

# Laser-Enhanced Ionization Spectrometry

*Edited by*

**JOHN C. TRAVIS AND GREGORY C. TURK**

Analytical Chemistry Division  
National Institute of Standards and Technology  
Gaithersburg, Maryland



**A WILEY-INTERSCIENCE PUBLICATION**

**JOHN WILEY & SONS, INC.**

**New York / Chichester / Brisbane / Toronto / Singapore**

## CONTENTS

<b>CONTRIBUTORS</b>	<b>xiii</b>
<b>PREFACE</b>	<b>xv</b>
<b>CUMULATIVE LISTING OF VOLUMES IN SERIES</b>	<b>xvii</b>
<b>CHAPTER 1 FUNDAMENTAL MECHANISMS OF LASER-ENHANCED IONIZATION: THE PRODUCTION OF IONS</b>	<b>1</b>
<i>Ove Axner and Halina Rubinsztein-Dunlop</i>	
1.1. Introduction	1
1.2. Thermal Ionization	3
1.2.1. Thermal Equilibrium	3
1.2.2. Processes Responsible for Thermal Ionization	5
1.2.3. The Thermal Ionization Rate of an Atom in a Heat Bath	6
1.3. Laser-Enhanced Ionization in the Rate- Equation Formalism	11
1.3.1. Representation of the Interaction Between Atoms and Laser Light	11
1.3.2. A Three-Level System Exposed to One- or Two-Step Excitation	14
1.3.3. The Number of Excited Atoms	15
1.3.4. The Ionization Rate for One-Step Excitation and Its Relation to Thermal Ionization	22
1.3.5. The Degree of Ionization for One- and Two-Step Excitation	27
1.3.6. The LEI Enhancement: A Relation Between the Two-Step and One- Step LEI Signals	30
1.3.7. Pulsed vs. Continuous-Wave Excitation	32

1.4. Comparison Between Collisional Ionization and Photoionization	41
1.5. The Ionization Efficiency of Excited Atoms in Flames	46
1.6. The Most Sensitive Transition for One-Step LEI: Signal Strength vs. Principal Quantum Number	51
1.7. The Number of Ions Produced vs. the Area of the Laser Beam	56
1.8. Anomalous Contributions from Atoms Outside the Interaction Region	60
1.8.1. Introduction	60
1.8.2. Some Experimental Examples: The Sr Anomaly	61
1.9. Anomalous Contributions from Two-Photon Transitions and Dynamic Stark Effects	70
1.9.1. Introduction	70
1.9.2. A Short Description of Two-Photon vs. Two-Step Excitation and Dynamic Stark Effects of Atoms in Flames	70
1.9.3. Experimental Evidence of Two-Photon vs. Two-Step Excitation and Dynamic Stark Effects for Atoms in Flames	73
1.10. Laser-Enhanced Ionization in the Density-Matrix Formalism	79
1.10.1. Introduction	79
1.10.2. Formulation of the Density-Matrix System of Equations	82
1.10.3. Solution of the Density-Matrix System of Equations	86
1.11. Comparison Between the Density-Matrix Formalism and Experimental Results	87
1.11.1. Density-Matrix Equation Simulated LEI Scans	87
1.11.2. Approximations in the Theory	91
1.11.3. Implications for LEI Spectrometry	92
Appendix: The Degree of Ionization for High-Chopping-Frequency Continuous-Wave Excitation	93
References	95

<b>CHAPTER 2 FUNDAMENTAL MECHANISMS OF LASER- ENHANCED IONIZATION: SIGNAL DETECTION</b>	<b>99</b>
<i>John C. Travis and Gregory C. Turk</i>	
2.1. Overview	99
2.1.1. Approaches to Deriving the LEI Signal Response in One Dimension	99
2.1.2. The One-Dimensional Approximation	100
2.1.3. Experimental Results	101
2.2. The Effect of an External Field on Ions and Electrons	102
2.2.1. Sign Conventions	102
2.2.2. Positive Ions in the Flame	102
2.2.3. Electrons in the Flame	103
2.3. The Effect of Ions and Electrons on the Field and Supporting Circuit	104
2.3.1. The Induction of Surface Charges on Parallel Plates	104
2.3.2. Laplace's Equation and the "Lines of Force" Construct	104
2.3.3. Poisson's Equation and the Interruption of Field Lines	107
2.3.4. The Effect of Free Charges on the Surface Charge and External Circuit	107
2.3.5. Image Charges and the Ionization Chamber Model	108
2.4. The Perturbation of a Flame by an External Applied Field	111
2.4.1. The Volume Ionization Rate and Three-Body Recombination Coefficient in an Ideal, Uniform Flame	111
2.4.2. Ionization Equilibrium	112
2.4.3. Perturbation of Ionization Equilibrium by a Field	113
2.5. The Perturbation of the Field by the Flame	114
2.5.1. The Positive Ion Space Charge, or "Sheath"	114
2.5.2. Extent of the Sheath	116
2.5.3. Electric Field "Saturation"— and Beyond	116

