LASER INDUCED BREAKDOWN SPECTROSCOPY ON SUSPENDED PARTICULATE MATTER IN AN ELECTRODYNAMIC BALANCE: INTERACTION PROCESSES AND ANALYTICAL CONSIDERATIONS

By

RICHARD ANDERSON WARREN JR.

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2013
All that is gold does not glitter,
Not all those who wander are lost;
The old that is strong does not wither,
Deep roots are not reached by the frost.

- J.R.R. Tolkien
ACKNOWLEDGMENTS

I thank my advisor and mentor, Doc (Nico) Omenetto, for his infinite patience, extensive experimental guidance, and unending knowledge in the field of spectroscopy and others of which I hope a small amount has rubbed off. His guidance and tutelage was invaluable both in my lab experience and life outside the lab. I want to thank him for entertaining my endless distractions, whims, and arguments. I truly enjoyed the science arguments, Doc. I also want to thank Ben Smith for his pats on the back and the words of encouragement both in the fun times and those others. It takes more than one person to get a Ph.D. I'm glad he was there. When I came into Doc's lab, after much asking, I met my new lab mates. I thank Jonathan Merten, who got me started with the project discussed here, for his help and technical assistance with my particle production and showing me a prototype EDB. I would like to apologize to Dan Shelby for walking in his lab and scaring him senseless almost on a daily basis. I now fully appreciate what that can do! Also, I greatly appreciate all the scientific debate and conversation, Dan. I'll never forget that it's a great place as long as you can live with the tilt. I would like to extend my appreciation to my family members who have supported me in many ways. My deepest thanks go to my mother for pushing me and not letting me back up (or fall down) and to my sister's understanding, patience and cell phone minutes, of which countless were undoubtedly used.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>4</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>8</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>9</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>11</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>16</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1 LASER INDUCED BREAKDOWN SPECTROSCOPY FOR AEROSOL ANALYSIS</td>
<td>18</td>
</tr>
<tr>
<td>Introduction</td>
<td>18</td>
</tr>
<tr>
<td>The LIBS Technique</td>
<td>18</td>
</tr>
<tr>
<td>LIBS Sampling Concerns</td>
<td>20</td>
</tr>
<tr>
<td>Matrix Effects</td>
<td>20</td>
</tr>
<tr>
<td>Aerosols</td>
<td>21</td>
</tr>
<tr>
<td>Aerosol Descriptors</td>
<td>22</td>
</tr>
<tr>
<td>Reynolds numbers</td>
<td>23</td>
</tr>
<tr>
<td>Optical Particle Analysis</td>
<td>24</td>
</tr>
<tr>
<td>Aerosol Charges</td>
<td>24</td>
</tr>
<tr>
<td>The Electrodynamic Balance for Single Particle Trapping</td>
<td>25</td>
</tr>
<tr>
<td>The Quadrupolar Field for Trapping</td>
<td>26</td>
</tr>
<tr>
<td>Paul Trap Variants</td>
<td>27</td>
</tr>
<tr>
<td>Trap Constants</td>
<td>29</td>
</tr>
<tr>
<td>Modes of LIBS Particle Experiments</td>
<td>30</td>
</tr>
<tr>
<td>Laser-Particle Interactions</td>
<td>31</td>
</tr>
<tr>
<td>Diagnostics for the Laser Particle Interaction</td>
<td>32</td>
</tr>
<tr>
<td>Simultaneous Multi-element Analysis: Signal Persistence</td>
<td>33</td>
</tr>
<tr>
<td>Conclusions</td>
<td>34</td>
</tr>
<tr>
<td>2 PARTICLE GENERATION AND CONFINEMENT</td>
<td>41</td>
</tr>
<tr>
<td>Introduction</td>
<td>41</td>
</tr>
<tr>
<td>Vibrating Orifice Aerosol Generator</td>
<td>41</td>
</tr>
<tr>
<td>Particle Charging</td>
<td>42</td>
</tr>
<tr>
<td>The Electrodynamic Balance and Particle Trapping</td>
<td>43</td>
</tr>
<tr>
<td>Trap Parameter Determination</td>
<td>44</td>
</tr>
<tr>
<td>Spring point</td>
<td>45</td>
</tr>
<tr>
<td>Experimental Results and discussion</td>
<td>45</td>
</tr>
<tr>
<td>Injection</td>
<td>45</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>2-1</td>
<td>Calcium chloride solutions used for particle generation.</td>
</tr>
<tr>
<td>2-2</td>
<td>Magnesium Chloride solutions used for particle generation.</td>
</tr>
<tr>
<td>3-1</td>
<td>Relationships between different mean reportable values for particle distributions.</td>
</tr>
<tr>
<td>3-2</td>
<td>Parameters for monodisperse particles generated from the TSI 3050 VOAG and the associated error from the calculated diameters.</td>
</tr>
<tr>
<td>3-3</td>
<td>The measured particle diameters were trapped and the spring point was measured.</td>
</tr>
<tr>
<td>4-1</td>
<td>Description of optics used for alignment, ablation, and signal collection to be used in conjunction with Figure 4-1.</td>
</tr>
<tr>
<td>6-1</td>
<td>Resonant atomic emission lines detected by the Leco Paschen-Runge polychromator.</td>
</tr>
<tr>
<td>6-2</td>
<td>Transition probabilities and energy levels for corresponding transitions of the six elements monitored with the polychromator.</td>
</tr>
<tr>
<td>6-3</td>
<td>Sodium chloride pellet composition.</td>
</tr>
<tr>
<td>6-4</td>
<td>Graphite pallet composition.</td>
</tr>
<tr>
<td>6-5</td>
<td>Neutral resonant lines monitored with six channels of the Paschen-Runge polychromator.</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Amorphic particle characterization</td>
<td>35</td>
</tr>
<tr>
<td>1-2</td>
<td>The LIBS event processes</td>
<td>36</td>
</tr>
<tr>
<td>1-3</td>
<td>The LIBS signal</td>
<td>37</td>
</tr>
<tr>
<td>1-4</td>
<td>3-D Quadrupolar bihyperbolic trap</td>
<td>38</td>
</tr>
<tr>
<td>1-5</td>
<td>The EDB</td>
<td>39</td>
</tr>
<tr>
<td>1-6</td>
<td>Vector Field in the Quadrupole</td>
<td>40</td>
</tr>
<tr>
<td>2-1</td>
<td>VOAG Schematic Representation</td>
<td>54</td>
</tr>
<tr>
<td>2-2</td>
<td>EDB Electrical Schematic</td>
<td>55</td>
</tr>
<tr>
<td>2-3</td>
<td>Frequency, $V_{AC}$, and $V_{DC}$ dependence for particle balancing</td>
<td>56</td>
</tr>
<tr>
<td>2-4</td>
<td>Bimodal distributions of particles</td>
<td>57</td>
</tr>
<tr>
<td>2-5</td>
<td>Control Window</td>
<td>58</td>
</tr>
<tr>
<td>2-6</td>
<td>Calibration curves for trap electrode voltages</td>
<td>59</td>
</tr>
<tr>
<td>2-7</td>
<td>General effects of field parameters on a two particle array within the EDB.</td>
<td>60</td>
</tr>
<tr>
<td>2-8</td>
<td>Anomolous trapping</td>
<td>61</td>
</tr>
<tr>
<td>3-1</td>
<td>Aerosizer</td>
<td>74</td>
</tr>
<tr>
<td>3-2</td>
<td>Scattering regimes</td>
<td>75</td>
</tr>
<tr>
<td>3-3</td>
<td>Light Scattering</td>
<td>76</td>
</tr>
<tr>
<td>3-4</td>
<td>Depiction of Babinet’s principle</td>
<td>77</td>
</tr>
<tr>
<td>3-5</td>
<td>Particle size distributions</td>
<td>78</td>
</tr>
<tr>
<td>3-6</td>
<td>Size distribution analysis</td>
<td>79</td>
</tr>
<tr>
<td>4-1</td>
<td>Optical setup for LIBS signal collection</td>
<td>100</td>
</tr>
<tr>
<td>4-2</td>
<td>Measurement of the breakdown threshold in laboratory</td>
<td>101</td>
</tr>
<tr>
<td>4-3</td>
<td>Laser Pulse Shapes</td>
<td>102</td>
</tr>
</tbody>
</table>
Anomalous plasma seeding ................................................................. 103
The HeNe signal used for targeting .................................................. 104
BBT Plasma formation and signal. ..................................................... 105
Representative spectra for BBT (a) and ABT (b) LIBS measurements..... 106
ABT and BBT RSD measurements. .................................................... 107
Ensemble averaged spectra ............................................................... 108
Particle diameter versus mass .......................................................... 109
Qabs versus particle size parameter .................................................. 110
Critical time for breakdown. ............................................................. 111
The first method for calculation of the correlation providing \( \rho(S,B) \) ...... 122
The second method for calculation of the correlation providing \( \rho(S,\lambda) \) ....... 123
ABT and BBT noise comparison ....................................................... 124
Nitrogen noise correlation ............................................................... 125
H(\( \alpha \)) noise correlation .............................................................. 126
Calcium noise correlation ............................................................... 127
Signal to background plots for two major calcium neutral and ion lines.... 128
Calcium Ion to neutral trends for ABT and BBT measurements. .......... 129
Optical setup for simultaneous multi-element analysis. ....................... 142
Emission traces generated from 6 samples ....................................... 143
Demonstration of the tuning ability for the Paschen-Runge spectrometer... 144
Calibration curves using various integration times .................................. 145
R\(^2\) and sensativity versus delay time ............................................. 146
Determinatin of optimal focal depth. ............................................... 147
## LIST OF ABBREVIATIONS

