. Furthermore, as a laser spark can be generated in a remote location, it has remote monitoring capability. In this section, LIBS is compared with some spectroscopic techniques commonly used in the laboratory, such as Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Atomic Emission (ICPAES), and X-ray Fluorescence Spectroscopy (XFS).

4.1. Sample preparation and sampling rate

AAS is used to detect the presence and amount of over 62 different metals in highly diluted solutions. It is widely used in laboratories that analyze the purity of water. The resonant wavelength of choice from a selected spectral lamp with cathode made on the metal being analyzed passes through the sample vapor. The atomized element absorbs the light energy over time. The concentration is determined through a calibration curve. The technique typi-

cally makes use of a flame to atomize the sample, but other atomizers, such as a graphite furnace, which contains the sample, are also used.

ICPAES measures the intensities of light emitted from each species as they are atomized and ionized in the plasma. As an atomic emission spectrometry technique, ICPAES has the capability of simultaneous multi-element measurement. Atomization is more complete than in the AAS system; therefore, limit of detection (LOD) values are generally lower for ICPAES than for AAS. In ICPAES, the sample may be an aerosol, a thermally generated vapor, or a fine powder. The sample is carried into the hot plasma by argon flowing. Typically, the sample is reduced to a solution that is sputtered into the system.

XFS is a spectroscopic method that is commonly used for liquid and homogeneous solid samples in which secondary X-ray emission is generated by excitation of a sample with X-rays. XFS can provide rapid quantitative analysis for various samples; however, it is not applicable to light elements (M<10) such as Be, B, and Li. Inhomogeneous samples must be pulverized or fused. Then the homogenized material can be dissolved for analysis as a liquid sample, pressed into grain form, or cast as a glass-like solid.

A typical sample preparation for these techniques often takes several hours while LIBS requires minimum sample preparation. As a result, a complete sample analysis takes minutes to hours. Generally, LIBS can yield useful results in 3-60 s.

4.2. Limit of detection

The detection limit is the minimum concentration that can in principle be measured. As multi-element techniques, LIBS, ICPAES, and XFS all rely on the capability of resolving spectral signals unique to each element. When signals of some elements are very strong, they start to interfere with weaker signals from the other elements, and it may be difficult to achieve the optimum detection limits. LIBS has poorer sensitivity in gas measurements due to the low concentration and small laser microplasma. Typical Limits of Detection (LODs) for LIBS are in the ppm range. For ICPAES, detection limits for most elements are on the order of 10 ppb. XFS is generally less sensitive than the various optical methods. It offers LODs from a few ppm to the percentage range. In AAS, the amount of light that is absorbed by a sample is directly proportional to the concentration of the ground state element of interest. A comparison of the LIBS results with the AAS analysis showed LIBS to be of comparable accuracy. Some samples may have matrix, chemical, and/or ionization interferences.

Generally, LIBS still cannot match completely the detection limits of most conventional analytical techniques in most cases. However, its ability to directly analyze samples without cumbersome sample preparation makes its application promising in practical field determinations of elements for environment and industrial samples.

4.3. Accuracy and precision

Precision and accuracy are generally used to determine the merit of a measurement technique. Precision is the measure of the degree of reproducibility of a measurement. Accuracy is used to determine the difference between the evaluated measurement method and a measurement by a standard method precision. Typical LIBS precision is 5-20%. Laser shot-to-shot variation causes differences in the plasma properties; therefore, it affects the magnitude of the element signal and hence degrades the LIBS precision. To improve LIBS precision, spectra from several laser shots have to be averaged in order to reduce statistical error due to laser shot-to-shot fluctuation. The accuracy of LIBS depends on sample composition, homogeneity, surface condition, and particle size. The sample matrix can affect the amount of

element ablated and hence the LIBS signal. As LIBS only analyzes a small amount of sample, the result might be biased if the composition of the ablated sample does not represent the composition of the bulk. Multipoint measurements can improve the LIBS accuracy for an inhomogeneous sample.

