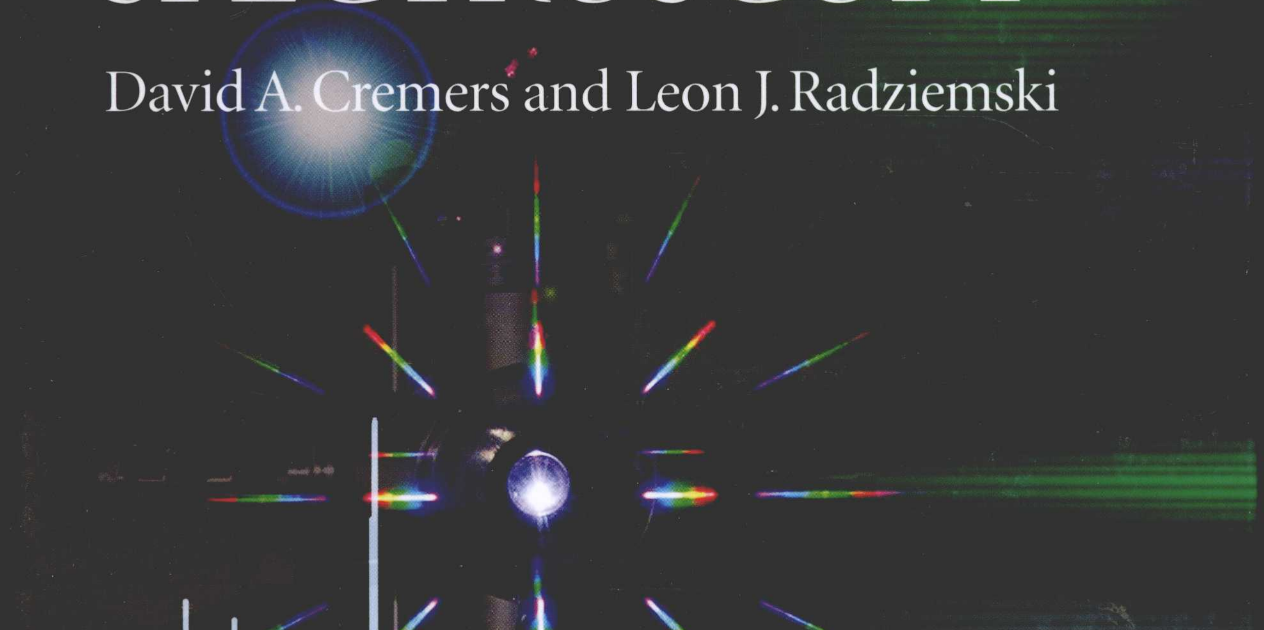
Second Edition

Handbook of LASER-INDUCED BREAKDOWN SPECTROSCOPY

David A. Cremers and Leon J. Radziemski



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Handbook of Laser-Induced Breakdown Spectroscopy

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To all those practicing LIBS throughout the world: may your experiments be rewarding and your applications successful.

Preface

The invention of the laser has resulted in many technological spin-offs. One that has emerged as a field-deployable, analytical technique is laser-induced breakdown spectroscopy (LIBS), sometimes called laser-induced plasma spectroscopy (LIPS) or laser spark spectroscopy (LSS). LIBS uses a low-energy pulsed laser (typically tens to hundreds of millijoules per pulse) to generate a plasma, which vaporizes a small amount of the sample. Spectral features emitted by the excited species, mostly atoms (but more recently molecules as well), are used to obtain quantitative and qualitative analytical information. Targets have included solids, gases, liquids, slurries, and aerosols. The first record of the observation of a LIBS plasma occurred in a meeting abstract in 1962. In the past 50 years, applications have been many. They range from sampling iron and steel, soil for contamination, metals used in nuclear reactors for degradation, artwork for dating, to the more recent analysis of soil and rocks on Mars and toxic substances like anthrax. Improved statistical techniques for analysis of LIBS spectra are being developed, and considerable LIBS instrumentation is now available commercially. Experiments have driven improved theoretical and computational models of plasma initiation and expansion.

