

David A. Cremers and
Leon J. Radziemski

Handbook of
LASER-INDUCED
BREAKDOWN
SPECTROSCOPY



 WILEY

Contents

Foreword	xi
Preface	xiii
Acronyms, Constants and Symbols	xvii
1 History	1
1.1 Atomic Optical Emission Spectrochemistry (OES)	1
1.1.1 Conventional OES	1
1.1.2 Laser OES	1
1.2 Laser-Induced Breakdown Spectroscopy (LIBS)	2
1.3 LIBS History 1960–1980	6
1.4 LIBS History 1980–1990	9
1.5 LIBS History 1990–2000	11
1.6 Active Areas of Investigation, 2000–2002	15
References	16
2 Basics of the LIBS Plasma	23
2.1 LIBS Plasma Fundamentals	23
2.1.1 Spectral Lines and Line Profiles	25
2.1.2 Determining Electron Densities from Spectral Line Widths	27
2.1.3 Plasma Opacity	30
2.1.4 Temperature and Thermodynamic Equilibrium	31
2.2 Laser-Induced Breakdown	36
2.2.1 Breakdown in Gases	36
2.2.2 Post-Breakdown Phenomena in Gases	39
2.2.3 Breakdown In and On Solids, Aerosols and Liquids	39
2.2.4 Post-Breakdown Phenomena on Solid Surfaces	41
2.3 Laser Ablation	43
2.4 Double or Multiple Pulse LIBS	47
2.5 Summary	49
References	50
3 Apparatus Fundamentals	53
3.1 Basic LIBS Apparatus	53
3.2 Lasers	54

3.2.1 Laser Fundamentals	54
3.2.2 Types of Lasers	55
3.2.3 Properties of Laser Light Important for LIBS	58
3.2.4 Generation of Additional Wavelengths	60
3.2.5 Double Pulse Operation	61
3.3 Optical Systems	62
3.3.1 Focusing and Light Collection	62
3.3.2 Lenses	63
3.3.3 Fiber Optic Cables	65
3.4 Methods of Spectral Resolution	69
3.4.1 Introduction	69
3.4.2 Spectral Resolution Devices	70
3.5 Detectors	83
3.6 Detection System Calibrations	88
3.6.1 Wavelength Calibration	88
3.6.2 Spectral Response Calibration	90
3.7 Timing Considerations	93
3.8 Methods of LIBS Deployment	94
References	96
4 Determining LIBS Analytical Figures-of-Merit	99
4.1 Introduction	99
4.2 Basics of LIBS Measurements	99
4.3 Precision	105
4.4 Calibration	107
4.4.1 Calibration Curves	107
4.4.2 Calibration Standards	113
4.5 Detection Limit	115
4.6 Accuracy	115
References	116
5 Qualitative LIBS Analysis	119
5.1 Introduction	119
5.2 Identifying Elements	119
5.3 Material Identification	122
5.4 Process Monitoring	125
5.4.1 Experimental	126
5.4.2 Results	127
5.4.3 Conclusions	133
5.5 Material Sorting/Distinguishing	133
5.5.1 Surface Condition	134
5.5.2 Type of Analysis	134
5.5.3 Sorting Materials of Close Composition	136
5.6 Site Screening Using LIBS	137
References	141

6 Quantitative LIBS Analysis	143
6.1 Introduction	143
6.2 Effects of Sampling Geometry	143
6.3 Other Sampling Considerations	147
6.4 Particle Size and Incomplete Vaporization	151
6.5 Use of Internal Standardization	152
6.6 Chemical Matrix Effects	153
6.7 Example of LIBS Measurement: Impurities in Lithium Solutions	155
6.7.1 Objective	155
6.7.2 Experimental	156
6.7.3 Results	158
6.7.4 Discussion of Results	163
6.8 Reported Figures-of-Merit for LIBS Measurements	164
6.9 Conclusions	168
References	168
7 Remote LIBS Measurements	171
7.1 Introduction	171
7.2 Conventional Open Path LIBS	173
7.2.1 Apparatus	173
7.2.2 Focusing the Laser Pulse	174
7.2.3 Collecting the Plasma Light	178
7.2.4 Results Using Conventional LIBS	179
7.3 Stand-off LIBS Using Femtosecond Pulses	182
7.3.1 Conventional Remote LIBS Using Femtosecond Laser Pulses	182
7.3.2 Remote Analysis by Femtosecond Pulse Produced Filamentation	184
7.3.3 Teramobile	185
7.3.4 Remote LIBS Using Femtosecond Pulses	186
7.4 Fiber Optic LIBS	187
7.4.1 Fiber Optics for Light Collection	187
7.4.2 Fibers for Laser Pulse Delivery	189
7.4.3 Applications of Fiber Optics	192
References	195
8 Examples of Recent LIBS Fundamental Research, Instruments and Novel Applications	197
8.1 Introduction	197
8.2 Fundamentals	197
8.3 Calibration-Free LIBS (CF-LIBS)	201
8.4 Laser and Spectrometer Advances	203
8.5 Surface Analysis	205

8.6	Double Pulse Studies and Applications	208
8.7	Steel Applications	210
8.8	LIBS for Biological Materials	211
8.9	Nuclear Reactor Applications	212
8.10	LIBS for Space Applications	214
	References	223
9	The Future of LIBS	227
9.1	Introduction	227
9.2	Expanding the Understanding and Capability of the LIBS Process	227
9.3	Widening the Universe of LIBS Applications	229
9.4	Factors that will Speed the Commercialization of LIBS	230
	9.4.1 LIBS Standardization and Quantification	230
	9.4.2 Routine LIBS use in Industrial Applications	230
	9.4.3 Availability of Components and Systems	231
9.5	Conclusion	232
	References	233
Appendix A	Safety Considerations in LIBS	237
A.1	Safety Plans	237
A.2	Laser Safety	237
A.3	Generation of Aerosols	238
A.4	Laser Pulse Induced Ignition	239
	References	239
Appendix B	Recommended Methods for Commencing LIBS Research on a Variety of Samples	241
	References	243
Appendix C	Representative LIBS Detection Limits	245
C.1	Detection Limits from the Literature	245
C.2	Uniform Detection Limits	263
	References	265
Appendix D	Major LIBS References	271
Index		275