As a result of the small sample volume used the analytical capabilities of LIBS are generally poorer than most conventional methods. However, various studies showed that LIBS is best for applications where standard laboratory instrumentation is not feasible, such as measurements in remote or harsh environments.

5. LIBS application areas

LIBS is a simple spark spectrochemical technique that has a broad capability for chemical analysis with an accuracy comparable to conventional techniques. LIBS is a simple inexpensive analytical technique for determining the elemental composition of a sample, regardless of whether the sample is a solid, a liquid, or a gas. The advantage of LIBS is its sensitivity to all elements with typical limits of detection between 0.1-200 ppm depending on the sample and the element of interest. No sample preparation is needed making it quick and easily adaptable to automated chemical monitoring equipment or portable units.

The main features of LIBS:

- remote and real time analysis, measuring distance of 1 cm–100 m
- static or moving samples, velocity of 0–3 m/s
- states of aggregation: solid, liquid, gaseous
- no sample preparation, small mass required (sub-μg)
- analyzed elements: all elements, simultaneous multi-element analysis
- high spatial resolution (2 μm)
- measuring frequency: 1 Hz – 1 kHz
- Single step for vaporization and excitation.

LIBS has a wide range of applications:

- Metallurgy (solid or molten metals, alloy composition, pyrometallurgy or hydrometallurgy processes monitoring, etc.)
- Pharmaceutical (analysis of active agents in tablets, lubricant, etc.)
- Mining and mineral industry (detection, mineral composition, prospecting, etc.)
- Microanalysis:
  - by sharp laser focusing 2D composition measurement at the micron scale
  - by using the material erosion produced by the laser, measurement of composition below the surface (3D-composition profile)
- Recycling (sorting of alloys or various grades)
- Polymers (rubber, pigments, stabilizing additives)
- Soil contamination
- Papers (pigment distribution, homogeneity)
- Security: detection of explosives, drugs, hazardous and toxic substances
- Environmental analysis: toxic metals
- Remote analysis: smokestack emissions
- Extreme environments: space, nuclear industry
- Art and archeology
- Research and design.

The LIBS technique can be used in a variety of more complex analyses, such as determination of alloy composition, origin of manufacture (by monitoring trace components), and molecular analysis (unknown identification). There is also the option of using LIBS as a stand-off analytical technique for harsh or hazardous environments (such as space, nuclear reactors) preventing risk to the operator as well as for military use in man-portable or robotics applications. LIBS was applied to many environmental situations. The major interests here are applications in environmental monitoring and in industrial process control. Other application areas, e.g., medicine and metals, are discussed elsewhere [24].

5.1. Environmental applications

5.1.1. Radioactive materials. A novel LIBS system was developed specifically for the quantitative analysis of gallium content in plutonium dioxide after processing via thermally induced gallium removal [25]. Gallium has two emission lines of high intensity: 403.299 and 417.204 nm. The line at 417.204 nm was found to be the most intense and best suited for analysis at low Ga concentrations. A nearby Pu emission line at 417.242 nm was chosen to ratio against the Ga line. Samples with gallium concentrations ranging from 34 to 8336 ppm were analyzed, and results were compared with the data of inductively coupled plasma-mass spectrometry. The Ga/Pu ratios resulting from LIBS analysis ranged from 0.288 to 9.92. Most of the data lie below 500 ppm and are quite linear in that range. However, the ratio appears to become nonlinear with a concentration above 1000 ppm. The nonlinearity is due largely to self-absorption of Ga emission within the plume. It may be possible to avoid this effect if a less intense Ga emission line can be used for analysis at higher concentrations.

Success in this application has prompted an expansion of the technique to other areas in nuclear industry, including determination of plutonium 239/240 isotopic ratios [25]. An atomic Pu emission line occurring at 594.522 nm was chosen for analysis. Pu-239/Pu-240 isotope shift of 0.355 cm^{-1} appears as two distinct emission lines. Two samples containing different ratios of 239/240 isotopes were chosen for analysis. For the metal sample, the observed ratio was found as 93.1/6.9, and the known ratio is 93/6. For the oxide sample, the observed ratio was 49.0/51.0, and the known ratio is 49.6/51.4. Analysis for many other impurity elements in plutonium metal and oxide is possible.

