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REVIEW ON LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

Farah Gamal Atshan
Department of Laser Physics ,College of Science for Girls, University of Babylon
Corresponding Author: umtamara199@gmail.com

ABSTRACT

This paper describes the fundamentals, instrumentation, applications and future trends of an analytical technique that is in its early stages of consolidation and is establishing its definitive niches among modern spectrometric techniques. The technique has been named Laser Induced Breakdown Spectroscopy (LIBS) and its main characteristic stands in the use of short laser pulses as the energy source to vaporize samples and excite the emission of electromagnetic radiation from its elements and/or molecular fragments. The emitted radiation is analyzed by high resolution optics and the intensities are recorded, usually by fast triggered solid state detectors. Together, these devices allow producing and registering a wide ranging emission spectrum of the short-lived phenomenon induced by the laser pulse. The spectrum contains qualitative and quantitative information which can be correlated with sample identity or can be used to determine the amount of its constituents. This review is divided in three parts. First, the relevant historical and theoretical concepts associated with LIBS are presented; then the main practical aspects of the several experimental and instrumental approaches employed for implementation of the technique are critically described; the applications related in the literature, including those making use of chemometrics, are classified and exemplified with relevant and recently published work.

Keywords: Laser Induced Breakdown Spectroscopy, LIBS, atomic emission spectroscopy.

Introduction

Analytical techniques based on emission of electromagnetic radiation produced after excitation of atoms, ions or molecules present in a sample have been around for quite a while. Usually, these techniques employ some type of energy source to promote the species present in the sample to higher energy levels from where they decay, emitting characteristic radiation that is collected, sent to a wavelength selector and detected. The sample can be a solid, liquid or gas. However, some of the emission techniques can not deal directly with the original samples and some type of treatment must precede their presentation for analysis. Although the measurement step is rapid, precise and sensitive, sample treatment is often slow, cumbersome and prone to induce errors due to contamination and losses. Furthermore, the necessity of sample treatment limits the use of these techniques in the field, a requirement increasingly under investigation to match the interests of the Environmental Chemistry, Process Analytical Chemistry, Forensic Analysis, Archaeological Analysis and many others areas of science that present sound arguments to make a reality of the dream of take the instrument to the untouched sample and not the inverse. This review describes a modern analytical technique based on emission spectroscopy that employs a short pulse of high energy radiation generated by a laser focused on a sample, in order to attain representative vaporization and excitation. The technique is named Laser Induced Breakdown Spectroscopy (LIBS) and numerous reviews1-11 and three recent text books12-14 have already been published addressing both general and specific aspects, in the relatively short period after the technique had undergone a renewed interest in the beginnings of the eighties. On the other hand, the technique has recently experienced an exponential growth in interest, reflected by an increasing number of publications, and, apparently, its niche in the general field of Analytical Chemistry are ready to be defined. Therefore, the expectation of the present review on the fundamentals, instrumentation and applications of LIBS, including most recent achievements, is to help those who want to be introduced to the technique while providing up-to-date information on instrumentation, applications and its real potential for micro and remote essentially non-destructive and direct analysis.

1. Historical summary

The laser is the fundamental and distinctive part of the LIBS instrument. Therefore, this technique's history passes, initially, by the theory of stimulated emission of radiation proposed by Einstein early in 1917,15 which later made the laser existence possible. The first insight on a laser operating in the visible spectrum range was due to Shawlow and Townes in 1958.(1) Maiman constructed the first ruby laser employing optical pumping in 196017 and two years later Brech and Cross detected, for the first time, the spectrum of a plasma induced in a material vaporized by a ruby laser.(2) However, an auxiliary spark source was employed to produce the plasma and subsequent spectral emission. The first direct spectral analysis made by LIBS can be attributed to Runge et al. in 196419 and the first model for the laser breakdown of a gas was proposed only one year later by Zel'dovich and Raizer.20 The first commercial instruments were fabricated by Jarrell-Ash and Carl Zeiss in the beginning of the 70's. However it should be mentioned that these instruments employed the energy of the laser pulse only to ablate the sample while excitation was made by an electric arc. The advent of more stable, fast and robust lasers, with better beam quality, high resolution/wide spectral range dispersion optics (such as the echelle based spectrographs), and sensitive gated image detectors based on arrays of intensified charge coupled devices (ICCD) provided strong impulses towards improving and applying LIBS since the beginning of the 80's.21,22 The last 26 years have witnessed the results of the efforts made by a number of companies and research laboratories towards the development of commercial instruments, of new applications and of theoretical models providing a profound insight into the fundamentals of LIBS and associated phenomena. In the last decade, for instance, the number of papers related to fundamentals and applications of LIBS reached about 600. The number of papers published on LIBS during the year of 2005 was about 350 and an exponential growth may be foreseen for this technique.(4).

