# LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

Laser-induced breakdown spectroscopy (LIBS) is an emerging technique for determining elemental composition in real-time. With the ability to analyze and identify chemical and biological materials in solids, liquids, and gaseous forms with little or no sample preparation, it is more versatile than conventional methods and is ideal for on-site analysis.

This is the first comprehensive reference book explaining the fundamentals of the LIBS phenomenon, its history, and its fascinating applications across 18 chapters written by recognized leaders in the field. Over 300 illustrations aid understanding.

This book will be of significant interest to researchers in chemical and materials analysis within academia, government, military, and industry.

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# LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

## Fundamentals and Applications

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# Preface

**Richard E. Russo and Andrzej W. Miziolek**

LIBS (laser-induced breakdown spectroscopy) has been described as "a future super star" in a 2004 review article by Dr. James Winefordner, a world-renowned analytical spectroscopist.[1] LIBS is the only technology that can provide distinct spectral signatures characteristic of all chemical species in all environments. LIBS can be used to chemically characterize any sample: rocks, glasses, metals, sand, teeth, bones, weapons, powders, hazards, liquids, plants, biological material, polymers, etc. LIBS can be performed at atmospheric pressure, in a vacuum, at the depths of the ocean, or extraterrestrially. LIBS can respond in less than a second, indicating if a spilled white power is innocuous or hazardous, using a single laser shot. A unique attribute of LIBS is that samples do not need to fluoresce, or be Raman or infrared (IR) active. It is the simplicity of LIBS that allows this diversity of applications; simply strike any sample with a pulsed laser beam and measure a distinct optical spectrum. The laser beam initiates a tiny luminous plasma from ablated sample mass. The plasma spectrum is a signature of the chemical species in the sample; spectral data analysis provides the chemical species composition and relative abundance. Because a pulsed laser beam initiates the LIBS plasma, there is no physical contact with the sample; laboratory and open-path standoff applications are readily employed. Simply put, the LIBS phenomenon represents an efficient engine to convert the chemical information of the target material to light information that can be captured efficiently and analyzed thoroughly by modern spectroscopic instrumentation and data analysis/chemometrics software.

LIBS has been aggressively investigated for environmental, industrial, geological, planetary, art, and medical applications since the early 1980s, although initial LIBS papers appeared with the discovery of the ruby laser in 1962.[1] A comprehensive source of literature describing LIBS research and applications can be found in *Applied Optics*,[2] which dedicated a special issue to this technology, as well as an extensive review in 2004.[3] Although traditionally classified as an elemental analysis technology, the use of broadband high-resolution

[1] J. D. Winefordner, I. B. Gornushkin, T. Correll, E. Gibb, B. W. Smith, and N. Omenetto, Comparing several atomic spectrometric methods to the super stars: special issue on laser induced breakdown spectrometry, LIBS, a future super star. *J. Anal. Atom. Spectrom.*, **19** (2004), 106–108.
[2] See *Appl. Opt.*, **42** (30) (2003).
[3] W. B. Lee, J. Wu, Y.-III Lee and J. Sneddon, Recent applications of laser-induced breakdown spectrometry: a review of material approaches, *Appl. Spectros. Rev.*, **39** (2004), 27–97.

spectrometers has recently extended LIBS applications to molecular species identification. The ability to detect molecular and elemental signatures with a single laser pulse offers unprecedented performance for emerging medical, biological, environmental, and security applications.

With the growth and evolution of LIBS phenomenon understanding and application areas there has been a corresponding increase in LIBS practitioners, both engineers and scientists, as well as a growth in LIBS commercial activities, in both instrument manufacturing and applications for hire. In fact, the world-wide LIBS community has established a tradition of international conferences on a two-year cycle that include LIBS 2000 (Tirrenia, Italy), LIBS 2002 (Orlando, USA), LIBS 2004 (Málaga, Spain), and LIBS 2006 (Montreal, Canada). The European LIBS community has also established the EMSLIBS (Euro-Mediterranean Symposium) series with EMSLIBS 2001 (Cairo, Egypt), EMSLIBS 2003 (Crete, Greece), and EMSLIBS 2005 (Aachen, Germany). In addition there have been a multitude of LIBS symposia associated with Optical Society of America, Pittcon, and FACSS meetings.