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABT</td>
<td>Above the air breakdown threshold</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AES</td>
<td>Atomic emission spectroscopy</td>
</tr>
<tr>
<td>BBT</td>
<td>Below the air breakdown threshold</td>
</tr>
<tr>
<td>CC</td>
<td>Correlation Coefficient</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge coupled device</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>iCCD</td>
<td>Intensified charge coupled device</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>LIBS</td>
<td>Laser induced breakdown spectroscopy</td>
</tr>
<tr>
<td>LIP</td>
<td>Laser induced plasma</td>
</tr>
<tr>
<td>LTE</td>
<td>Local thermodynamic equilibrium</td>
</tr>
<tr>
<td>MPI</td>
<td>Multiphoton ionization</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>pLTE</td>
<td>Partial local thermodynamic equilibrium</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative standard deviation</td>
</tr>
<tr>
<td>S/N</td>
<td>Signal to noise ratio</td>
</tr>
<tr>
<td>Stk</td>
<td>Stokes Number</td>
</tr>
<tr>
<td>Constants</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>$c$</td>
<td>Speed of light in vacuum: $2.9979 \times 10^8$ m s$^{-1}$, [LT$^{-1}$]</td>
</tr>
<tr>
<td>$e$</td>
<td>Elementary charge: $1.6022 \times 10^{-19}$ C, [Q]</td>
</tr>
<tr>
<td>$eV$</td>
<td>Electron volt, $1.6022 \times 10^{-19}$ J, [ML$^2$T$^{-2}$]</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravitational field strength: 9.81 m s$^{-2}$, [LT$^{-2}$]</td>
</tr>
<tr>
<td>$h$</td>
<td>Plank constant: $6.626 \times 10^{-34}$ J•S, [ML$^2$T$^{-1}$]</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Plank constant over $2\pi$: $1.055 \times 10^{-34}$ J•S, [ML$^2$T$^{-1}$]</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant: $1.3807 \times 10^{-23}$ JK$^{-1}$, [ML$^2$T$^{-2}$K$^{-1}$]</td>
</tr>
<tr>
<td>$m_e$</td>
<td>Electron rest mass: $9.1094 \times 10^{-31}$ kg, [M]</td>
</tr>
<tr>
<td>$m_p$</td>
<td>Proton rest mass: $1.6726 \times 10^{-27}$ kg, [M]</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro's constant: $6.022 \times 10^{23}$ mol$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Electric permittivity in vacuum: $8.8542 \times 10^{-12}$ F•m$^{-1}$, [ML$^{-1}$T$^{-2}$Q$^{2}$]</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>Magnetic permeability in vacuum: $4\pi \times 10^{-7}$ H•m$^{-1}$, [MLQ$^{-2}$]</td>
</tr>
</tbody>
</table>
Symbols

\( A_{ki} \)  
Spontaneous emission transition probability, \([T^{-1}]\)

\( a \)  
Radius of a particle, \([L]\)

\( B \)  
Magnetic flux density, \([MT^{-1}Q^{-1}]\)

BPP  
Beam parameter product

\( C \)  
Stark effect coefficient

\( C_a \)  
Vapor concentration in equilibrium with a particle surface, \([ML^3]\)

\( C_i \)  
Vapor concentration of \( i \), \([ML^3]\)

\( C_0 \)  
Dimensional trap constant

\( C_s \)  
Slip correction factor, [null]

\( C^\infty \)  
Vapor concentration far from the particle, \([ML^3]\)

\( D_0 \)  
Beam diameter, \([L]\)

\( d_a \)  
Aerodynamic particle diameter, \([L]\)

\( d_d \)  
Droplet diameter, \([L]\)

\( d_{\text{min}} \)  
Minimum particle diameter, \([L]\)

\( d_p \)  
Dried particle diameter, \([L]\)

\( D_{ij} \)  
Diffusivity for vapor \( i \) in gas \( j \) \([L^2T^{-1}]\)

\( D[1,0] \)  
Length moment mean, \([L]\)

\( D[2,0] \)  
Number surface mean, \([L^2]\)

\( D[3,0] \)  
Number volume mean, \([L^3]\)

\( D[3,2] \)  
Surface area moment mean, \([L]\)

\( D[4,3] \)  
Volume moment mean, \([L]\)

\( E \)  
Electric field strength, \([MLT^{-2}Q^{-1}]\)

\( E_i \)  
Atomic energy levels, \([ML^2T^{-2}]\)

\( E^\infty \)  
Ionization energy, \([ML^2T^{-2}]\)
g  Statistical weight, [Null]
H(α)  Balmer α line (656.3 nm)
Im  Imaginary component of a complex number*
l†  Length†, [L]
m†  Mass†, [M]
M²  Ratio of BPP to an ideal Gaussian beam, [Null]
Mᵢ  Molecular weight of I, [M]
Nₑ  Electron number density, [L⁻³]
Nᵢ  Number density of ith state or type, [L⁻³]
Nₜ  Total particle number density, [L⁻³]
p  Electric dipole moment, [LQ]
P  Electric polarization, [M²Q]
pᵢ  Vapor pressure of I, [ML⁻¹T⁻²]
q  Charge, [Q], [M¹/²L³/₂T⁻²]
Q_{abs}  Absorption efficiency, [Null]
Q_{ex}  Extinction efficiency, [Null]
Q_{scat}  Scatter efficiency, [Null]
rₒ  Radial dimension parameter, [L]
Re  Reynolds number / Real component of complex number, [Null] / [*]
t⁺  Time⁺, [T]
T  Temperature, K = [ML²T⁻²]•kB⁻¹
Uᵣ  Nozzle gas flow, [LT⁻¹]
V_{AC}  Voltage of alternating current, [ML²T⁻²Q⁻¹]
V_{DC}  Voltage of direct current, [ML²T⁻²Q⁻¹]
V_p  Particle velocity, [LT⁻¹]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^0$</td>
<td>Direct current offset voltage required for a given m/z</td>
<td>$[ML^2T^{-2}Q^{-1}]$</td>
</tr>
<tr>
<td>$z_0$</td>
<td>Vertical dimension parameter</td>
<td>$[L]$</td>
</tr>
<tr>
<td>$Z_r$</td>
<td>Distance required for beam to increase by $2^{1/2}$</td>
<td>$[L]$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Scattering angle / Polarizability</td>
<td>$[\text{Radian}] / [M^{-1}T^{-2}Q^2]$</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Electric permittivity</td>
<td>$[M^{-1}L^{-3}T^2Q^2]$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Refractive index / Viscosity</td>
<td>$[\text{Null}] / [MT^{-1}L^{-1}]$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Correlation coefficient</td>
<td>$[\text{Null}]$</td>
</tr>
<tr>
<td>$\theta_{dw}$</td>
<td>Divergence</td>
<td>$[\text{Radian}]$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Drag parameter</td>
<td>$[\text{Null}]$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Measured wavelength</td>
<td>$[L]$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Magnetic permeability</td>
<td>$[MLQ^{-2}]$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Frequency</td>
<td>$[T^{-1}]$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Charge density / Impact parameter / Particle density</td>
<td>$[QL^n] / [L] / [ML^n]$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Cross section</td>
<td>$[L^2]$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Dimensionless time variable</td>
<td>$[\text{Null}]$</td>
</tr>
<tr>
<td>$\chi_e$</td>
<td>Electric susceptibility</td>
<td>$[M^{-1}T^{-2}Q^2]$</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
<td>$[T^{-1}]$</td>
</tr>
<tr>
<td>$\omega_s$</td>
<td>Stark width</td>
<td>$[T^{-1}]$</td>
</tr>
<tr>
<td>$\omega_d$</td>
<td>Doppler Width</td>
<td>$[T^{-1}]$</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>Unperturbed frequency / Minimum beam radius</td>
<td>$[T^{-1}] / [L]$</td>
</tr>
</tbody>
</table>

$n$ | Order of dimensionality |

* | Variable dimensionality |

† | Denotes fundamental unit |
Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

LASER INDUCED BREAKDOWN SPECTROSCOPY ON SUSPENDED PARTICULATE MATTER IN AN ELECTRODYNAMIC BALANCE: INTERACTION PROCESSES AND ANALYTICAL CONSIDERATIONS

By

Richard Anderson Warren Jr.