2. The LIBS concept and related phenomena

2.1 Initiation of the induced plasma

Recently, it has been accepted that the acronym LIBS should be used to refer to the spectroscopic technique that employs a laser pulse as the only source of energy to simultaneously prepare the sample and produce an emission spectrum of analytical value. The name of the technique does not include a "plasma" term. The main reason for this omission is in the fact that the LIBS is not always characterized by plasma formation.(5). A Debye number with values equal or higher than unity (in order to achieve a plasma condition) is not always observed in a LIBS experiment. Therefore the acronym LIPS where the "P" states for "plasma" is not recommended,(6). although it is still possible to find, in the specialized literature, papers employing this acronym for the same technique as LIBS. The LIBS concept, which distinguishes the technique from others based on induced spectral emission, is that of using a laser pulse to ablate a minute quantity of the material to a condition that may then be excited by the energy supplied by the same pulse or by a subsequent pulse. This latter case involves the double-pulse technique, also described in this work. Of course, if the material is already in the gaseous phase, part of the energy does not need to be spent in sample vaporization. Many of the distinct characteristics of LIBS, such as its quasi-nondestructive and micro-analytical character, speed, in field and remote applications for both conductive and non conductive samples, which can be liquids, solids and gases or even in aerosol forms, come from this concept. The basic phenomena that need to be considered to understand and control a LIBS experiment for its evolvement into a useful analytical tool are: first, those related with the laser interaction directly with the sample; then, later, the laser interaction with the ablated material (electrons, molecules, atoms, ions and tiny particles) and the coupling of its remaining pulse energy are of primordial importance to reach a condition of reproducible and sensitive excitation and spectral emission. The irradiance is a very important paramenter regarding the effects caused by the laser interaction with the sample and plasma evolution. The average irradiance of a stigmatic collimated pulsed laser beam at the focusing area (beam waist) is given by:

$I\ f = \pi EL\ D2 / 4\tau L\ f\ 2\ \lambda 2\ (M\ 2\ )\ 2$. (7).

where If is the irradiance (usually expressed in W m-2), EL is the energy of the laser pulse, D is the diameter of iluminated aperture of the focusing lens (or the laser beam diameter), τL is the pulse duration, f is the lens focal length, λ is the laser wavelength, and M 2 is the the beam propagation ratio. For a beam ideally Gaussian, M 2 is equal to 1. Typical values for beams produced by Nd:YAG lasers are between 2 to 10. Fluence is the time integrated value in J m-2. , schematically, what happens at and near the point where a short duration laser pulse of sufficient energy strikes the surface of a solid sample. The sequence of events starts with the breakdown of the material, local heating occurs and a high pressure vapor is produced while a shock wave, propagating at supersonic speed, is created as the vapor expands. (8).This initial interaction of the laser beam with a material is not a simple matter and depends on many characteristics of both the laser and the material. From this first moment on, the evolution of the plasma depends on a series of other factors related, for instance, to the irradiance of the laser (W m-2), to the size of the vapor bubbles and the vapor composition and to the composition and pressure of the atmosphere surrounding the sample, as well as, to the laser wavelength. The breakdown of the target material, occurring at the initial moments after the laser pulse strikes the sample target (up to few ps), is reached when the density of free carriers (electrons) reaches about 1018 cm-3. The existence of such a quantity of free electrons promotes a high optical absorption in the plasma, allowing it to be extended in direction of the beam which sustains it for the remainder of the laser pulse.(9)..