In the early 1980s, there were few groups working on LIBS. In the past decade, however, the field has expanded greatly with many international groups now investigating and developing the method for a variety of applications. The first international conference solely on LIBS was held in Pisa, Italy in 2000. Subsequently, international meetings have been held every 2 years, and regional meetings in the odd years in North America, Europe, and the Middle East. Beginning in 2011, annual LIBS meetings have been held in China. Recently, LIBS 2012 was successfully held in Luxor, Egypt. The 2014 international meeting is scheduled for Beijing, China.

Several books and book chapters published in the last 7 years have provided snapshots of the status of LIBS at the time of their publication. Our goals are different. LIBS differs from a standard laboratory analytical tool, such as the inductively coupled plasma (ICP) which operates at high power, continuously, with a homogeneous sample feed. In contrast, the laser typically generates a low-energy, short duration, low duty-cycle plasma, often on an inhomogeneous sample. Whereas the ICP is restricted mainly to laboratory use, LIBS is especially useful in field applications. However, its use as an analytical tool requires special consideration as to its characteristics. Choosing an appropriate temporal regime and portion of the plasma for observation, and using new statistical tools can enhance its capability considerably. Hence we begin by reviewing and summarizing the principles of plasma spectroscopy, analytical spectrochemistry, and instrumentation as it applies to LIBS. We then go on to review current and upcoming applications. Included in this 2nd edition are new data and archival material to assist experienced as well as new users. Embedded are comments on the advantages of the method along with its limitations, to provide the reader the ability to judge whether or not LIBS can be applied in a particular situation. A new addition to this edition is sets of problems (and solutions) on the material in Chapters 2–5. These are designed to give the reader practice in the actual computations involved in applying basic concepts.

In the first chapter, we present a historical review of LIBS development through the year 2012, based on the peer-reviewed literature. We focus on the earliest time an innovation or application appeared on the scene, rather than tracing every development through to the present day. Of course, continuous improvements in apparatus, techniques, and fundamental understanding drive the reexamination of old applications, and the emergence of new applications spurs improvements in a recurring spiral of progress. Chapter 2 contains a review of the basic principles of plasma atomic emission spectroscopy, updated with references to databases and analysis tools now available on the web. A plasma is a local assembly of atoms, ions, and free electrons, overall electrically neutral, in which the charged species often act collectively. Natural light-emitting plasmas, like the sun, are very familiar. Electrically induced plasmas have been generated in the laboratory since the 1800s, and laser-induced plasmas have been investigated since the 1960s. In Chapter 2, we deal with the intricacies of LIBS plasma formation, lifetime, and decay, in and on a variety of media, focusing on spectral information as the primary diagnostic technique. An example of using the Boltzmann plot for temperature determination utilizes the spectrum of once-ionized uranium. Newer concepts in laser ablation found in recent literature, such as "ablation sensitivity," are reviewed. Recent published advances in nanosecond and femtosecond multiple pulse LIBS are noted.

Each important element of a LIBS apparatus is discussed in turn in Chapter 3. The unique characteristics of LIBS originate from the use of one or more powerful laser pulses to "prepare" the target sample and then "excite" the constituent atoms to emit light. To generate and capture those signals, LIBS requires a combination of modern laser, detector, timing, and data-gathering instrumentation, teamed with traditional spectroscopic apparatus including spectrometers and their optics. New developments in fiber optics (including fiber lasers) and detector technology (such as the electron-multiplying CCD) are highlighted. The calibration of wavelength and spectral response is treated, along with methods of LIBS deployment from basic setups to more advanced configurations.

The next three chapters deal with fundamental concepts in spectrochemical analysis, and how they apply to and are modified by the conditions under which LIBS operates. Analytical figures of merit are used to benchmark the capabilities of an analysis method and to compare the performance of distinct analytical techniques using a common set of parameters. These include limits of detection, precision, accuracy, sensitivity, and selectivity. In Chapter 4, we present a discussion of the more important figures of merit, how they are used to characterize LIBS, and how they are determined. A section on calibration-free LIBS has been added because of the expanding use of this technique. The basic element of any LIBS measurement is the emission spectrum recorded from a single plasma. Each firing of the laser atomizes a portion of the sample in the focal volume and produces a plasma that excites and re-excites the atoms to emit light. This is then applied either to qualitative analysis as discussed in Chapter 5 or to quantitative measurements as presented extensively in Chapter 6. In the former, some basic and practical methods of element and material identification are presented. In the latter, we discuss the ultimate goal to provide a highly quantitative analysis, hence to determine with high precision and accuracy the concentration of a species in a sample or the absolute mass of a species. We treat how LIBS interacts with different forms of samples, internal standardization, and matrix effects. A detailed example of measuring impurities in a lithium solution is presented. Swipe analysis is treated in a new section, and the comparison of LIBS results with other standard methods, such as ICP, has been augmented.