The Applied Photonics Ltd used LIBS for the remote characterization of the contaminant material that is known to form during the reprocessing of spent fuel from nuclear reactors at fuel reprocessing plants [26]. Routine hot camera inspections identified an accumulation of unknown solid material. Radiometric measurements were taken to identify the radionuclide inventory of the deposit, but since they yielded no information on the non-radioactive components, full characterization was not possible. Due to the difficulties in taking an active sample from behind the biological shield and the subsequent difficulties with laboratory analysis, a remote method for analysis was applied. Optical access to the material was possible by directing the laser beam of a telescope LIBS instrument via a 1-m-thick lead-glass radiation shield window. The results of the LIBS measurements combined with the radionuclide analysis confirmed that zirconium molybdate was formed in a processing hot cell.

5.1.2. Off-gas emission. The recent years were characterized by an increased awareness of and public interest in the health risks associated with toxic metals, specifically, smokestack emissions from industrial furnaces and hazardous waste incinerators, as well as the concentration levels of toxic metal species in ambient air. In particular, urban areas may be subject to additional public health risks resulting from a larger concentration of stationary and mobile

emission sources. Hazardous air pollutant metals, i.e., beryllium, cadmium, arsenic, chromium, lead and mercury, were designated by the U.S. Environmental Protection Agency as the primary metals of interest for the development of advanced continuous emission monitoring technologies. The LIBS technique is applicable for the detection and analysis of these six toxic elements [2].

Element/line, nm	As (228.81)	Be (313.1)	Cd (226.50)	Cr (425.44)	Hg (253.65)	Pb (405.78)
Limit of detection, $\mu g/m^3$	400	10	60	30	230	190

Listed detection limits for the elements of interest in the form of metal-based aerosols are consistent with new U.S. standards for emissions from existing hazardous waste incinerators.

5.1.3. Biological objects. Detection and identification of microbiological samples, such as bacteria, molds, or pollens, has become a critical application for either military and civil defense or environmental surveillance. In [27] was demonstrated time-resolved LIBS analysis of bacteria with femtosecond laser pulses. A comparison between femto- and nano-LIBS in the near infrared region demonstrates attractive features related to the use of ultrashort pulses for the LIBS analysis of a biological sample. These attractive features are related to the lower and faster decaying temperature of the femtosecond laser-induced plasma. For femto-LIBS, a less interference with emissions from ambient air and a igher contrast for the detection of trace elements in a bacterial sample were shown. Also, a higher ratio between molecular and atomic emissions implying a large concentration of molecular fragments in femtosecond laser-induced plasma was observed.

In particular, native C-N bonds released by a bacterial sample can be characterized by a short decay time of its band intensity. This allows an unambiguous distinction with respect to CN radicals formed by recombination with atmospheric nitrogen, which can be commonly observed in carbon-containing nonbiological samples, for example, graphite, hydrocarbons, etc. The strong emission of the C-N bands in a femto-LIBS spectrum, together with its time evolution and rapid decay behavior, provides a quick, certainly not definitive, indication of a bacterial sample, some kinds of first warning that triggers other more detailed and more sophisticated analysis. Such detailed analysis can be provided by trace mineral elements from a bacterial sample, which can be detected with a high sensitivity using femto-LIBS. These trace elements should contribute to the characterization of a specific bacterium, since they participate in the metabolism of the bacterium and affect their structure. Molecular and atomic spectra thus provide together valuable data for a specific bacterium to be either detected from a natural environment or distinguished from other biological species.

5.1.4. Characterization of recycled materials. High-order recycling of waste materials plays an important role for a sustainable use of resources. Up to now, in the field of construction waste recycling, the material is used for low-value recycling (down-cycling), e.g., street fillers, covers for landfill sites. An example for high-order recycling is the use of concrete-broken-sand as an additive for new concrete. In 1998 the amount of construction waste was 77.1 million tons in Germany only, and the fraction of recycled material was more than 70%, mainly for road constructions [28]. The high amount of building waste material requires innovative strategies for high-order re-use of the material. Since building waste is a mixture of different materials, which might as well be contaminated, it is a precondition to characterize and to sort the material depending on the further use.