May 2013

Chair: Nicoló Omenetto
Major: Chemistry

Laser induced breakdown spectroscopy (LIBS) has become increasingly popular as a sampling technique since its inception following the invention of the laser. In what is typically an atomic emission method, a single laser pulse performs the sample ablation, vaporization, and excitation in a single step allowing any phase of matter to be rapidly, qualitatively studied for the presence of numerous elements. Minimal sample preparation and the relative simplicity of the typical LIBS instrument make it appealing as both an analytical tool for the laboratory and for commercial-industrial applications.\(^1,2,3\) LIBS has a tremendous potential in the area of aerosol analysis as it provides a method for \textit{in situ} analysis of the density and composition of environmental aerosols which few methods can accomplish as rapidly and remotely. Quantification of sample compositions is possible with LIBS, but requires careful consideration of the complex mechanisms controlling the sample ablation and excitation mechanisms. Though the physical arrangement for a LIBS aerosol measurement can be quite simple the processes involved are all but\(^4,5\) Aerosols are composed of small discrete particles which, when sampled in the lab or in the field, are difficult to control.\(^6\) Variations in the
measurements on these particles can be caused by laser-particle scattering, particle to particle matrix defects and effects, spectral interferences and particle-photon resonances which are not seen in continuous samples.$^{2,3}$

This research focuses on the two problems listed above: sample control issues and sources of signal variation, which limit analyte quantification. The electrodynamic balance, which has been used by previous researchers for optical characterization of aerosols$^7$ is used here for LIBS measurements. This technique provides complete control of confined, charged aerosol particles. With this precise handling capability, consistent laser-particle and plasma-particle interactions are observed with both spectrally integrated / time resolved and time integrated / spectrally resolved detectors to provide details on the processes involved for micrometer sized charged aerosol particles.
CHAPTER 1
LASER INDUCED BREAKDOWN SPECTROSCOPY FOR AEROSOL ANALYSIS

Introduction

This research involves careful handling of charged, micro-aerosol particles for highly controllable application of laser radiation in the vicinity of the sample. Several previous studies in this area have focused on interactions of robust laser-gas plasmas interacting with particulate matter.\textsuperscript{8,9} It is felt that the direct understanding of the effects of the local plasma conditions and sample composition would be better obtained through techniques offering more control over the conditions leading up to the plasma event as well as the resulting plasma-laser-particle interactions.

To accomplish the level of control required between the particle-laser and particle-plasma interaction, an electrodynamic balance (EDB) will be used to spatially confine these charged micro-particles produced from aerosolized solutions as described in several previous Raman and fluorescence studies.\textsuperscript{10,11} In this way, laser radiation at pulse energies which would otherwise not form a plasma in air at laboratory conditions can be used to initiate plasmas from a direct laser-particle interactions. The resulting plasma environment can be studied for effects of species fractionation and the persistence of different species within. Three detector systems are incorporated in order to provide temporal, spatial, and light scattering data. The work performed here will focus on charged aerosolized matter generated from salt containing liquids.

The LIBS Technique

Laser Induced breakdown spectroscopy, an atomic emission technique that is capable of identifying and quantifying the composition of a substance regardless of its physical state as a solid, liquid, or gas was made possible by the creation of the laser
source. Laser Induced Breakdown Spectroscopy instruments can contain as few as 3 elements: a focused laser beam, a sample, and an optical detector capable of providing wavelength v. intensity data. This can prove to be relatively inexpensive when compared to other instruments which provide the same service.

The LIBS technique rapidly followed the invention of the laser, but for some 20 years was limited primarily to studies on the physics of plasma formation. By 1980 there was a growing interest in the analytical possibilities and the field of LIBS as we know it began. It was quickly recognized that while this rising superstar in atomic emission spectroscopy had a plethora of advantages over its sister methods with ease of sampling, lack of preparation, standoff measurement capability, and using a single laser source to accomplish heating, vaporization, atomization and excitation.

A typical LIBS measurement involves focusing a pulsed laser into a sample with sufficient irradiance to cause the vaporization, atomization and subsequent excitation of the sample. (FIGURE 1-2) This is convenient as all of the sampling steps are performed by a single laser source. The LIBS signal is transient by nature; it changes over time and only persists for a finite time depending on many variables including the sample composition, ambient pressure, and laser power and frequency. This transient emission signal, either whole or by parts, is collected and analyzed to provide information on the nature of the sample. (FIGURE 1-3) Spectroscopic measurements are typically performed during the early cooling stages when both neutral and ionized species are present in the plasma but after the continuum has decayed. Several factors lend to LIBS’s overall utility as an analytical technique. One of the most enticing of these is the sample preparation or lack thereof. Sample homogenization is often the only step
necessary, and in the case where the study’s intention is to analyze sample inconsistencies even this step is unnecessary. Some consider this to be a non-destructive technique\textsuperscript{14} since the laser pulse typically removes pico-nanogram quantities of material. This is a completely subjective argument since the cases of particulate analysis and in combustion studies, there is clearly an irreversible sample perturbation. The aerosol’s particle mass can be on the same orders of magnitude as the mass removed and chemical processes can completely change the sample.\textsuperscript{15}

**LIBS Sampling Concerns**

Aside from its potentially destructive nature, there were also some other inherent issues that arose with the LIBS methods. First, each laser pulse and emission collection is necessarily an independent experiment, essentially collecting information about a new sample with each laser pulse, providing measurement to measurement variations on any analysis. This type of variance is often attributed to changing the sample site / laser interactions or to inhomogeneities within a sample.\textsuperscript{2} Secondly, there are variations in sample to sample measurements. Among these are what are known as matrix effects as well as the problems associated with thermodynamic considerations for plasma diagnostics.

**Matrix Effects**

Matrix effects are one source for spurious signals when attempting to quantify concentrations of species in samples with differing matrices.\textsuperscript{16,17} Consider the hypothetical scenario where a researcher is attempting to identify a copper concentration in both an iron sample and an aluminum sample, both containing the same mole fraction of copper. It is likely that while both samples clearly contain the same amount of copper, the integrated intensity collected for copper emission for each
are likely vastly different. This results from differences in the materials, or matrices, in which the copper is included. This is actually a rather simplistic view of the matrix effect. In fact, these effects are not only due to factors such as absorption cross section, material density, lattice binding affinities, differing heats of fusion, vaporization, ionization, which are solely dictated by the sample but also on factors such as laser pulse width, wavelength and sampling rates which are source dependent.\textsuperscript{5,2} The source dependencies are discussed at length in the appendix. In general all of these differences are classified under the general term “matrix effects” when speaking of cross sample studies and would seem to require that for quantization of sample contents a need for a set of matrix matched standards to derive calibration data. These matrix matched standards do not exist for many samples. Matrix effects in LIBS and the impossibility of having matrix matched standards for all imaginable samples is currently the Achilles heel to the technique when it comes to absolute quantization.\textsuperscript{3} Fortunately, rigorous plasma diagnostics may offer a better understanding of the intricate interplay of all of these factors and allow for the correction or even negation of the effects.

**Aerosols**

Specifically, aerosols are a suspension of solid or liquid particles which exists long enough to be measured.\textsuperscript{18} The aerosol is the gaseous analogue to the hydrosol and has its naming origins from the Greek meaning roughly “air solution”. We know aerosols by many common names: smoke, fog, smog, dust, mist, cloud, and fumes among others. While these are colloquial terms they still give information about the specific types of particles suspensions we are referring to. We know clouds are typically liquid suspensions while dust is a solid. The rigorous classification of these aerosols takes place at several levels of observation and have been formally described by
several authors by their size, phase, macroscopic composition, chemical composition and origin. Dust for example originates from the mechanical degradation of a solid, is representative compositionally and chemically of the bulk material and may range in size from .1 micrometer to .1 millimeter in diameter.

Aerosol Descriptors

A typical discussion about an aerosol will quickly come to a description of size in terms of the particle’s representative diameter, volume, or mass. Each of these values gives information relevant to describing how the bulk aerosol may disperse as well as how this aerosol may react with its environment. The particle size is not a trivial or simplistic value. As particles can take on many geometries such as spheres, rods, ellipsoids, cubic, and heterogeneous agglomerations and aggregations of these shapes, measuring an implicit mass or diameter becomes more difficult. (FIGURE 1-1) One dimensional parameter completely describes the size of a sphere or cube while it takes two for a cylinder and three or more for higher order geometrical shapes. Because of this, equivalent diameters, equivalent volumes and equivalent masses are often used. The equivalent parameter given for a particle is the comparison to a spherical droplet which has some identical property to the particle in question. The analogy to spheres is used because analytical solutions to the theoretical equations representing responses to external fields exist and can be calculated in situ. Since the response to an external field can be well described we can generate techniques which can be used to describe a generic aerosol. The interaction with gravitational fields and electromagnetic fields are employed for these analyses.

Gravity is an ever present, locally measured vector field that has the effect of pulling particles contained in an aerosol toward the earth or any other massive body.
The rate at which particles fall to the earth over time outside a vacuum is dictated primarily by the force applied by the field, \( g \), the particle size parameter, \( d_p \), and density the particles in the media being traversed, \( N_p \). We are all familiar with the term “terminal velocity as it applies to falling skydivers. If in a vacuum, the skydiver would constantly accelerate to the ground even after opening his or her parachute as there would be no resistive force to counteract the force applied by gravity. Fortunately for our skydivers the density of air is such that it provides a drag force which rapidly equilibrates upon the diver’s exiting of the plane. The average skydiver falls at a rate of 60 m/s which would not make for a comfortable landing. The parachute when opened provides additional aerodynamic drag which slows the diver to a comfortable landing speed. These principles are directly applicable to aerosol gravimetric analysis and behaviors in the EDB.

The parameters which describe the interaction of our particles and our skydiver are those of Stoke’s and Reynolds.

