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Laser-Induced Breakdown Spectroscopy:

Basic Fundamentals, Principle, Measuring Parameters and Applications.

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***Abstract*— Since 1980s, Laser-Induced Breakdown Spectroscopy (LIBS) has been developed, (LIBS) is a type of atomic emission spectroscopy which uses a highly energetic laser pulse as the excitation source. The laser is focused to form a plasma, which atomizes and excites samples. The formation of the plasma only begins when the focused laser achieves a certain threshold for optical breakdown, which generally depends on the environment and the target material. The versatility of (LIBS) has been demonstrated in various industrial application. Laser-induced breakdown spectroscopy will be discussed in this article including its fundamentals, industrial applications, and challenges.**

***Keywords*— LIBS; Plasma parameters; Applications**

I. INTRODUCTION

Laser radiation is a high-quality form of electromagnetic energy enabling a multitude of new methods and applications, such as material processing, biomedical and communication technologies, and measuring methods. The advantages of lasers in measuring technologies are the noncontracting measurement, high flexibility, and high measuring speeds. Due to these features, laser measuring methods and applications have encountered a dynamic development during the last years. Laser measuring methods were introduced successfully in production technology, process engineering, quality assurance, environmental technology, and life sciences. The most important measuring quantities are:

•Geometrical quantities, such as distance, contour, shape, roughness, strain

•Dynamic quantities, such as velocities, vibration modes

•Thermodynamic and chemical quantities, such as temperature, density, concentration and chemical bonds. The above-mentioned quantities are determined preferably with the use of spectroscopic methods.

From the very first the invention of laser was tightly linked with spectroscopic questions **[1]**. The special properties of laser radiation enable a variety of new spectroscopic methods to analyze the chemical constituents of a substance or to determine their physical state. Examples are laser absorption spectroscopy, light detection and ranging (LIDAR), laser-induced fluorescence (LIF), and coherent antistokes Raman spectroscopy (CARS) **[2-3]**. On the one hand, the tunability of the laser wavelength to atomic or molecular transitions allows for a high selectivity, and on

the other hand the high spectral brightness of laser radiation enhances the detection sensitivity enabling the

determination of traces. Laser spectroscopic methods are a powerful tool for fundamental investigations, such as high-resolution spectroscopy within the Doppler width to study the fine structure of excited states **[4]**. Femtosecond laser pulses allow observing directly the dynamics of chemical reactions. The Nobel prize for physics in the year 1999 was awarded to A. Zerwail for his pioneering work in this field **[5]**. In an increasing degree laser spectroscopy enters into new application fields. Among these are the remote investigation of harmful substances in the atmosphere, the monitoring of combustion processes or material-dependent production processes, and the quality assurance of semi-finished products **[6-7-8-9]**. For technical applications, laser spectroscopic methods are of special interest as they are able to determine several species simultaneously with minimum equipment. Laser-induced breakdown spectroscopy (LIBS) belongs to these methods **[10].** Fundamentals and applications of LIBS are the subject of this book. LIBS is able to analyze solid, liquid, and gaseous substances. In principle, laser absorption spectroscopy and LIF are also able to determine several species, but in this case different laser wavelengths are necessary, which cause a corresponding high instrumental effort for technical applications.

- **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, selfabsorption effect, signal enhance- ment, and some other fundamental researches have been studied extensively to promote LIBS technique **[11-15]**. 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 param- eter. 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 404 Plasma Science and Technology - Progress in Physical States and Chemical Reactions 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 **[16]**. 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 acquis- ition 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 **[17]**. 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 **[18]**. 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 **[19]**. 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 **[20]**. 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 **[21-23]**. Besides signal enhancement, there were also some other studies worth mentioning. The selfabsorption in laser-induced plasma was studied. The results suggested that the selfabsorption effect could be alleviated by the selection of suitable atomic line, operating at higher pulse energy and detecting with longer delay **[24]**. The pressure effect on the plasma emission from fundamental 0.1 to 40 MPa in bulk seawater was investigated **[25]**. 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. Industrial Applications of LaserInduced Breakdown Spectroscopy .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 **[26,27]**. 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 **[28-30]**. 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 **[31-36]**, 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 analytic 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 **[37]**. 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. **[38, 39]**. 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 406 Plasma Science and Technology - Progress in Physical States and Chemical Reactions alloys **[40]**. 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) are 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 **[41,42]**. 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 Setup for LIBS and Measuring Procedure**
- **3.1 Setup**