Recycled material must not endanger people or environment; therefore, the contamination with organic or inorganic substances must be identified and harmful material must be separated in advance. Concrete is an inhomogeneous material, and a recycling material is even more inhomogeneous. Nevertheless, it is important to know the elemental composition, especially the ratio of Si, Ca, Al, Mg, and Fe as the main components, to guarantee the quality of products and to minimize the energy used for their production.

With LIBS both the elemental composition of building materials and contaminating trace elements can be determined with a real-time measurement, even on-site and in a harsh industrial environment. For the characterization of cement and concrete with respect to heavy metals, measurements of the content of Pb, which is the most important contaminant in mortar, were made in the ppm concentration range. Lead has a spectral line at 405.8 nm. In Fig. 4, the values for the relative amount of Pb in mortar determined from the LIBS measurements are compared with values determined with a standard analytical method, i.e., AAS. Four series correspond to mortar samples with different contents of zeolites. The dependence shown in Fig. 4 is nearly linear. Concrete specimens made with additives of concrete-broken-sand were investigated. The spectra demonstrate the change in Si, Ca, and Al line intensities due to the matrix inhomogeneities. The experiments and the results obtained show the successful application of LIBS for concrete analysis. Trace elements and main components can be measured simultaneously with the LIBS technique. In the recycling of building materials, LIBS can be applied in a first step to ensure the absence of harmful contamination with trace elements (e.g., heavy metals, chloride).

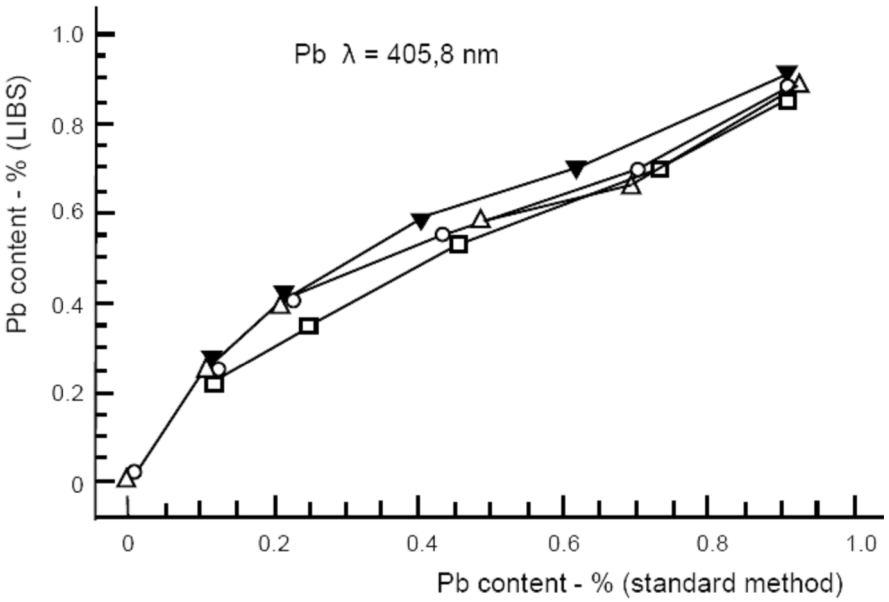

Fig. 4. Relative amount of Pb in four different cement mortar samples with different contents of zeolites. Comparison between LIBS and standard chemical method (AAS) data.

Depending on the further use, the material can be characterized in a second step due to its main components. Therefore, LIBS can act as quality assurance and allows the specific addition from other material necessary for a high order re-use.