**Reynolds numbers**

The Reynolds number is a unit-less term which relates the effects inertial forces and viscous forces have on flow. Three regimes exist: laminar flow, turbulent, and intermediate or slip flow. The Reynolds number is calculated from equation (1-1) shown in its simplified form when dealing with normal laboratory conditions. Flows with numbers <10 fall into the laminar flow regime while numbers greater than 2000 are turbulent. The drag force which decelerates falling particles in the micrometer range, \( \text{Re}(10^{-4}) \) in a gas is laminar and caused by momentum transfer processes between collisions of the particle and the gas molecules. The effect particles experience is a direct descent following the gravitational force.\(^1\)
\[ Re_p = \frac{\rho g V d_p}{\eta} = 6.5 V d \]  

(1-1)

**Stokes law**

Particles fall at different rates through the atmosphere. This rate is dependent on the particle density, \( \rho_p \), the atmosphere’s density, \( \rho_a \), size parameter, \( d_p \), and the viscosity of the continuous fluid, \( \eta \). This dependency gives rise to the term aerodynamic diameter, \( d_a \), which equates any measured value to the diameter of a spherical droplet of water which settles at the same rate and can be calculated using Stokes Law, (1-2), which provides a general description for bodies interacting with a continuous fluid medium.\(^1\)

\[ F_{drag} = 3\pi \eta V d_p \]  

(1-2)

**Optical Particle Analysis**

Optical techniques are some of the most theoretically complex measurements due to the dependence on temperature, refractive indices, angles of detection, wavelength of light used and even the polarization and intensity distribution of the source. Yet, because of the detection efficiency and rapid rates of parameter determination, these are often employed in laboratory settings as cost effective tools for particle characterization.\(^2\) Most useful for this work are scattering measurements to determine \( d_p \).

**Aerosol Charges**

Most aerosols carry a net charge, whether naturally produced or artificially induced. The principles of electro-neutrality apply to particles and in either case this charge tends to diminish over time due to exposure to UV radiation, collisions with particles of gas and other aerosolized particles when dealing with non-radioactive
aerosols. There are some detrimental effects of the charge on these particles as the rates of sedimentation are enhanced due to coulombic and image forces. In these studies only particles of common electrical charge are used for analysis. As they have a tendency to disperse from each other, the effects of agglomeration and aggregation are reduced.

Generically, The attractive and repulsive forces for charged particles in the Stokes regime can be described by eq 1-3 and the terminal velocity of a particle in a field are given by eq 1-4 when these particles are introduced into an electric field. The terminal velocity of a charged particle is highly important in the electric field of the EDB.

\[
F = \frac{n_1 n_2 e^2}{r^3} \hat{r} \tag{1-3}
\]

\[
V_{elec} = \frac{neEC_c}{3\pi \eta d_p} \tag{1-4}
\]

The Electrodynamic Balance for Single Particle Trapping

Aerosols have been collected through mechanical confinement methods using filters and solutions for a well over a hundred years. Impactors, impingers, and konometers with windows coated with petroleum jelly, submerged in exotic solutions and consisting of convoluted series of plates and springs, reminiscent of the finest Rube Goldberg machines were the state of the art in aerosol analysis up until the late 1950’s. Over time newer and more refined devices have been developed to sample aerosols. One such device forms the centerpiece for this research.

Since Milliken’s oil drop experiments in 1909 to determine the fundamental charge on the electron which used levitation, several techniques have been developed to confine charged particles against the force of gravity and flows. As a matter of semantics and for our purposes, levitation refers to the application of a force which
counteracts the force of gravity. The levitated body is free to move in the X-Y plane. Confinement refers to the application of a force such that motion in all three dimensions is limited. For either case the levitated and confined masses can range from 10’s of ions in an ion cyclotron resonance cell to thousands of tons of mag-lev trains racing down electro-magnetic rails at hundreds of miles per hour. These methods use the magnetic field component to do the work of counteracting gravity. Another set of devices works off of the electric field component and include devices like 3-d hyperbolic, (Figure 1-4), linear quadrupolar, planar traps, and the relatively new orbitrap. These devices are electrodynamic.

Electrodynamic balances, EDB’s, originated with Wolfgang Paul and Steinwedel’s design of the quadrupole trap for ionic research. Subsequently Straubel and Wuerker created electrodynamic balances for microparticles. Simpler designs such as the Paul-Straubel trap can both confine micro and macro charged-particles in and out of vacuum (Figure 1-5). Originally these EDBs were used for aerosol array analysis, but over time they were used for single particle analysis. Here we combine these two paralleled research areas into one: LIBS on confined aerosols.

**The Quadrupolar Field for Trapping**

As mentioned, there is a distinct difference between the electrostatic particle levitator used by Milliken and the particle traps used today which are electrodynamic. Milliken’s device used a static DC field between two plates to suspend oil droplets. The droplets, while levitated, were free to move about in the axial directions as there is no horizontal stabilization force. Recent work by Dutouquet employs such a method of levitation for analysis of nanoparticles in vacuum conditions. Confinement is preferred to levitation for these studies.
Quadrupole fields were first proposed for use and developed by Nobel laureate Wolfgang Paul and his group in 1953 while working at the University of Bonn. Such fields are generated by many mechanisms but are all uniquely defined by having four poles of alternate phase. Three dimensional bihyperboloidal and linear quadrupole traps are typical for mass analyzers in modern electric sector mass spectrometric analyzers and ion trapping systems.

The advantage of using the bihyperboloidal quadrupole over the linear variety is the ability to have vertical stabilization forces as well restorative forces in the radial directions. In both devices there exists a set of electric field parameters that provide either stable or unstable trajectories for a given m/z. To see how the field stability parameters give rise to selective stability regimes, a DC and AC potential are applied to the quadrupole in Figure 1-4, and the equations of motion for a particle in the field are solved. The solutions for stable trajectories give rise to the familiar Mathieu stability diagram. Note that stability regimes are defined solely by the parameters $a_z$ and $q_z$ which are proportional to the AC field frequency and magnitude and DC field magnitude. The shaded areas are regions of stability while the unshaded area represents unstable regimes with respect to mass to charge ratios.

**Paul Trap Variants**

Since its invention, many variations of fields and geometries have been developed. The Paul-Straubel traps are what are known as planar traps, i.e. their confinement fields are generated by planar structures.\textsuperscript{27} The electrodes in this variety of trap are supplied both alternating current and direct current in order to provide a radial stabilization and a balancing force to confine charged matter within. The double ring
electrodynamic balance it a hybrid design with components of both Paul and Straubel and is essentially a stack of planar traps capable of 3-d confinement.

The general theory of operation of the EDB is described by the solutions to the equations of motion for a charged mass in a quadrupolar field and in the limit of the center of the trap, the solutions are identical to those of the homogenous Mathieu equations. Another consideration for the EDB is that the radial and vertical components of the field are 90 degrees out of phase and that the EMF in the vertical direction will always be twice that of the horizontal. For particles and clusters confined in these fields, any destabilization of the trajectories will occur along Z and thus, only the conditions which form stable trajectories along Z need be considered. The vector field in the Paul trap has been calculated at t= 0 and t=ω/2 to demonstrate the restorative forces (Figure 1-6).

$$\frac{d^2\mu_j}{dt^2} + (a_j - 2q_j \cos(2\cdot\tau))\cdot\mu_j = 0 \quad j = 1, 2, 3$$

While the Mathieu equation’s analytic solution only holds in the limit of the geometric center of the Paul trap, stable trajectories are also possible which involve clusters and arrays outside that center. Davis et. al. studied numerical solutions to these scenarios through imposing boundary conditions to the general equation, eq 1-6, predicting accurately the formation of coulombic crystals and particle arrays within the traps. Here the unit-less parameters describe the drag, AC field and gravitational imbalance.

$$\frac{d^2Z}{dt^2} + \delta \frac{dz}{dt} - 2\beta Z \cos \tau = \sigma$$
These clusters and arrays can be manipulated within the balance by careful adjustment of the DC and AC fields of the balance electrodes having the effect of extending, compressing, rotating, and even selectively destabilizing particles in the cluster due to the stability parameters, a and q, found in eq. 1-7 and 1-8. Mapping the boundary for values of \( a_z \) and \( q_z \) which yield convergent solutions to the equations of motion produces the Mathieu stability diagram. \( V_{AC} \) provides no time averaged force within the trap and thus it is necessary to equate \( F_z \) using \( V_{DC} \).

\[
a_z = \frac{8QU_0}{Md^2\Omega^2} \quad (1-7)
\]

\[
q_z = -\frac{4QV_0}{Md^2\Omega^2} \quad (1-8)
\]

This selective stability allows for the collection of many charged aerosol particles and subsequent selection of one individual particle with known parameters for LIBS analysis. (Figure 1-7) The trap used in all of the experiments described in this text is the bi-tauroidal 3-d Paul trap and was selected for its optical access, ease of construction and cost effectiveness. With the level of control given by the Paul trap, individual charged particles from a single electron to fifty micrometers or more can be trapped for study, theoretically. Once confined, a single particle can be analyzed to determine the mass, charge and diameter using a laminar gas flow and measurement of the \( V_{DC} \) required to stabilize the particle.\(^29\) This relationship is shown in equation 1-9

\[
-q \frac{V_{dc}}{z_0} = mg \quad (1-9)
\]

**Trap Constants**

The DC field within the trap is not uniform and requires that a trap constant or geometrical constant, \( C_0 \), be used to determine the actual field strength. Davis et al. have tabulated these values for several trap geometries including the double ring EDB.
These trap constants are dependent on the radius, $a$, and vertical separation, $2z_0$, of the trap rings. In the center of the trap volume equation 1-10 can be used to calculate the balancing voltage.

$$E_{dc} = -C_0 \frac{V_{dc}}{z_0}$$  \hspace{1cm} (1-10)

**Modes of LIBS Particle Experiments**

There are at least two distinct types of interaction that can be had when performing aerosol LIBS measurements in the electrodynamic balance. One possible scenario is to use a high energy, pulsed laser to produce a robust laser plasma in the medium containing trapped aerosolized particles. The second scenario involves using a lower power pulse so that dielectric breakdown of the carrier gasses containing the aerosol particles does not occur in the pure gas.