2.6. The Point Charge Model for LEI Using Pulsed Lasers	117
2.6.1. The Electron Pulse	117
2.6.2. The Ion Pulse	119
2.7. Numerical Modeling	120
2.7.1. Diffusion and the Continuity Equation	120
2.7.2. Electron Charge Profiles for Laser-Induced Charges in a Fixed Field	121
2.7.3. Electron Current Induction for Laser-Induced Charges in a Fixed Field	123
2.7.4. Positive Ion Charge Profiles for Laser-Induced Charges in a Fixed Field	125
2.7.5. Positive Ion Current Densities for Laser-Induced Charges in a Fixed Field	126
2.7.6. Field-Distortion Effects for Large Laser-Induced Charge Densities	126
2.7.7. Current Pulse Distortions	128
2.7.8. Modeling the Flame Background	131
2.8. Relationship of Theory to Laboratory Results	133
2.8.1. Current vs. Voltage Curves in Analytical Flames	133
2.8.2. Pulsed LEI Peak Shapes and Induced Charge Apportionment	136
2.8.3. Matrix Effects and Recovery Curves	138
2.8.4. Evolution of Electrodes	140
2.8.5. Sheath-Displacement Imaging	141
2.8.6. Translated-Rod Imaging	142
2.8.7. Modulated Continuous-Wave Current Profiles	142
2.8.8. Advantages of Continuous-Wave Lasers	147
2.9. Unfinished Business	149
2.9.1. Electrode Design	149
2.9.2. High-Frequency Detection	150
2.9.3. Draining of Easily Ionized Elements	150
2.9.4. Other Plasmas	150
2.9.5. Ion Mass Selectivity	151
2.10. Conclusion	152

Appendix: A Computer Program to Model LEI Charge Transport and Current Generation	152
References	159
 <b>CHAPTER 3 ANALYTICAL PERFORMANCE OF LASER-ENHANCED IONIZATION IN FLAMES</b>	 <b>161</b>
<i>Gregory C. Turk</i>	
3.1. Introduction	161
3.2. Instrumentation	161
3.2.1. Flames	162
3.2.2. Lasers	164
3.2.3. The Ionization Probe	170
3.2.4. Electronics	172
3.3. Noise Characteristics	176
3.3.1. Multiplicative Noise	177
3.3.2. Additive Noise	181
3.4. Limits of Detection	186
3.4.1. Theoretical Detection Limits	186
3.4.2. Compilation of Measured Detection Limits	187
3.5. Spectral Interferences	199
3.5.1. Line Overlaps	199
3.5.2. Broadband Spectral Interferences	201
3.6. Summary and Future Directions for LEI Spectrometry	207
References	208
 <b>CHAPTER 4 APPLICATIONS OF LASER-ENHANCED IONIZATION SPECTROMETRY</b>	 <b>213</b>
<i>Robert B. Green</i>	
4.1. Introduction	213
4.2. LEI Spectrometry of Real Samples	214
4.2.1. General Analysis	215
4.2.2. Diagnostic Measurements	223
4.3. Conclusions	230
References	231

## **CHAPTER 5 NONFLAME RESERVOIRS FOR LASER- ENHANCED IONIZATION SPECTROMETRY 233**

*Nikita B. Zorov*

5.1. Introduction	233
5.2. Atmospheric Pressure Electrothermal Atomizers	233
5.3. Hybrid Combinations of Flame and Electrothermal Atomizers	239
5.3.1. Analysis of Orthophosphoric Acid	245
5.3.2. Determination of Indium in Cd-Hg-Te Alloy	247
5.3.3. Determination of Copper in Germanium	247
5.3.4. Determination of Gold in Silver Nitrate	248
5.3.5. Analysis of $\text{NH}_4\text{F}$ and $\text{NaF}$	249
5.4. Electrothermal Atomization in a Low-Pressure Noble Gas Atmosphere	249
5.4.1. Figures of Merit	251
5.4.2. Interferences	251
5.5. Resonant LEI of Atoms in an Inductively Coupled Plasma	252
5.5.1. ICP Plasma Diagnostics	254
5.6. Other Plasma Atomization Systems in LEI Spectrometry	254
5.6.1. Helium-Microarc-Induced Plasma	254
5.6.2. Microwave-Induced Active Nitrogen Plasma	255
5.6.3. Microwave Resonant Cavity in Flames	256
5.7. LEI in Laser-Generated Plumes	256
5.8. Conclusions	259
References	260

## **CHAPTER 6 IONS AND PHOTONS: INTERPLAY OF LASER-INDUCED IONIZATION AND FLUORESCENCE TECHNIQUES IN DIFFERENT ATOMIC AND MOLECULAR RESERVOIRS 265**

*Nicolò Omenetto and Paul B. Farnsworth*

6.1. Introduction	265
6.2. General Theoretical Considerations	267

6.3. General Experimental Considerations	277
6.4. Analytical Studies	280
6.4.1. Evaluation of the Total Number Density by Means of Saturated Fluorescence	280
6.4.2. Resonance Ionization Detection of Photons	283
6.5. Spectroscopic Studies	290
6.5.1. Simultaneous Fluorescence and Ionization Measurements: Power Dependence of the Signals	290
6.5.2. Optical Detection of LEI and Multiphoton Ionization	299
6.5.3. Evaluation of Fundamental Ionization Parameters by Fluorescence-Dip Spectroscopy	306
6.5.4. Simultaneous Molecular Ionization and Fluorescence Spectroscopy	312
6.5.5. Time-Resolved Studies	315
6.5.6. Miscellaneous Applications	320
6.6. Conclusions	322
References	323
<b>INDEX</b>	<b>327</b>