5.1.5. Discrimination of explosive materials and hazardous agents. The direct analytical detection of energetic materials and explosive residues in real time is a particularly challenging problem. Interest in overcoming the difficulties associated with detection of explosives

has grown over the past decades. The military has a vital interest in the development of field-portable sensors to detect land mines, improvised explosive devices, remotely detonated munitions, hidden armaments, and unexploded ordnance. Homeland security requires an analytical capability for the detection of trace amounts of explosives or their residues in a variety of different situations (e.g., in airplane, train, or ship passenger luggage, in vehicles, and within transport containers).

Energetic and explosive materials are pure substances or mixtures that chemically react to rapidly liberate large amounts of heat and gas. Today, about 150 different formulations are used in military, commercial, and illegal manufacture of explosives. Many explosives consist of a fuel component (usually a hydrocarbon) and an oxidizer (typically an oxide of nitrogen), which may be contained within the same molecule. To be of broad utility, a sensing technique must have the capability to rapidly detect and identify the wide variety of different constituents that are present in energetic materials and explosives.

Although some methods for detecting bulk explosives, such as X-ray analysis, neutron activation or scattering (which measures quantities of carbon, nitrogen, and oxygen), and terahertz imaging, are currently used or undergoing development, many of these systems are quite large and expensive. One of the most pressing needs is the stand-off detection of explosives. As a result of drastically reduced sensitivity at increasing distances and the generation of potentially harmful ionization radiation, neither X-ray imaging nor neutron activation is practical at stand-off distances. Although terahertz imaging is a promising technique that employs non-ionizing radiation, absorption of water vapor and other species in the atmosphere could potentially limit its application to stand-off detection. Most trace explosive detection techniques, such as ion mobility spectrometry and gas chromatography, rely on vapor detection. Unfortunately, at room temperatures, the vapor pressures of many common explosives are extremely low (ppb or less), and attempts to conceal the explosives by sealing them in packaging materials can decrease the vapor concentrations by as many as three orders of magnitude.

Of all optical techniques that have been applied to trace explosive detection (Raman spectroscopy, photoacoustic spectroscopy, photofragmentation followed by resonance-enhanced multiphoton ionization or laser-induced fluorescence) only Raman has been demonstrated on solid explosives at stand-off distances (10 to 50 m), although long integration times (i.e., multiple laser shots) were required to improve the signal-to-noise ratio.

LIBS is an alternative optical technique for the detection of explosives with determination of composition of the sample, based on elemental and molecular emission intensities under close-contact laboratory conditions and for the stand-off detection as well. LIBS spectra of a large variety of energetic materials have been acquired at the US Army Research Laboratory (ARL) using laboratory, field-portable, and stand-off systems [29]. The laser-induced microplasma has never initiated detonation of any of bulk energetic materials because the short-lived spark provides an insufficient ignition source. However, detonation of materials that are especially shock sensitive is possible as well as ignition of reactive gaseous mixtures. The ability of LIBS to detect trace amounts of materials with a single laser shot is especially important for residue detection, since the first shot can ablate all or most of the residue. One possible way to extend LIBS as a practical approach to the detection and identification of explosives at an operational level is through spectral matching based on a predetermined and assembled spectral library of reference materials of interest. Another approach to detection and identification of explosives is through the use of the stoichiometry of the compound for discrimination by taking a ratio of the elemental peaks of interest. The strength of the carbon, hydrogen, oxygen, and nitrogen atomic emission lines obtained with LIBS (which span the ultraviolet to near infrared regions) and linear correlation techniques are commonly used to identify organic com-

pounds and allow sorting of a variety of plastics, including polystyrene and high-density polyethylene [30]. Subtle differences in the carbon and hydrogen intensities enabled successful identification of 90% to 99% of samples. In addition to the absolute intensities of the atomic emission lines, the peak intensity ratios of these lines (C:H, C:O, C:N) were used to analyze samples [31, 32]. The ratios determined from the calibration curves were compared with the actual stoichiometries and showed high accuracy with uncertainty of 3% on average.