In this first case there is always going to be a laser plasma formed, but there will not always be a particle enveloped by the plasma. This type of measurement can produce direct particle hits, laser particle interactions, or can produce a plasma which subsequently engulfs the particle. This is the scenario most often described experimentally by Windom, Carranza, and Hahn.\(^8\),\(^{30,31}\) Gornushkin and coworkers have worked on theoretical modeling these plasma analyte interactions as well.\(^{32,33}\) Noll and his group describe size resolved analysis using 20-800 nm CaCl\(_2\) aerosols and note the relationship between signal intensity and particle diameter.\(^{34}\) Hahn and his group report an effective upper particle limit on the order of 2.11 µm and note that current reports are <10 µm\(^{35}\) for linear analyte response. The requirements for complete particle vaporization are explicitly stated conditions for Hahn’s study.\(^{15}\)
In the second scenario where insufficient irradiance for clean gas breakdown is provided, there is only one possibility to produce a LIBS signal: the direct laser particle interaction. The methodologies described here provide means to identify the energy transfer mechanisms between the plasma and the particle versus the laser and the particle and identify differences in the resulting plasma involving the dissociated particle matter.

**Laser-Particle Interactions**

Energy must be transferred into the sample via mechanisms which are dependent on the timescale of the laser pulse used. An accepted mechanism of transfer between laser and bulk samples using nanosecond, infra-red pulses on solid, bulk samples is that of Multi-photon absorption leading to initial ionization. Upon the formation of free electrons, a transfer of energy deposition mechanisms occurs from those of laser-sample to laser-plasma processes. Inverse Bremsstrahlung processes cause cascade collision ionization processes, forming a robust plasma.$^{1-4}$

Phase explosions due to rapid heating of a material past the boiling point can occur in samples.$^{34}$ An overheated zone is confined to its given phase by elevated pressures generated by the rapid vaporization of surrounding material. When the pressure drops the superheated material rapidly changes phase via phase explosion. This explosion produces a high pressure, rapidly expanding plume of hot dense material which inhibits the further removal of material from the surface.$^{36}$ Laser heating and conductive heat dissipation through a sample does not proceed to a large extent as the heat dispersion processes are much slower than the timescale of the laser pulse. The general process shown in Figure 1-2 can be applied to particles as well.
In aerosols, the laser energy is scattered by the particle and explosive plumes erupt from the particle while heating and vaporization ensue. It has been shown that the dielectric breakdown threshold decreases with the seeding of a sampling cavity and that this threshold is also lowered as the size of the particles used to seed the cavity increases. Laser particle interactions can be assured through the collection of spectra created when our laser is fired below the breakdown threshold, BBT. If the laser is operated above the breakdown threshold, ABT, we must ensure that the particle lies within the focal volume of the laser.

**Rayleigh length**

The Rayleigh length is the characteristic length along the axis of propagation that is required for the doubling of the beam waist diameter. It is the focal volume produced by the product of the beam waist and the Rayleigh length that will be taken into consideration for laser particle versus plasma particle discussions. When sufficient power is available to produce a plasma, If the particle lies within the focal volume, it is considered a laser hit while if the particle is outside the focal volume, it will be considered a plasma hit.

**Diagnostics for the Laser Particle Interaction**

Plasma diagnostic techniques which rely heavily on the thermodynamic properties of plasmas offer direct insight into the mechanisms which produce and define the life of the LIBS plasma. Researchers have used these types of analysis to attempt to determine the causes of matrix effects and subsequently correct for them. The plasma parameters which can readily define the plasma’s state sans external fields are the excitation temperature governing the velocity distribution of particles within the plasma, $T_{ex}$, the electron temperature, $T_e$, and the electron number density, $N_e$. A set of
relationships exist from which these values can be experimentally determined, most of which are derived from an assumption of equilibrium which one should take into consideration when attempting to apply them to the laser induced plasma.\textsuperscript{2,39} Most commonly used are the Saha-Boltzmann relationships in association with Stark broadening parameters to determine electron number densities and excitation temperatures.\textsuperscript{3}

**Simultaneous Multi-element Analysis: Signal Persistence**

Since the introduction of the intensified charge coupled detector, iCCD, many research groups have adopted them as the detector of choice. With high speed gating on the order of nanoseconds in current systems and the ability for both high signal gains and infinitely-variable gates, ever finer slices of the transient plasmas may be captured while providing highly resolved spectral windows when coupled to an appropriate spectrometer. Using a series of images collected, the average life of a representative laser-sample interaction can be assembled. The disadvantages to this method are: 1) Each LIBS plasma is a different experiment and convolving spectra does not give direct insight into the shot to shot variations. 2) Using large gate widths provided by iCCD camera systems causes a significant loss of temporal resolution.

In order to get a better representative sample for the aerosol measurements, a broadband and continuous-in-time detector will be used. A Paschen - Runge polychromator capable of monitoring up to 32 individual elements simultaneously will be used for some measurements. Photomultiplier tubes, PMT’s, provide time resolved and spectrally integrated waveforms representative of the persistence of an emitting species within the laser plasma. This method of collection has been recently reported by Noll for rapid compositional analysis of recyclable alloys and for very fast, 1kHz, acquisition of
Simultaneous observation of and recording from a single plasma event provides shot to shot discrimination of varying plasma parameters throughout the plasma lifetime at the cost of spectral resolution.

**Conclusions**

Plasma particle interactions have been described by several research groups in the LIBS field. Currently there is no method for consistently observing laser-particle interactions with aerosolized matter. The incorporation of LIBS with the electrodynamic balance provides the level of sample control required for diagnostic measurements to be made on the laser particle and plasma particle interaction in order to determine the degree of material incorporation, diffusion, and the plasma parameters which differ between the two events. By spatially confining a charged particle in 3 dimensions interactions of plasma and particle as well as laser particle can be studied with a consistency unattainable by other means.

A clear advantage to using the EDB for these studies is that the stability characteristics of the balance allow for arrays of particles to be confined and possibly selectively ejected. Using the parameters pioneered and defined by Davis and his group\(^7\) we can use the EDB to size particles and monitor the consistency of m/z for the aerosols under study eliminating the need for separate instrumentation for these verifications.
Figure 1-1. Amorphic particle characterization can take on many descriptors. Maximum and minimum diameters, equivalent weights, diameter and volumes are all used to describe the size. Chemical characterization is also possible.
Figure 1-2. The LIBS event processes through several phases starting with the laser pulse and ending with deposition of the ablated material.
Figure 1-3. The LIBS signal is integrated either in its entirety or in time resolved slices using an initial delay, $T_d$, to avoid continuum emission and a gate with a width of $T_g$. 
Figure 1-4. 3-D Quadrupolar Bihyperbolic Trap. This type of trap consists of a ring electrode and two end caps, all electronically isolated. In mass spectrometric applications the DC bias voltage is often left at ground potential leaving stability solely dependent on the AC frequency, often in the MHz range.
Figure 1-5. The EDB. Here two ring electrodes are energized with a DC voltage superimposed on an AC field. These traps stability regimes can be approximated by the Mathieu equations when close to the center of the trap.
Figure 1-6. Vector Field in the Quadrupole at $t=0$, top, and $t=\omega/2$, bottom. This demonstrates that the EMF applied to the center is null. Plots are generated using Mathcad software.
CHAPTER 2
PARTICLE GENERATION AND CONFINEMENT

Introduction

The instrument for single particle analysis consists of elements facilitating three primary functions: particle generation and charging, particle trapping and selection, and data acquisition. These three custom elements combined make the single-particle LIBS system. The parameters of liquid aerosols are more easily controlled than those solid aerosols due to the tendency for liquid droplets to form spherical structures. A vibrating orifice aerosol generator is employed for the particle production which can produce monodisperse aerosol flows of liquid droplets. The aerosol flow produced by the VOAG is charged in order to interact with our EDB fields. The charging of aerosol particles and the subsequent interactions with the EDB must be characterized for the sake of consistency in LIBS measurements.

Vibrating Orifice Aerosol Generator

Charged particle generation is accomplished with a TSI 3050 vibrating orifice aerosol generator (VOAG) unit which has been custom modified for our application by removing the unit from its factory enclosure, building a custom desolvation chamber and adding a conductive exit plate for inductive aerosol charging. The VOAG, Figure 2-1, uses a piezoelectric ceramic crystal to perturb a liquid jet, ideally producing a monodisperse flow of particles. The liquid jet is formed by creating sufficient head pressure behind interchangeable pinholes which can range in diameter from 10-50 um. Changing pinholes produces liquid jets, and subsequently particles, of varying diameter. The dependence on the diameter of the liquid jet, the flow rate, and the drive frequency applied to the piezoceramic crystal can be seen in equation 2-1. The theoretical
diameters, $D_d$, and dried particles, $D_p$, can be calculated using both equations 2-1 and 2-2, assuming spherical droplets and dried particles. Masses of the droplets and subsequent desolvated particles are calculated from the volumetric concentrations of the solutions and salts. Here $D_d$ is the droplet diameter, $Q$ is liquid flow rate, $f$ is the drive frequency for the piezo, and $C$ is volumetric concentration of the solute.\(^{42}\)

$$D_d = \left(\frac{6Q}{\pi f}\right)^{1/3} \quad (2-1)$$

$$D_p = C^{1/3} D_d \quad (2-2)$$

Thus the particle size can be manipulated by changing the drive frequency or the initial solution concentration. While the particles which dry from the solutions may not be spherical, they will always have a known mass, determined from the original droplet size and the concentration of the solutions. Particles ranging from 4-25 microns have been generated, trapped, and studied.