Figure (1) shows the principal setup for laser-induced breakdown spectroscopy. A mirror guides the pulsed laser radiation to a focusing lens. The sample to be analyzed is placed in a measuring chamber. As a rule, the incident direction of the laser radiation is oriented perpendicularly to the sample surface. The focused radiation generates a plasma at the sample surface. The emission of this plasma is observed in a direction, which includes an angle ¸O to the incident direction of the laser radiation. In figure (1), the measuring radiation is transmitted via a fiber optics to a spectrometer, where it is spectrally dispersed and converted to electrical signals. The measuring chamber is gas tight. Laser radiation and measuring radiation are transmitted via built-in windows. Via gas fittings the type of gas filling as well as the gas pressure and gas exchange rate can be adjusted in a defined manner. A translation stage moves the sample in relation to the incident laser beam to measure at different locations on the sample surface. The use of a measuring chamber is not a necessary precondition for laser induced breakdown spectroscopy. For inline analyzing tasks, the measuring chamber is often set aside and the measurement is performed under atmospheric conditions. In this case, the usable measuring radiation is limited to wavelength greater than 190 nm, since air absorbs shorter wavelength strongly. For quantitative measurements with high requirements on measuring precision and uncertainty, a measuring chamber is used to adjust the ambient gas conditions and the gas exchange at the interaction region in a defined way.

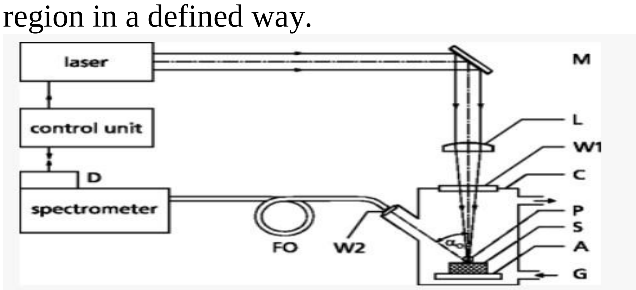

Figure1: Fig (1) Setup for laser-induced breakdown spectroscopy; M= mirror, L = focusing lens, W1 = window of the laser radiation, C = measuring chamber, P = laser-induced plasma, S = sample, A = translation stage, G = gas fitting, ¸o = observation angle, W2 = window for the measuring radiation, FO = fiber optics, D =detectors

A control unit triggers the laser and reads the signals of the detectors. To improve the signal-to-noise ratio the plasma radiation is recorded only during the life time of the plasma. For this purpose, the spectrally dispersed radiation is detected time resolved and integrated over a time gate within the life time of the plasma. The control unit adjusts the position and duration of that time gate. Figure (2) shows schematically the arrangement of components in an analyzing system based on LIBS.

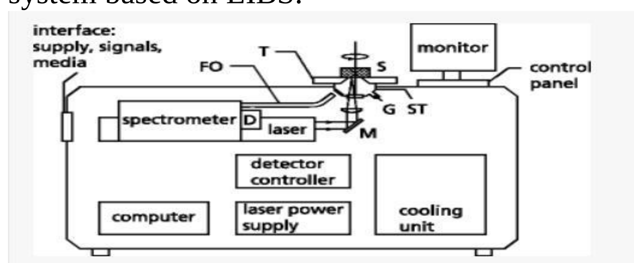

Figure2: Fig(2) Arrangement of components in a LIBS-based analyzing system; T = sample table, S = sample, ST = sample stand, FO = fiber optics, G = gas supply, D = detector, M = mirror.

The sample is positioned on a sample table. The laser beam is focused onto the bottom side of the sample. The sample table can be set into rotation, whereby the rotational axes and the optical axes of the incoming laser beam are parallel and shifted laterally. Due to this eccentricity, a relative motion between sample and laser beam occurs, where the locations of laser irradiation lie on a circle. By this a spatial averaging is realized. Sample table and measuring chamber are parts of the so-called sample stand. Figure (3) shows a view of an analyzing system. The sample stand can be seen on the left side at the top of the system

Figure2: Fig (3) Analyzing system based on LIBS. Left: sample stand

3.2 Measuring Procedure

A measuring procedure comprises the following steps: 1. Definition of a measuring method or retrieval of a measuring method which was already defined. Putting the sample on the sample stand 2. Start of the measurement 3. Evaluation of the spectral signals 4. Display of the measuring results A measuring method is defined in particular by the selection of measuring parameters and their temporal sequence, cf. Sect. 11.1. Measuring parameters are, e.g., the laser pulse energy, the number of prepulses and measuring pulses, and the gas flow in the measuring chamber. These various parameters influencing the measuring process will be discussed in more detail in Chap. 3. A typical measuring sequence for a quantitative analysis of a sample including data evaluation takes about 30 s–2 min. For an identification testing of work pieces, inspection times of a few seconds or even fractions of a second are achievable, cf. [43].

• 4. LIBS Applications

LIBS is useful in a wide range of fields, namely, those which can benefit from a quick chemical analysis at the atomic level, without sample preparation, or even in the field. This paragraph compiles the most important applications at this moment.