This book describes the history, current research in understanding fundamental processes, research to improve measurement performance, and examples of numerous applications requiring parts per million (p.p.m.) and parts per billion (p.p.b.) detection levels. Several chapters describe research efforts dedicated to improving detection capabilities. Achieving sub-p.p.b. levels would allow LIBS to compete with vacuum-based mass spectrometric measurements, without requiring a vacuum. As described throughout this book, there is a tremendous international effort to advance the LIBS technology, by addressing multiple laser pulses, short duration laser pulses, and new instrumentation. One area to increase sensitivity would be to utilize ablated mass more efficiently; current LIBS analysis detects only a fraction of the mass ablated and excited to optical emission. Focused fundamental research on laser-induced plasmas will provide advanced knowledge for efficiently generating, exciting, and detecting mass. There is a large body of supporting literature on laser ablation for other applications (micromachining, materials fabrication, nanotechnology, thin-film deposition) that is germane to LIBS; the fundamental mechanisms are the same, but the optimum parameters for application are not. Optimum parameters need to be established for analyzing diverse samples, for example organic residues compared with inorganic refractory bulk samples. Understanding plasma physics can provide new approaches for increased sensitivity by using external (for example light, radio frequency, magnetic fields) means for producing longer-lived, hotter, and denser plasmas. There have been numerous efforts to study the influence of the laser beam properties (pulse duration, wavelength, energy, and number of pulses) on LIBS analytical performance. The laser beam can deliver energy from femtoseconds to microseconds in duration. On the other hand, the LIBS plasma duration is generally several microseconds, although research needs to establish laser–plasma–property time relationships.

Most LIBS applications are based on using a laser with wavelength of 1064 nm. Wavelength contributes to plasma heating with nanosecond pulses, but research needs to establish if IR is best when using short pulsed (femtosecond and picosecond) lasers, and the role of Bremsstrahlung absorption. The use of double and triple pulses is being aggressively investigated for improving sensitivity and reducing ambient interferences. Currently, the UV–IR (ultraviolet–infrared) spectral region is interrogated for analysis, but other spectral regions, such as hyperspectral, may provide enhanced measurement capabilities. Just as the broadband spectrometer opened new vistas in LIBS applications, understanding measurement principles will advance performance specifications for existing and new LIBS applications.

Implementation of LIBS in a suite of applications requires diverse yet similar instrumentation. For example, LIBS can be used with a simple lens to focus the laser beam within a few millimeters from the laser, with an optical fiber to carry the laser beam to a remote physical location, or by using a telescope for open-path standoff applications. Improved LIBS systems for long-distance standoff measurements will benefit from advanced optical configurations. Other spectroscopic technologies (Raman, fluorescence, absorbance, light scattering) perform in open-path configurations, although they do not possess the versatility of LIBS. However, it would be easy to integrate LIBS with Raman and laser-induced fluorescence for additional measurement capabilities. An integrated system could use light scattering to identify a suspect particle based on its morphology and then Q-switch the same laser for simultaneous LIBS – all in the same system. A concern for open-path standoff laser-based analysis is eye safety. Although the FDA in the USA has established limits for pulsed exposure, these limits are for unfocused laser beams; LIBS requires a focused laser beam. As research progresses to advance LIBS sensitivity using various laser wavelengths, low-level eye-safe operation will be viable.

New applications of LIBS are expected in medical, biological, security, and nanotechnology. With the international effort to fabricate nano-devices, -structures, and -particles, new technologies will be required to ensure that these systems abide by their design criteria. LIBS can fulfill this requirement, but will need to operate on smaller spatial scales and with enhanced sensitivity. The widespread utilization of LIBS for these applications will require development of comprehensive spectral databases and data manipulation algorithms. Spectral libraries can be established for voluminous chemical species and rapidly be evaluated to determine distinct signature for classes of species. Mass spectroscopy, Raman spectroscopy, fluorescence, IR, NMR (nuclear magnetic resonance), and almost all spectral analytical technologies benefit from the use of spectral libraries – as will LIBS.

This book challenges you to benefit from the current expertise and to imagine new applications and ideas for advancing LIBS. The chapters present the current status of fundamental and applied LIBS studies, from a community excited by the numerous capabilities and possibilities. Chemical analysis is a critical component of world survivability – for understanding nature, contamination, health, climate, microelectronics, terrorism, advanced materials, and other things. We believe that LIBS will play a dominant role in every aspect of society for chemical analysis. With continued research and application, LIBS is becoming a future super star of analytical spectroscopy.