Dispersion gases are used to prevent droplet aggregation while a flow of dry nitrogen is used to desolvate and dilute the droplet stream, producing dried particles. While particles produced from different solutes may dry to different final geometries as in the case of sodium chloride particles, the masses of the different particles can be directly calculated from solute concentration and initial droplet diameters.

**Particle Charging**

Uniform charging of the particles is achieved inductively. The resulting charge on the particle produced from conductive liquids can be calculated using equation 2-3

$$q = q_0 \frac{2\pi \varepsilon_0 L d_p a V_c}{eH} \quad (2-3)$$
where \( q_0 \) is the initial charge, \( \varepsilon_0 \) is the permeability of free space, \( L_B \) is the breakup length of the liquid jet and \( d_p \) is the droplet diameter which can be calculated from equation 2-4. \( V_C \) is the charging voltage, and \( e \) is the fundamental charge. \( H \) is the headspace gap from the generator to the charging electrode and \( \alpha \) is a correction factor for the nonuniformity of the electric field. This value has been determined to be 0.8 by Reischl et al. for our geometry.\(^{43}\)

The VOAG has been retrofitted with a stainless steel inductive charging plate, electronically isolated from the piezo body, which enables the application of potentials up to 200 \( V_{DC} \). Particles, once charged, are introduced into the trap through a sealable orifice above the trap assembly for confinement and study. The particles used for study are produced from the chloride salts of sodium, calcium, and magnesium dissolved in 50/50 V/V isopropanol and water solution. The VOAG and this charging method are described at length in TSI documentation and by Reischl and Davis.\(^{43,44,45}\)

**The Electrodynamic Balance and Particle Trapping**

In the double ring electrodynamic balance, EDB, manipulation of the drive frequency and the amplitude of both the drive and DC ring voltages is critical to stabilizing or ejecting particles and arrays confined in the trap volume. The AC source is a HP arbitrary function generator whose signal output is amplified using a Realistic 100W audio amplifier. The amplified signal is sent to a step-up transformer producing AC amplitudes of up to 2200V b-p. This signal is divided into two channels for the upper and lower ring electrodes. A schematic is presented in Figure 2-2.
Each electrode DC potential can be controlled both simultaneously (bias) and independently (offset) to manipulate particles into the path of a HeNe targeting laser awaiting ablation. These two types of DC manipulation have different effects of the particles in the trap. Offset voltages are used to counteract the downward forces on the particle. Bias is applied to squeeze or compress arrays and to change the levitation height within the trap. This is represented in Figure 2-3.

**Trap Parameter Determination**

Determining the diameters of particles in the balance at any given time is essential. Imaging of particles in the trap can provide information which is used to determine the exact properties of the balance through characterization of the fields. A HeNe laser co-propagates with the ablation laser for alignment purposes and to determine when a particle is in the trap’s center. This allows for accurate measurements of balancing voltages on a per-particle basis. With a centered particle and known AC and DC voltages the calculation of the trap constant, \( C_0 \), and the inductive charging efficiency for the system can be performed. This calculation requires particles whose diameters are already known. Plotting the square of the radius, \( a^2 \), versus the trap’s offset DC voltage divided by the radius, \( V_{dc}/a \), results in a linear trend according to Equation 2-5 and can be used for the determination of \( C_0 \).\(^{29}\) The images of arrays and clusters also provide information about the mass to charge distribution of the species being generated, as can be seen in Figure 2-4.

\[
a^2 = \frac{2c_0q}{4\pi \rho g} \cdot \frac{V_{dc}}{a} + \frac{9\mu u q}{2\rho g} \tag{2-5}
\]
Spring point

When the offset $V_{DC}$ voltage does not exactly balance the m/z, as described by equation 1-9, for particles in the trap violent vertical oscillations of can be observed.\textsuperscript{46} This lower threshold value is known as the springpoint and provides direct measurement of the mass to charge ratios for the aerosol particles. Using 1-9, 1-10, 2-5 and particles of known mass allows for complete characterization of the balance.

Experimental Results and discussion

The chloride salt of calcium and the nitrate salts of potassium and magnesium were used to make solutions of varying concentrations in 50/50 V/V solutions of HPLC grade water and filtered, reagent grade isopropanol. Selection of the salts stems from both convenience and that several studies have been performed using aerosols from these salts.\textsuperscript{47,48} Solution concentrations were calculated and made to yield various dried particles diameters in order to determine the minimum and maximum particle diameters capable of being stably confined in the balance. Table 2-1 and 2-2 give concentrations and operational parameters for the system. The impurity of the solids and solvents were neglected in the calculations of the particle diameters because of the reagent purity used for preparation. There was no measurable effect of this assumption.

Injection

These solutions were loaded into standard plastic 25-cc syringes and injected into the vibrating orifice aerosol generator after filtration using .25 μm inline filters. Any particle on the size order of the orifice used in the VOAG results in device failure or, at best, intermittent operation. The effects of inefficient filtration and filter failures were observed as multiple jets emitted from the VOAG instead of a single, homogenous flow.
A syringe pump provided a constant flow and backpressure through the VOAG. Pressures were monitored using an attached pressure gauge for diagnostics as well as to maintain normal startup and operational conditions, NOC. High pressures are often required to initiate the liquid jet, but are undesired for normal operation. This higher pressure is developed by temporarily increasing the desired flow rate by a factor of 10. Once the liquid jet was observed the flow rate was decreased to NOC. After system equilibration, charging voltages were applied and particles introduced into the trap.

Charging voltages were varied from 0-100 V\(_{\text{DC}}\) as was required by the solution being used. It was found that, for all calcium solutions, the charging voltage required was 20-25% that required for magnesium solutions. Insufficient charging voltage created particles with very high mass to charge ratios and subsequently required high DC offset values and AC field values to stabilize the particles. Using the maximum voltage, 100 V\(_{\text{DC}}\), did not produce particles with sufficient charge to cause the drying particles to disintegrate from coulombic forces. The phenomena is known as coulombic explosion and unfortunately was not observed.\(^\text{23}\)

**Trapping**

Trapping of a single particle began with the introduction of a cascade of particles into the chamber with the trap energized. Initially arrays of particles find stable trajectories in the trapping fields. To isolate a single particle, the magnitude of the AC trapping field is lowered while simultaneously adjusting the offset voltage which destabilizes the array and causes particles to be ejected. Coulombic repulsions work favorably for this process. Squeezing particles into an ever smaller space increases the inter-particle repulsions and causes destabilizations. Once only one particle remains,
the AC field magnitude is increased and the offset and bias voltages adjusted to maximize the HeNe back scatter signal detected at the spectrometer.

**Trap Parameters**

The EDB is an air tight, optically accessible chamber. Both the trap and charging apparatus were controlled by LabView Vi’s, Figure 2- 5. This interface is coupled via RS232 to a SR-245 computer interface. The DC voltage for charging and the electrodes is sent through a fast 10X voltage amplifier prior to signal mixing with the AC voltage applied to the ring electrodes and the charging plate on the VOAG. The 10x amplifier was designed and built by Steve Miles of the UF Dept. of Chemistry Electronics Shop. This amplifier allows all dc voltages the range of -100 to +100 VDC.

The electrodes for the electrodynamic balance were constructed of .045” 308 stainless steel round rods delicately curved around a .375” mandrel and brazed to a support shaft 2” in length of the same material. There are miniscule differences in the exact curvature and in the surface morphology of the individual ring electrodes which made an observable effect on the performance of the balance with respect to the geometric field center. Acid polishing, fine sand blasting and extensive sonicating were used to diminish these effects to an appreciable degree, though there were mixed results.

**VAC Variations**

The AC frequency v. primary and secondary voltage response was recorded with a high frequency, high voltage probe at the ring electrodes and is presented in Figure 2-6. As expected, when the drive frequency increases, the efficiency of the transformer increases and produces higher gain on the secondary over the frequency range.
monitored. Also, as the primary voltage amplitude is increased the secondary voltage amplitude increased.

Higher AC field strengths exacerbate the violent oscillations observed on unbalanced particles. The force on the particle is proportional to the magnitude of the AC field and the charge on the particle. This result is not abnormal and was seen by Davis and others.\textsuperscript{7} Within the range of particles observed, 4-20 micrometer, and in the frequency range used, 60-400 Hz, higher frequencies tend to increase the radial displacement of the particle in the trap from center. These trends are shown in Figure 2-7 for a two particle array.