2.2. Plasma evolution and termination

Although the initial phenomena involved in the establishment of the initial breakdown plasma differ as a function of the nature of the target sample, its further evolution apparently occurs in a similar way.(10). The ablated material expands at supersonic velocities producing a shock wave which propagates from the surface towards the surrounding atmosphere. The laser plume continues to absorb energy from the laser during the duration of the pulse, the species are excited producing an emitting plasma that is visible to the naked eye. Then the plume starts to reduce its velocity of propagation due to collisions with the surrounding gas, and slows down to speeds close to that of sound. The plasma will then cool down by self absorption (quenching) and recombination between electrons and ions, generating neutral species and clusters after plasma extinction. A typical time elapsed since the initiation of the process of plasma formation, shortly after the laser pulse reaches the sample surface, till its extinction, is from a few tenths of microseconds to a few milliseconds.(11)

3 .Wavelength Selectors

Spectrographs based on different set-ups of diffraction gratings, lenses and mirrors, such as the well known Czerny Turner and Paschen Runge designs, have been intensively employed in LIBS for many years and are still used.94,132,136-138 However, due to the high complexity of LIBS spectra, with multiple emission lines (many sometimes at very close wavelengths) from the vacuum ultraviolet to the near infrared (according to the elements present in the sample), an ideal wavelength selector for LIBS should have the capability of covering large wavelength ranges simultaneously and with high resolution, which is not the case with conventional grating spectrographs. These wavelength selectors can either cover a short wavelength range with high resolution, decreasing the capability of multielement detection, or cover a wide wavelength range with lower resolution, sometimes resulting in problems of detection of specific emission lines due to their overlapping with other lines. In order to overcome these limitations and to avoid more expensive instrumentation,(12). Body and Chadwick136 employed up to four grating-based spectrographs, simultaneously covering different spectral regions with high resolution, to analyze the radiation emitted by the plasma. In spite of the limitations, grating spectrographs are still important in designing low cost instruments, such as that described by Neuhauser et al. 137 using a Paschen Runge design in a Rowland circle type spectrograph. Another important feature is the capability to be compacted in miniaturized devices coupled to detecting systems composed of a linear array of sensors (discussed later). These kinds of spectrometers, available commercially, have been used in many works.(13). In the last years, a kind of spectrograph already used in other atomic emission spectroscopic techniques since the 1990s,139,140 called echelle spectrograph, which comprises a special kind of grating in a specific design, is being increasingly used in LIBS. It is also compact and, associated with appropriate detectors, constitutes a spectrometer covering a wide range of wavelengths (commonly from 200 up to 1000 nm) with a high resolving power ($\lambda/\Delta\lambda$ up to above 10000). The echelle technology has been developed since about the early 1950s,(14,15) and the first applications of echelle spectrographs in LIBS date from the late 1990s.(16,17).

4. Medical and Biological Applications

Samek et al. 285-287 reported on quantitative LIBS analysis to study the presence of trace minerals in teeth. In these papers, selections of teeth from different age groups were investigated. The samples showed a series of elements normally present in trace amounts in biological specimens. The authors concluded that the concentrations of aluminium found in the teeth under investigation could most likely be attributed to the use of toothpaste with whitening additives as well as the presence of fillings. Samek et al. (17).reported on the application of LIBS to the analysis of important minerals and the accumulation of potentially toxic elements in calcified tissue to trace the influence of environmental exposure and other medical or biological factors. This paper exemplified quantitative detection and mapping of Al, Pb, and Sr in representative samples, including teeth and bones. They studied this approach in detail for traces of Al, Pb, and Sr in over 50 specimens. Sun et al. (18). investigated the feasibility of using LIBS as a quick and simple technique to analyze trace elemental concentrations in the stratum corneum of human skin. A 60 mJ pulse-1 Nd:YAG laser operating at 1064 nm (pulse duration of 5 ns) was used to form the laser-induced plasma. An analytical curve with a linear correlation coefficient of 0.998 and a detection limit of 0.3 ng cm-2 were obtained for Zn.(19). The results indicate that Zn was absorbed through the skin and the concentration decreased exponentially with depth into the skin. Corsi et al. (20). analyzed the concentration of the main minerals present in human hair by calibration-free laserinduced breakdown spectroscopy (CF-LIBS). The results showed that CF-LIBS can be considered as a very promising technique for hair tissue mineral analysis. This technique allows for the determination of relative concentrations of the most interesting elements in hair, at levels of a few mg per 100 g of materials. Fang et al(21). used the LIBS technique to analyze and identify elemental constituents of urinary calculi. The results showed that the elements detected with this study were: Ca, Mg, Na, Sr, K and Pb. In this study they concluded that the technique offers the possibility of accurate measurements of trace elements in such stones without the need for any elaborate sample preparation, but for quantitative measurements the system needs to be calibrated for each elemental species.(22),