Chemometrics describes the use of mathematical models and statistical principles in the field of analytical chemistry. Because of the growth of statistical techniques for LIBS analyses, a new Chapter 7, authored by Dr Jennifer Gottfried, has been added. Chemometric analysis techniques have traditionally been applied to spectroscopic data for two primary purposes: (1) experimental design (i.e., selection of the optimal experimental procedures) and (2) extraction of the maximum relevant information from chemical data. The use of chemometrics enables multivariate analysis of complex spectral data. By considering multiple variables simultaneously, a number of advantages can be realized, including the ability to extract more information from the data, noise reduction, neglecting the effects of interfering signals, and the exposure of outlier samples. Applications are discussed, and many references are included to guide the reader to detailed information on specific methods. Terms commonly used in chemometrics are defined, and a tutorial approach to developing models is presented. Steps in the model development are illustrated with figures from specific applications, with particular emphasis on the advantages and limitations of chemometrics. In addition to describing ways to ensure accurate model development, techniques such as receiver operating characteristic curves for developing and testing models are presented.

The ability to make remote measurements in field environments is one of the principal advantages of LIBS. This application and three basic techniques for its use are treated in Chapter 8. In the first method, the laser beam is directed over an open path (through air, gas, or vacuum) to the target on which a plasma is formed, and then the plasma light is collected at a distance. In the second method, the laser pulses are injected into a fiber optic and transported to the remotely located target sample, while in the third method, a compact probe containing a small laser is positioned next to the remotely located sample and the plasma light is sent back to the detection system over a fiber optic cable. We discuss topics such as conventional stand-off analysis, the development of very long distance analysis, and details of the physics, engineering, and applications of fiber optics.

Chapter 9 has been completely revised, focusing on what LIBS does best, solving difficult and exotic problems, usually in the field, such as stopping terrorism, assessing nuclear proliferation, and exploring the solar system. The detection of Chemical, Biological, Radiological, Nuclear, and Explosive (CBRNE) threats by LIBS has received attention because of LIBS ability to perform analyses at a distance, *in situ*. LIBS instruments can be configured as person-portable devices or larger instruments intended for stand-off detection which are transported to the field in a vehicle. LIBS has the ability to determine isotope ratios of actinide atoms because of their relatively large isotope shifts. Simple molecules, however, have vibrational and rotational structures which can yield much larger isotope shifts than atoms. This newer technique for isotopic analysis is discussed. A transportable LIBS instrument is reviewed with considerable detail on the design and performance. The chapter concludes with a review of LIBS for space missions to planets, comets, and asteroids. The issue of calibration methods for such projects is discussed. The LIBS-based

ChemCam instrument on the Mars Science Laboratory rover is briefly described along with initial results.

The Appendices contain reference and original material that will be useful to the LIBS community. They include (a) a discussion of the essentials of basic safety considerations for LIBS operations; (b) a list of references to major LIBS publications and papers referencing international and regional LIBS meetings; (c) updated tables of published detection limits and the relevant references, and a unique table of element detection limits using a uniform method of analysis developed for this text; and (d) traces of LIBS spectra in air, on metals, turkey skin, trinitite, and synthetic silicates.

Starting from fundamentals and moving through a thorough discussion of equipment, methods, and recent and coming applications, we believe that the 2nd Edition of the *Handbook of Laser-Induced Breakdown Spectroscopy* will provide a unique reference source that will be of value for many years for this important analytical technique.