**V\textsubscript{DC} variations**

V\textsubscript{DC} offsets are introduced after power amplification of the AC field. Each of the two offset V\textsubscript{AC} channels is coupled to the balance electrodes. Individual particles for these experiments were trapped using a drive frequency ranging from 60 hz to 400 hz and an amplitude of 1310-1550 V\textsubscript{AC}. DC offsets are controlled with custom LabView VI’s and a Stanford Research Systems SR-245 computer interface. This allows for the rapid manipulation of the parameters to accommodate particles of varying m/z.

Increasing the V\textsubscript{DC} in the balance controls the vertical position of the particle. With a voltage required to balance the mass in the trap equal to V\textsuperscript{0}, a voltage below this causes the particles to reside below the mid-plane, oscillating normal to the AC field lines while voltages greater than V\textsuperscript{0} put them above. When the V\textsubscript{DC} equals V\textsuperscript{0} particles or arrays of monodisperse particles hover, virtually stationary in the mid-plane.

**Evaporation**

As the particles are generated from solvated salts, there is a finite amount of time required to evaporate the solvent from the particles. This is seen in the trap volume as a
change in \( V^0 \) over time. This phenomenon has been reported and observed by Lin, Campillo, Davis, Liu and others and can be described in the continuum regime by isothermal diffusion controlled quasi-steady-state evaporation of a sphere whose relationships were originally derived by Maxwell.\(^{20,49}\) Assuming ideal vapor-gas relationships, the concentrations may be expressed as vapor pressures and integrated.

\[
\frac{da}{dt} = \frac{D_{ij}}{\rho_p} (C_a - C_\infty) \quad (2-6)
\]

\[
C_i = \frac{M_i P_i}{RT} \quad (2-7)
\]

This relationship demonstrates that over time the radius of the particle will reduce with the square root of time. The total charge on the particle is left unperturbed resulting in a change in mass to charge, m/z. This is observed in the balance as \( dV^0/dt \) and must be taken into account before assuming that particles are desolvated.

\[
a^2 = a_0^2 - \frac{2M_i D_{ij} P_i^0(T_a)}{\rho_p R T_a} (t - t_0) \quad (2-8)
\]

Upon initial confinement, wet particles require rapid changes in \( V^0 \) to remain balanced. This is likely caused from local heating from the HeNe used for observation and alignment. Once evaporation was complete, \( V^0 \) stabilized.

**Stable Particle Diameters**

Particles from 2 – 20 micrometers were produced from solutions using the VOAG, charged and introduced into the balance. As a general rule, the larger the particle, up to about 50 micrometers, the broader the stability regime in the \( a_z \) and \( q_z \) plane on the Mathieu diagram. Hence, there is a much greater tolerance for \( V_{AC} \) and \( V_{DC} \) parameters to keep any given charged particle in the trap. Since mass grows with the cube of the radius and the charge can grow with the square, there is an upper limit
of liquid particle diameter whose desolvated counterpart will possess sufficient charge to be trapped within the limits of our $V_{DC}$ range. As well, particles with sufficient charge can disintegrate due to Coulombic repulsion upon desolvation. The bounds theoretical limits are presented by Aardahl et al.\textsuperscript{45}

On the opposite end of the range spectrum, with small particles, particle-gas interactions become dominant. Local flows and eddies cause destabilization, and subsequently, the particles cannot be confined. Field imperfections have ever increasing effects on small diameter particles as well. As our instrument was not precision machined, these local field anomalies are real and caused observable issues on particles below four micrometers.

**Trap with Cylindrical Confinement Fields**

The EDB was originally designed to be operated with symmetric AC fields on both electrodes. At some point during the operation of the balance it was observed that no particles were being trapped in the volume between the rings regardless of $V_{AC}$ or $V_{DC}$ amplitudes and frequencies. Particle production and charging were confirmed to be normal as well as the AC and DC outputs from the signal mixer. Video acquisition was verified as being real time.

Analysis of the acquired images (Figure 2-8) showed that arrays of particles were confined radially atop the upper ring and that these particles' trajectories were affected by both the magnitudes of the $V_{AC}$ and the $V_{DC}$. In an analogous manner to the particles which could be confined within the trap, increasing the $V_{AC}$ amplitude accentuates the displacement and increasing $V_{DC}$ affects the mean distance from the ring electrode. The difference between the two trapping situations lies in the symmetry of the motions.
It was discovered that a fault in the RG-6 cable supplying the $V_{AC}$ to the upper electrode had created a situation where the upper electrode was being inductively charged by the lower electrode. This faulty line and inductive charging created a new type of trap with cylindrical symmetry. When the observation camera and illumination was adjusted to monitor the event, arrays of particles were observed to accumulate in a ring formation with even spacing between one another. When some minimum inter-particle separation was achieved, confinement of additional particles displaced ones already in the field.

Sufficient $V_{DC}$ was not available to balance the particle from the lower ring and attempts were not made to apply $V_{DC}$ to the upper ring and $V_{AC}$ to the lower ring, though this methodology should provide sufficient $V_{DC}$ to reach the spring point. This trapping method requires at least two independent rings. When one ring is used, the symmetry becomes planar and follows the principles Paul-Straubel planar trap.

**Conclusions**

An electrodynamic balance consisting of two toroidal rings and operating at atmospheric pressure is an effective tool to confine and study aerosol particles on the order of four to twenty micrometers in diameter as either arrays or as individual particles. We successfully trapped particles as small as 2 µm and as large as 20 µm, though the smallest particles are rather difficult to consistently confine due to the conditions of atmospheric pressure and field inhomogeneity.

While operating in reduced pressure or a vacuum would lower the minimum size limit it would also greatly increase the complexity of the device. Sample introduction, gas routing and temperature regulation would be all but impossible using the current system. The system is highly sensitive to any gas flow in the chamber. Another side
effect of pressure adjustments it the associated change in dielectric breakdown threshold. After all, in a pure vacuum one cannot form a plasma as there is no material to be ionized.

As our aerosol particles are generated from solution, it is important to allow adequate time for evaporative processes to occur to ensure that no liquid solvent remains. The effects of the desolvation process can be observered and the rate quantified through the relationship of $dV^0/dt$. These desolvated particles generated from the VOAG demonstrate a small SD in $V^0$ once allowed to dry in the trap, indicating consistent m/z. While the m/z is determined from the balance, the diameter of the particles produced should be verified by other means.

The double ring cylindrical balance provides several notable results. First, the observation of uniform inter-particle spacing provides evidence of the consistency of the inductive charging arrangement used. Secondly, the uniformity of the vertical displacement while $V_{dc}$ is below the springpoint shows the consistence of the mass to charge ratio of the particles. As a logical deduction, with uniform charging and uniform mass to charge, the particles are necessarily of uniform mass. This is a new and novel approach to simultaneously verify charge, mass to charge, and mass of an aerosol flow. Finally, this type of trap offers, through a slight modification, the development of a compact accelerator with no upper ring or turning electrodes. The implications of this new electrode configuration deserves further consideration. Solving the EOM for this device could provide a new method of charged particle analysis and reaction mechanisms.
Table 2-1. Calcium chloride solutions used for particle generation. Calculated using a frequency of 60 kHz and a flow of .140 ml/min.

<table>
<thead>
<tr>
<th>$D_d$</th>
<th>Mass (g) /250 ml 50/50 ISO/Water</th>
<th>Orifice diameter (μm)</th>
<th>$D_d$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4.890</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>9</td>
<td>4.890</td>
<td>20</td>
<td>42</td>
</tr>
<tr>
<td>12</td>
<td>12.71</td>
<td>20</td>
<td>42</td>
</tr>
<tr>
<td>15</td>
<td>24.826</td>
<td>20</td>
<td>42</td>
</tr>
</tbody>
</table>

Table 2-2. Magnesium Chloride solutions used for particle generation. Interchangeable orifices allow for one solution to produce two particle diameters.

<table>
<thead>
<tr>
<th>Diameter ($D_p$)</th>
<th>Mass (g) /500 ml 50/50 ISO/Water</th>
<th>Orifice diameter (μm)</th>
<th>$D_d$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>17.026</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>13.5</td>
<td>17.026</td>
<td>20</td>
<td>42</td>
</tr>
</tbody>
</table>
Figure 2-1. VOAG Schematic Representation.
Figure 2-2. EDB Electrical Schematic. T1 is a step-up transformer. Vdc 1 and Vdc 2 are terminal connections for independent V_{DC} offset voltages. L1 and L2 are inductors acting as chokes, preventing V_{AC} feedback into the V_{DC} sources. C1 and C2 are 47 nF capacitors providing infinite resistance to DC current. J1 and J2 connect to the upper and lower balance electrode.
Figure 2-3. Frequency, $V_{AC}$, and $V_{DC}$ dependence for particle balancing and graphical demonstration of the spring-point (bottom two tiles). The off-axis motion is due to field asymmetries caused by small defects in the balance.
Figure 2-4. Bimodal distributions of particles can be seen in (a). Manipulation of the array lead eventually to a single, confined particle illuminated by the HeNe laser.
Figure 2-5. Control Window. This is a custom I/O for the electrodynamic balance which allows simultaneous Laser and spectrometer control, visualization of the trap interior and control of all trap parameters including $V_{\text{bias}}$, $V_{\text{offset}}$, $V_{\text{charging}}$, and polarity of the electrodes.
Figure 2-6. Calibration curves for trap electrode voltages. Trap electrode voltages are sensitive to both input frequency and primary amplitude. The vertical deviations are lines of constant voltage from .1 to 2.1 volts on the primary in .1 V increments.
Figure 2-7. General effects of field parameters on a two particle array within the EDB. Higher frequencies tend to accentuate the motion of the particle and pull it close to the ring electrode. Raising and lowering the DC voltage changes the vertical position in the trap with $V_{DC} = V^0$, creating the condition of balance.
Figure 2-8. The particles confined above the upper ring of the EDB provide insight into the charge distribution and the mass to charge distributions.
CHAPTER 3
DIMENSIONAL ANALYSIS OF THE AEROSOL PARTICLES

