Preface

*Laser-Induced Breakdown Spectroscopy* (LIBS) also known as laser-induced plasma spectroscopy (LIPS) or laser spark spectrometry (LSS) is a relatively new type of atomic emission spectroscopy made possible by the invention of the laser. More precisely, the use of laser-induced spark emission for elemental analysis of materials originated from the pioneering work of D. A. Kremers and L. J. Radziensky at Los Alamos National Laboratory (USA) in the early 1980s, about 20 years after the invention of the laser. Since then, LIBS has developed into a major analytical tool capable of providing real-time measurements of constituents in almost any kind of material.

The LIBS principle of operation is quite simple, although the physical processes involved in the laser–matter interaction are complex and still not completely understood. The technique relies on the use of a pulsed laser source (with energy per pulse ranging from tens to hundreds of mJ and pulse durations typically smaller than 10 ns) and a measuring chain for the analysis of the plasma emitted spectrum. In detail, the laser pulses are focused down to a target (solid, liquid as well as gas samples have so far been analyzed) so as to generate a high-temperature plasma that vaporizes a small amount of material. A portion of the light emitted by the excited atomic and ionic species in the plasma is then collected and spectrally analyzed to determine the sample elemental composition. Quantitative LIBS analysis can also be performed when the assumptions of local thermal equilibrium (LTE) and optically thin plasma are satisfied.

Because of its unique features, like the absence of sample preparation, the ability to perform real-time, and in situ analysis as well as the quasi non-destructive and micro-analysis character of the measurements, the number of LIBS applications has dramatically increased in the last years. For this reason, the main purpose of this book is to provide an overview of the latest developments and applications of the LIBS technique as well as to recall (especially for readers not familiar with these topics) some theoretical and experimental aspects of the laser–matter interaction in LIBS experiments.

The book is divided into two main parts: the first part deals with some fundamental aspects of the technique and the second part is dedicated to the description of the most important applications of LIBS in different disciplines and areas of interest. In Part I of the book (Fundamentals of LIBS), the physical processes occurring during the formation and expansion of a laser-induced plasma
are described in the Chap. 1, where the role of the various effects characterizing
the energy flow from the laser pulse to the observed spectroscopic quantities (e.g.,
thermal diffusion, electron and ion temperatures, particle ablation, and kinetics)
are elucidated. Other aspects of the same topic are also discussed in Chap. 2 where
different features of the physical mechanisms involved in optical emission spec-
troscopy (OES) are analyzed in equilibrium and non-equilibrium conditions. The
content of Chap. 3 deals with the instrumental aspects of LIBS. The purpose of this
chapter is to provide a description of the basic components of a LIBS system (laser
source, focusing optics, ablation chamber, and detection system) and how their
technical features as well as their experimental arrangement may affect the mea-
surements. New developments in laser sources and fiber optics technology are also
highlighted. LIBS performance under non-standard pressures and with surrounding
atmospheric gases other than air is the content of Chap. 4. The interest for this
topic has been mainly driven by the applications of LIBS for space exploration
(described in more detail elsewhere in the book) but the gained experience has
proved fruitful in improving LIBS measurements. In fact, altering the atmospheric
pressure and gas composition can dramatically change the observed spectra, such
as modifying (and in many cases improving) the spectral resolution, the signal
intensity, and the overall signal-to-noise ratio. More recent LIBS techniques where
multiple laser pulses and ultrashort laser pulses are used to excite the plasma are
also discussed in this section (Chaps. 5 and 6). Chapter 5 covers several important
aspects of double and multiple pulse LIBS, including the physical principles of the
laser–target plasma interactions, an overview of the currently available instru-
mentation, and some examples of representative applications of this technique
(e.g., the analysis of metallic alloys, soils, underwater materials, etc.). Chapter 6
deals with the use of femtosecond lasers in LIBS. Since the duration of a femto-
second laser pulse is shorter than the electron-to-ion energy transfer time and the
heat conduction time in sample lattice, the resulting laser ablation and heat dissipa-
tion mechanisms are very different from those observed when more conven-
tional nanosecond laser pulses are used. The basics of femtosecond laser ablation
processes and the application of this technique are presented in this chapter.

Part II of the book (Applications of LIBS) shows how LIBS can be conveniently
used to provide analytical information about different disciplines. Applications of
LIBS to the analysis of solid targets, like metals and different alloy types, is the
subject matter of Chap. 7, while LIBS analysis of liquids at gas–liquid interface
as well as the underwater analysis of both solid and soft targets are described in
Chap. 8. The use of LIBS for determining the chemical composition of aerosols is
presented in Chap. 9 where particular emphasis is given to the analysis of fine and
ultra-fine aerosols. Space utilization of LIBS, one of the more exotic applications of
this technique, forms the subject matter of Chap. 10. In this chapter the capabilities
of LIBS for geological analysis at close-up and stand-off distances as well as for
atmospheric pressures and compositions (simulating the Mars, Venus, and Moon
environments) are discussed. The elemental analysis of soils and the geochemical
fingerprinting using LIBS are the content of Chaps. 11 and 12. Although apparently
very similar, these two topics cover two different aspects of ground analysis.
While soil testing and analysis has an impact on both crops yield and environment, the importance of geochemical fingerprinting stems from its ability to determine the geographical provenience of a large variety of minerals, gemstones, and volcanic rocks. The detection of explosives in traces by means of LIBS is discussed in Chap. 13. The advantages and disadvantages of using LIBS as a technique for forensic evidence analysis are presented in Chap. 14 together with examples of current applications of LIBS to the analysis of materials of forensic interest (e.g., paper and inks, counterfeit currency, gun-shot residues, fingerprints, etc.). Chapter 15 deals with the utilization of LIBS for the identification of organic compounds (in particular polymer materials) while Chap. 16 includes the applications of LIBS in research related to globally important aspects such as climate change, carbon sequestration, phytoremediation, and dendrochemistry. Life science applications of LIBS are the subject matter of Chap. 17 where the use of LIBS for the elemental signature of biomedical specimens is discussed. Combustion applications of LIBS as well as the use of LIBS for the analysis of coal are discussed in Chaps. 18 and 19. Both these chapters are of great interest in view of the future developments in LIBS-based diagnostic techniques aimed at improving the efficiency of industrial boilers utilized in coal-fired power plants. Analysis of cultural heritage materials by means of LIBS is the content of the last chapter of the book. In this chapter, in addition to a number of case studies (such as the use of LIBS techniques in museums, in archeological conservation labs, and in excavation sites), particular emphasis is given to mobile/portable instrumentation to be used in outdoors applications.

We believe that this book will be of interest to the large community of consumers, researchers, and developers of the LIBS technique, working in academic institutes, research centers, as well as in industrial laboratories.

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Milan Sergio Musazzi
Umberto Perini
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