David A. Cremers
Leon J. Radziemski

Acronyms, Constants, and Symbols

Item	Definition	Value, units, or comments
$\alpha(\lambda)$	Absorption coefficient as a function of wavelength	cm^{-1}
AD	Array detector	
AOTF	Acousto-optic tunable filter	
APD	Avalanche photodiode	
APXS	Alpha-proton X-ray spectrometer	
c	Speed of light in vacuum	299 792 458 ms^{-1}
CBRNE	Chemical, biological, radiological, nuclear, and explosive	Suite of WMD threats
CCD	Charge-coupled device	Two-dimensional array of light-sensitive pixels
CDC	U.S. Center for Disease Control	
CF-LIBS	Calibration free-LIBS	
ChemCam	Name of the LIBS instrument on Curiosity rover	
COD	Continuous optical discharge	
CONOPS	Concept of operations	
CRM	Certified reference material	Used to calibrate LIBS
CW	Continuous wave	
DPSS	Diode-pumped solid state	A solid-state laser which is optically pumped using laser diodes (compare to a flashlamp-pumped laser)
e	Electron charge	$1.60217653 \times 10^{-19}$ C
eV	Electron volt	$1.60217653 \times 10^{-19}$ J; also: 1 eV (energy) = 8065.544 cm^{-1}; 1 eV (temperature) = 11 600 K (from kT)
$\varepsilon(\lambda)$	Emissivity as a function of wavelength	
ε_0	Vacuum permittivity	$8.854187817 \times 10^{-12}$ Farads m^{-1}
EMCCD	Electron-multiplying CCD	
f/#	*f*-number of an optical system	e.g., *f/#* = *f/d* = (lens focal length)/(lens diameter)
FOC	Fiber optic cable	
FOM	Figures-of-merit	A set of parameters to benchmark the performance of an analytical method
FWHM, Γ	Full-width at half maximum	width of a spectral line at the points of half maximum intensity, units of wavelength, wavenumber or frequency

Item	Definition	Value, units, or comments
HWHM	Half-width at half maximum	Half-width of a spectral line at the points of half maximum intensity
h	Planck constant	$6.6260693 \times 10^{-34}$ J-s
$\hbar$	Planck constant/2π	$1.0545717 \times 10^{-34}$ J-s
ICCD	Intensified CCD	
ICP	Inductively coupled plasma	Radio-frequency-powered continuous plasma source
IPDA	Intensified PDA	
IR	Infra-red	Refers to a spectral region, $\lambda > 700$ nm
k	Boltzmann constant	$1.3806505 \times 10^{-23}$ JK^{-1}
LIBS	Laser-induced breakdown spectroscopy	
LIDAR	Light detection and ranging	Optical methods of remote sensing of materials in the atmosphere
LIF	Laser-induced fluorescence	
LIPS	Laser-induced plasma spectroscopy	Alternate name for the LIBS method
LOD	Limit of detection	
LOQ	Limit of quantification	LOQ = 3.3LOD, usually
LSC	Laser-supported combustion	Type of plasma wave
LSD	Laser-supported detonation	Type of plasma wave
LSR	Laser-supported radiation	Type of plasma wave
LSS	Laser spark spectroscopy	Alternate name for the LIBS method
LTE	Local thermodynamic equilibrium	
LTSD	Lens-to-sample distance	
LV	Latent variables	Chemometric term
λ	Wavelength	µm, nm, Angstroms (Å); 1 µm = 1000 nm = 10 000 Å. In tables such as NSRDS-NBS 68, below 200 nm wavelengths are vacuum wavelengths, above 200 nm they are air wavelengths. $\lambda_{vac} = n\lambda_{air}$, where n is the index of refraction of air at that wavelength
m	Electron rest mass	$9.1093826 \times 10^{-31}$ kg
MCP	Microchannel plate	Intensifier for a CCD and PDA
NA	Numerical aperture	
ND	Neutral density	Usually used to describe a filter that reduces the intensity of a range of wavelengths of light equally; ND = $-\log_{10}(I/I_o)$
Nd:YAG	Neodymium YAG laser	Type of solid-state laser typically used for LIBS
NIR	Near-IR	Refers to a spectral region between 700 and 3000 nm
OES	Optical emission spectroscopy	
PC	Principal component	Chemometric term
PCA	Principal components analysis	Chemometric term
PD	Photodiode	
PDA	Photodiode array	One-dimensional array of photodiodes