References

1. Song, K.; Lee, Y.; Sneddon, J.; Appl. Spectroc. Rev. 1997, 32, 183.
2. Rusak, D.A.; Castle, B.C.; Smith, B.W.; Winefordner, J.D; Trends Anal. Chem. 1998, 17, 453.
3. Martin, Z.M.; Cheng, M.D.; Martin, R.C.; Aerosp. Sci. Technol. 1999, 31, 409.
4. Sneddon, J.; Lee, Y.; Anal. Lett. 1999, 32, 2143.
5. Radziemski, L.J.; Spectrochim. Acta, Part B 2002, 57,1109.
6. Song, K.; Lee, Y.; Sneddon, J.; Appl. Spectrosc. Rev. 2002, 37, 89.
7. Tognoni, E.; Palleschi, V.; Corsi, M.; Cristoforetti G.; Spectrochim. Acta, Part B 2002, 57, 1115.
8. Song, K.; Lee, Y.; Sneddon, J. In Advances in Atomic Spectroscopy-Volume 7; Sneddon, J., ed.; Elsevier Science: Amsterdam, 2002, ch. 6.
9. Winefordner, J.D.; Gornushkin, I.B.; Correll, T.; Gibb, E.; Smith, B.W.; Omenetto, N.; J. Anal. At. Spectrom. 2004, 19, 1061.
10. Vadillo, J.M.; Laserna, J.J.; Spectrochim. Acta, Part B 2004, 59, 147.
11. Santos Jr., D.; Tarelho, L.V.G.; Krug, F.J.; Milor, D.M.B.; Martin Neto, L.; Vieira Jr. N.D.; Rev. Analytica, 2006, 24, 72.
12. Cremers, D.A.; Radziemski, L.J.; Handbook of Laser-Induced Breakdown Spectroscopy, Wiley: New York, 2006.
13. Misiolek, A.W.; Palleschi, V.; Schechter, I. eds.; Laser Induced Breakdown Spectroscopy, Cambridge University Press: Cambridge, 2006.
14. Singh, J.P.; Thakur, S.N. eds.; Laser Induced Breakdown Spectroscopy, Elsevier Science:Amsterdam, 2006.
15. Einstein, A.; Phys. Z. 1917, 18, 121.
16. Shawlow, A.L.; Townes, C.H.; Phys. Rev. 1958, 112, 1940.
17. Maiman, T.H.; Nature 1960, 187, 493.
18. Brech, F.; Cross, L.; Appl. Spectrosc. 1962, 16, 59.
19. Runge, E.R.; Minck, R.W.; Bryan, F.R.; Spectrochim. Acta, Part B 1964, 20, 733.
20. Zel'dovich, Y.B.; Raizer, Y.P.; Sov. Phys. JEPT 1965, 20, 772.
21. Radziemski, L.J.; Loree, T.R.; Cremers, D.A.; Hoffman, N.M;. Anal. Chem. 1983, 55, 1246.
22. Cremers, D.A.; Radziemski, L.J.; Anal. Chem. 1983, 55, 1252.