The appropriateness of LIBS for identifying organic compounds based on atomic emission intensity ratios led researchers to investigate characteristics of LIBS spectra of explosive compounds. Carbon, hydrogen, oxygen, and nitrogen are found in most military explosives. A common characteristic of most explosives is their high nitrogen and oxygen content relative to the amount of carbon and hydrogen. By tracking the amounts of oxygen and nitrogen in a sample relative to the other elements, it is possible to determine if a compound is energetic or non-energetic. LIBS spectra for explosive Hexahydro-1,3,5-trinitro-s-trazine (RDX) and a non-explosive (diesel fuel) were obtained. Figure 5 shows the O/C ratio calculated from each individual spectrum collected with single-pulse LIBS for the diesel fuel and the RDX residue. Everything above a certain O/C threshold is classified as an energetic material while everything below is classified as a non-energetic. Instead of relying on one ratio, we can use all the atomic emission ratios associated with the energetic material calculated from the LIBS spectra (O/C, O/H, N/C, N/H, and O/N).

Although explosive residues can be identified on the base of elemental ratios of carbon, hydrogen, nitrogen, and oxygen, the entrainment of atmospheric oxygen and nitrogen into a laser-induced plasma complicates the discrimination of energetic and non-energetic materials.

To minimize oxygen and nitrogen contribution from the atmosphere, it is necessary to track the true amount of oxygen and nitrogen relative to carbon and hydrogen in a LIBS spectrum. Two methods for diminishing the atmospheric interference have been studied: displacing the atmosphere with an inert gas and double-pulse LIBS.

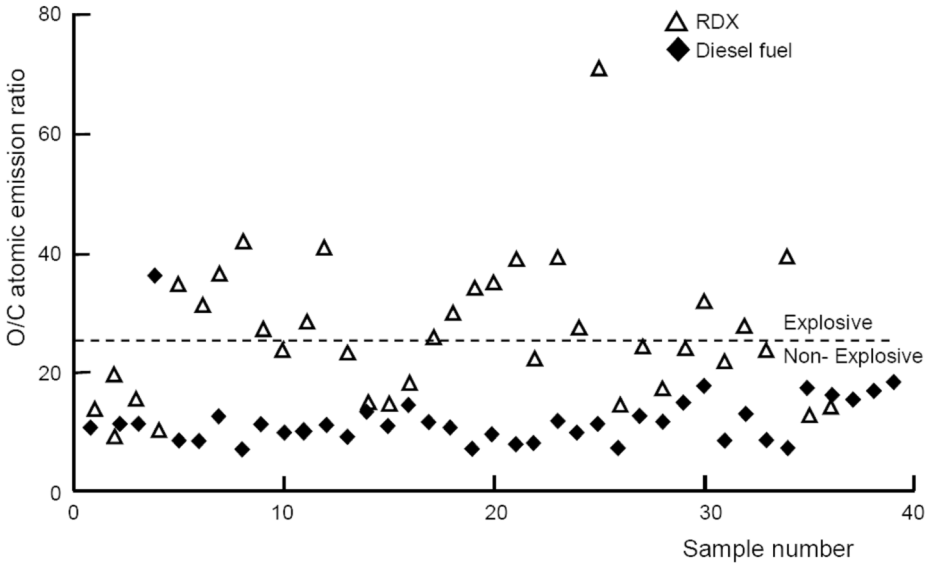

Fig. 5. O/C peak atomic emission ratio for single-pulse LIBS spectrum taken of RDX and diesel fuel samples. (The dotted line represents the rating threshold).

The formulation of Hexahydro-1,3,5-trinitro-s-trazine (RDX) has equal amounts of O and N. Air alone has more nitrogen (80%) relative to oxygen (20%). Displacing the surrounding atmosphere with argon eliminates all atmospheric nitrogen and oxygen.