Item	Definition	Value, units, or comments
PLS-DA	Partial least squares discriminant analysis	Chemometric term
PMT	Photomultiplier tube	Optical detector
ppm	Parts-per-million	Concentration unit, usually stated as wt to wt; also stated as $\mu g g^{-1}$
ν	Frequency	s^{-1}, Hz
n_e	Electron density	cm^{-3}
RDD	Radiological dispersal device	
R-FIBS	Remote filament-induced breakdown spectroscopy	
RM	Reference material	Used to calibrate LIBS
RMI	Remote micro imager	
RMSEC	Root mean square error of calibration	Chemometric term
RMSEP	Root mean square error of prediction	Chemometric term
ROC	Receiver operating characteristic	Chemometric term
RSD	Relative standard deviation	
σ	Wavenumber	cm^{-1}
s	Standard deviation	
SIMCA	Soft independent modeling of class analogies	Chemometric term
SNM	Special nuclear materials	
S/N	Signal to noise ratio	
T	Absolute temperature	Degrees Kelvin (K)
t_b	Gate width	Time period over which the plasma light is recorded
t_d	Delay time	Time period between arrival of the laser pulse at the sample to form the plasma and the start of recording of the plasma light signal
units of pressure	Torr, bar, Nm^{-2}, Pascal	1 atm = 760 Torr = 1.013 bar = 1.013×10^5 Nm^{-2} = 0.1013 MPa
UV	Ultraviolet	Refers to a spectral region, $200<\lambda<400$ nm
VIP	Variable importance in projection	Chemometric term
VIS	Visible	Refers to a spectral region, $400<\lambda<700$ nm
VP	Vehicle transportable prototype	
VUV	Vacuum ultraviolet	Refers to a spectral region, $\lambda<200$ nm
w_o	Beam waist radius	
Wavenumber	$= 1/\lambda$	Units of cm^{-1}. Usually wavenumbers come from differences of energy levels and correspond to vacuum wavelengths, not air wavelengths
WMD	Weapons of mass destruction	
XRF	X-ray fluorescence	Method of element detection using their X-ray emission
z_R	Rayleigh range	Distance from the beam waist (w_o) at which w_o increases by a factor of $\sqrt{2}$

Constant values from: Mohr, P.J., and Taylor B.N. (2005). CODATA recommended values of the fundamental constants: 2002. *Review of Modern Physics* 77: 1–108.

Contents

1

Introduction

1.1 Atomic Optical Emission Spectrochemistry (OES)

1.1.1 Conventional OES

Since the early 1800s, scientists realized that elements emitted specific colors of light. As atomic theory developed, spectroscopists learned that those colors, wavelengths, or frequencies were a unique signature for each atom and ion. Hence spectra became the fingerprints of the emitting atomic species. This is the basis for atomic spectrochemical analysis.

Early sources of spectra were the sun, flames, and gas discharges, such as the old Geissler tube. These were plasma sources, with varying degrees of ionization depending on the source conditions. Against the 5000 K photosphere of the sun, we see the Fraunhofer absorption lines due to neutral and once ionized species. In the solar corona, highly ionized spectra are observed because of plasma temperatures that reach into the hundreds of thousands of degrees.

Many sources have been developed for spectrochemistry, but two workhorses have been the conventional electrode spark and, more recently, the inductively coupled plasma (ICP). These are illustrated in Figure 1.1, which also contains a photograph of the laser spark. The electrode spark has excitation temperatures of up to 50 000 K, while the argon ICP temperature is more typically about 10 000 K. Usually these sources are used for laboratory analyses, but occasionally they are pressed into service for situations requiring more rapid data acquisition. For example, the conventional spark has been used for decades to monitor the steel-making process by withdrawing a molten sample that is then solidified and transported to a laboratory located in the plant for rapid analysis. Decisions on additives are made based on the resulting spectroscopic data.

1.1.2 Laser OES

As soon as the laser was developed in the early 1960s, spectrochemists began investigating its potential uses (Radziemski, 2002). An early observation was that a pulsed laser

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