4.1. LIBS in Archeology and Cultural Heritage.

Samples with archeological or cultural value are sometimes difficult to analyze. These samples cannot usually be moved or destroyed for analysis, and some chemical techniques to prepare the sample or a controlled environment in a laboratory are needed. In the first place, portable LIBS devices can be used, solving the problem when the sample cannot be moved. In the second place, LIBS do not need contact to analyze the sample, avoiding damage in valuable samples. Although LIBS ablates an amount of the sample, the crater is nearly microscopic and practically invisible to the eye. In addition, this microscopic ablated surface improves the spatial resolution, providing accurate spatial analysis and even a depth profile analysis of the sample. The sample does not need to be prepared; hence the analysis is clean and fast. Besides, LIBS probes based on optical fibers allow the analysis of samples with difficult access. Despite these facts, LIBS is a microdestructive technique and the researcher should pay attention to experimental parameters in order to avoid critical damage in valuable samples. Many cultural heritage artifacts can be analyzed with the right LIBS set-up. LIBS is feasible with virtually all types of materials, for instance ceramics, marble, bones, or metals, usually applying quantitative analysis. The most common analysis attempts to determine the elemental composition of the sample in order to help to date it **[74– 77]**, but it works with bones for analysis of paleodiet **[75]**. LIBS has been used with delicate samples such as Roman coins **[78]** or other metallic alloys like bronze [74], even under water **[79]**. In the field of painting, it can determine the elements that compose the pigments. This analysis of pigments can help to date and authenticate frescos or paintings [80]. Moreover, LIBS can be used, combined with other techniques, in order to sum the potential of them, such as Raman or X-ray fluorescence (XRF) **[78, 81, 82].**

4.2. LIBS in Biomedical Applications.

Biomedicine and LIBS are fields that have not been working together for long. For that reason, this field may provide a large number of new developments in a few years. LIBS can analyze chemical compositions of biological samples such as human bones, tissues, and fluids **[83]**. LIBS can help to detect excess or deficiency of minerals in tissue, teeth, nails, or bones, as well as toxic elements **[83, 84]**. In the same way, cancer detection is possible with LIBS and it can provide a surgical device which can detect and destroy tumor cells at the same time **[85]**. In addition, classification of pathogenic bacteria or virus is possible too **[86, 87]**. The analysis of samples from plants is difficult, because they need a difficult preparation of the sample based on acid digestion processes in order to obtain accurate analysis of micronutrients. LIBS can provide a fast analysis tool with easy sample preparation, for instance in micronutrient analysis of leaves **[88].**

4.3. LIBS in Industry.

LIBS has been targeting many industrial processes for many years, because it is a fast analytical tool well suited to controlling some manufacturing process. Moreover, LIBS can work at a large range of distances, allowing analysis of samples in hazardous and harsh environments. For example, remote detection of explosives has been assessed with LIBS **[89]**, even at trace levels **[90]**. In the nuclear energy industry, the effects of radiation on living beings and devices are widely known. LIBS can work far away from nuclear waste or reactors, using stand-off configuration or with fiber optic probes, avoiding dangerous radiation levels **[91, 92]**. In the metallurgical industry, smelters, and final products can reach high temperatures, and LIBS can analyze the alloy compositions in production line or detect impurities in other production sectors, such as the automotive industries **[93–95]**. LIBS can also be useful to detect toxic products like heavy metals in industrial wastes **[96]**. These waste products should be recycled or stored, and knowing the elements in them can provide key data to reduce the environmental impact of the process. In the renewable energy field, analysis and detection of impurities in solar cells can be a useful tool to improve the manufacturing processes or to achieve high efficiency solar panels. There are recent research works in this field **[97]** although there is a huge amount of work to do.ISRN Spectroscopy 9

4.4. LIBS and Geological Samples.

The Analysis of some kinds of minerals is possible using LIBS, in particular, of soils and geological samples in situ **[98]**. Sample features can strongly affect the experimental conditions and reduce the accuracy, but quantitative analysis is still possible **[99]**. LIBS analysis can detect traces of toxic material in soils, rocks, or water without sample preparation and in the natural environment of the sample. LIBS can work in a wide range of environmental conditions and with different atmospheres, from air to vacuum. This feature, coupled with the capability to analyze soil samples and the possibility to build a portable set-up, enables the possibility to work in the space. Recently, a spacecraft has been launched to Mars to provide spectral analysis of Mars, geological samples **[100]**. This spacecraft contains, among other things, a hybrid LIBS-Raman spectrometer

II. CONCOLUTION

In this paper, we firstly designed a framework consists of goals, benefits, security requirements and a flow diagram for the assessment of a New Authentication Protocol FPE for Smart Card Using Fingerprint

Finally, we have analyzed and compared both the schemes

according to the desired criteria of the framework and proved that our proposed scheme is far better than other hash based authentication schemes.

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