The nitrogen and oxygen atomic emission lines in the LIBS spectra collected from samples under argon buffer gas are reliable characteristics of the material composition. Double-pulse LIBS can be used to reduce the amount of air entrained in the laser-induced plasma and improve the discrimination of energetic and non-energetic materials. Eliminating the nitrogen and oxygen contribution from the air using double-pulse LIBS results in a larger O:N ratio characteristic of an explosive material that is much closer to the true ratio value of the sample than the ratio obtained from single-pulse LIBS [33]. For double-pulse LIBS was obtained more than 90% detection of RDX compared to 25% with single-pulse LIBS. The double-pulse technique, although not quite as effective as displacing the atmosphere with an inert gas in order to minimize atmospheric oxygen and nitrogen interference, has the advantage of being applicable to stand-off LIBS systems. The data from the double-pulse LIBS based on several atomic emission ratios represent 100% identification of RDX with 0% false positive rate.

Single-shot spectra of nerve agent simulants (dimethyl methyl phosphonate DMMP, $C_3H_9O_3P$ and diisopropyl methyl phosphonate DIMP, $C_7H_{17}O_3P$) and interferents (plant food fertilizer and liquid detergent) were acquired at 20 m using the stand-off LIBS system. Even though both simulants contain the same elements, the ratios of the atomic/molecular emission lines can be used to discriminate between them. Single-shot spectra of the anthrax surrogate *Bacillus subtilis* (also known as *Bacillus globigii* or BG*)*, the ricin surrogate ovalbumin, and 24 potential interferents, such as dust, sugar, and fertilizer, were acquired at 20 m using a LIBS system. The samples were tested against a mathematical model for discriminant analysis and correctly identified [34].

Stand-off LIBS is an extremely promising technology for security applications (including chemical and biological hazard detection as well as explosives detection. Recent work at ARL demonstrated the detection and discrimination of explosive residues and explosive-containing mixtures as far as 50 m with a stand-off double-pulse LIBS system designed to minimize the air entrainment in the LIBS plasma. A ruggedized LIBS system with a 16-inch military-specified telescope, more powerful lasers, and effective stand-off limit >100 m is currently undergoing development and is expected to provide an important new tool in the fight against terrorism [34].

6. Conclusions

The results presented suggest that LIBS is a useful diagnostic tool for “in situ” chemical analysis by studying the atomic and ionic emission spectra from laser-induced plasma.

LIBS is completely optical technique; therefore, it requires only optical access to the sample. This is of major significance as fibre optics can be employed for remote analyses. Being an optical technique, it is non-invasive, non-contact and can even be used as a stand-off analytical technique when coupled to an appropriate telescopic apparatus. These attributes have significance for the use in areas from hazardous environments to space exploration. Additionally LIBS systems can easily be coupled to an optical microscope for micro-sampling adding a new dimension of analytical flexibility.

Since such a small amount of material is consumed during the LIBS process, the technique is essentially non-destructive or minimally-destructive. There is almost no specimen heating surrounding the ablation site. Due to the nature of this technique, sample preparation is typically minimized to homogenization or is often unnecessary if heterogeneity is to be investigated or where a specimen is known to be sufficiently homogeneous. This reduces the possibility of contamination in chemical preparation steps.

One of the major advantages of the LIBS technique is its ability to depth profile a specimen by repeatedly discharging the laser in the same point, effectively going deeper into

the specimen with each shot. This can also be applied for the removal of surface contamination, where the laser is discharged a number of times prior to the analyzing shot. LIBS is also a very rapid technique giving results within seconds, making it particularly useful for high volume analyses or on-line industrial monitoring.

Specialized optics or mechanically positioned specimen stage can be used to rater the laser over the surface of the specimen allowing spatially resolved chemical analysis and the creation of "elemental maps". This is very significant as chemical imaging is becoming more important in all branches of science and technology.

LIBS is one of several analytical techniques that can be deployed in the field as opposed to pure laboratory techniques. Recent research in LIBS is focusing on compact and portable systems. Portable LIBS systems are more sensitive, faster and can detect a wider range of elements (particularly the light elements) than competing techniques such as portable X-ray fluorescence. LIBS does not employ ionizing radiation to excite a sample, which is both penetrating and potentially carcinogenic.

In recent years, some techniques have been developed to improve the LIBS sensitivity, such as oblique incidence of laser upon the sample surface, dual-pulse excitation, LIBS at reduced pressures, use of magnetic field to confine laser-induced plasmas, etc.

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