Introduction

Particle size analysis is an active area of research in chemistry, chemical engineering and environmental sciences. The size and structure of particles in aerosols control how the environment and biological organisms will react to exposure. Miners were among the first populations to recognize long term health risks associated exposure to aerosols as a side effect of hard rock mining, though the true causes were not understood until the mid-19th century.\textsuperscript{19} With an understanding of the problem come solutions. Dust particles created by mining process were analyzed for size and morphology using konometers and microscopes. It was discovered that dust with certain aerodynamic diameters would become trapped in the lungs causing silicosis. Particles with a diameter of roughly one micrometer are the most hazardous to human health as they are most easily deposited in the tissues within the lung. Environmental impacts of industrial and combustion exhaust are of great concern to environmental scientists and ecologists. Nucleation and accretion of industrial and automotive exhaust, salt aerosols from sea spray, and the chemistry that follows their entry into the atmosphere are under observation for clues to local and global environmental impacts. In all of these cases the absolute size of the particles, as much as the composition, affect the outcomes of the chemical and physical processes.\textsuperscript{19}

There exist numerous methodologies to determine size and compositional aspects of various aerosols and are discussed at length in the first three chapters of a book by Spurny\textsuperscript{21} and in a recent review of single particle measurements by Miles et. al.\textsuperscript{50} Few techniques are practically accomplished in the field due to the size and
elaborate nature of most measurements. Here the theory behind the techniques directly applicable to the particle LIBS experiments conducted in an EDB are presented and include scattering measurements, time of flight techniques, and electronic metering. With the increasing uses of portable LIBS systems, in situ measurements for particle analysis may well be accomplished with a field portable aerosol analyzer / LIBS analyzer as well in the near future.

**Time of Flight Measurements**

Time of flight measurements quantify the time required for an object to traverse a given distance. If the kinetic energy of the object is known, the mass can then be measured from the velocity, \( \frac{dx}{dt} \), where \( x \) is the distance traversed. This is the basic operational principle of the TSI aerosizer, which is used to calibrate the EDB and the VOAG. The aerodynamic particle sizer, Figure 3-1, uses two gas flows to introduce particles into an observation area. One flow contains the particulate samples while the other contains clean, dry carrier gas identical to that containing the sample. Particles are accelerated through a nozzle and subsequently pass through two detectors spaced a known distance apart. As the particle occludes the laser beams, the decrease in signal at the detector marks the time to traverse the distance, providing the time of flight used to calculate the size.\(^6\)

Particles are accelerated at different rates in flows according to their Stokes number, \( stk \). The velocity of the particle is calculated from the gas flow within the nozzle, \( U_g \), the transit time, and the transit time of a small particle in the free molecular regime. The Bernoulli equation for compressible flow can be used to calculate the gas flow within the nozzle. Using \( U_g \), \( v_p \), and \( Stk \) the aerodynamic velocity can be calculated from equation 3-1.
\[ U_g = \sqrt{\frac{2RT}{M} \ln \left( \frac{P}{P-\Delta P} \right)} \] 

(3-1)

**TSI Aerodynamic Particle Sizer (APS)**

The TSI 3603 APS works on the principle of aerodynamic time of flight. A differential pressure is driven against the opening of the nozzle in these instruments which acts as a critical orifice. This critical orifice creates a sonic flow and supersonic expansion on the detector side. Dahneke and Chen showed that the particle in this supersonic expansion reaches terminal velocity rapidly.\(^{51}\) Detection is accomplished as described previously. The terminal velocity is a function the particle size and density.

The system is intended to be calibrated using polystyrene spheres or other solid micrometer sized particles of well-defined size. Monodisperse aerosols such as those generated by the TSI 3450 may also be used to calibrate the instrument per TSI\(^{44}\), though issues were reported by Chen et al. that involve the irregular acceleration of droplets which can lead to incorrect calibration.\(^{52}\) The acceleration of liquid droplets causes them to deform into ellipsoids, broadening the response signal and also leading to aerodynamic diameters smaller than the stationary particle. As our particles begin as liquid droplets, the effects of particle elongation on the reported diameter values should be taken into consideration. Also noteworthy is that while there is single particle detection, it takes some thirty seconds to generate the distribution report on an aerosol flow. No individual particle may be sized with this instrument.

**Light Scattering**

Another useful technique to determine particle properties is light scattering. Strictly speaking light has but a few interaction processes with matter, though the interactions can become quite complex. According to the accepted solutions to
Maxwell’s equations concerning the interaction of light with a sphere developed by Gustav Mie and Lorentz, the solutions lead to two matrices which completely describe extinction and scattering. Beautifully simple solutions they may be, incredibly complex they can become. Thus arise the immediate pitfalls of scattering measurements: assumptions and complexity. One can base analysis on many theories which include many levels of assumption.

The real advantages to light scattering methods are the speed of measurement and simplicity of most analytical methodologies used to acquire data. The utility of these methods stem from the fact that particles of varying size scatter light with differing angular intensities. Rayleigh correctly described the scattering of light for particles with diameters much smaller than the wavelength of the incident light. Here the electric field is assumed to be homogenous around the scattering particle. This creates an oscillating dipole, scattering the light both forwards and backwards with respect to the incident light. Rayleigh scattering’s intensity decreases as $1/\lambda^6$. Hence photons in the blue are scattered more efficiently than photons in the red. This is observable when we go outside on a clear day. Other theories exist for particles which are of the same order to larger than wavelength of incident light. These theories can describe particles with diameters of micrometers to hundreds of meters in diameter.\textsuperscript{53} See Figure 3-2. The decision to refer to matter as a particle, bulk, or even a wave, after all, is simply a matter of semantics and/or perspective. To describe the effects of objects on light we begin with the approach: the basis for classical light scattering and Fresnel.

**Fresnel Theory**

For particles much larger than the wavelength of light, a theory must be applied which is different than that of the oscillating dipole of Lord Rayleigh. Let us consider
diffraction which is described as a small deviation from rectilinear propagation. This phenomenon occurs when light passes a sharp edge or when waves on the ocean encounter an obstacle such as a jetty or a pier. Lines of minimum and maximum intensity can be seen on a projection plane placed downfield from the source and interfering body. Huygen proposed that this effect was due to plane waves being composed of spherical radiators. This theory was put into a formalized mathematical form by Fresnel known as Fresnel’s formulation of Huygen’s principle and describes the location of the minima and maxima observed when considering angles not far from that of propagation. This theory can describe scattering of light by a planar object such as a knife edge or the orifices used by the VOAG.

\[
u_{II} = \frac{q}{l} e^{-ikl} \iint_{-\infty}^{\infty} u_{II} e^{-ik(x^2+y^2)} \, dx \, dy \]  (3-2)

**Babinet’s Principle**

When coherent light passes a knife edge or a pattern in a screen a diffraction pattern can be seen on a downfield screen. Babinet proposed that for any arbitrary pattern in the screen, the diffraction pattern of the original pattern and the complimentary pattern should necessarily be identical yet of differing phase. In Figure 3-3 it can be seen that solving fresnel’s equations for the two situations yield the same diffraction pattern. In this case the two fields generated are indeed out of phase such that adding the two field yields the original incident field.

Hence, the size of the object with respect to the wavelength of light being scattered defines the appropriate theory to consider when performing an analysis. Just as the obstruction’s size matters, so does the shape. Fresnel theory only includes information about the incident radiation on the determination of the scattered field and
not of the obstruction itself. It can only describe these fields within small angles of propagation, as well. Larger aerosol particles have a more complex interaction with the radiation. The field is not uniform about the particle and responds differently. The particle may reflect, absorb, or refract the incident light and as such a different theory must be applied which considers the boundary and curl conditions described by Maxwell. For spherical particles, Maxwell’s equations were solved by Lorentz and Mie.\textsuperscript{53}

**Lorentz-Mie Theory**

Another more rigorous theory which involves both the characteristics of the incident electromagnetic wave and the medium impinging the field must be considered for three dimensional shapes. Maxwell’s equations of electromagnetic propagation can in theory be solved for any shape in an electromagnetic field. In this case, there is no restriction on angle, or on dimensions of the interfering body. Lorentz and Mie solved Maxwell’s equations for a plane wave incident on a spherical homogenous particle. The solutions to this problem describe the fields both inside and outside of the sphere. The functions indicate that spherical waves propagate which are angularly and polarization dependent. Several programs have been written most notably by Bohren, Huffman, and Laven. These programs provide the ability to rapidly calculate the efficiency matrices $Q_{ex}$, $Q_{Scat}$, and $Q_{abs}$ for arbitrary particles as well as angular distribution functions.\textsuperscript{54}

**Size Descriptions**

Distribution analysis can be described in several ways. Take for example a given series of particles of 1, 2, 3, 4, and 5 length units in diameter. The size of these particles can be discussed as a simple diameter average, a cross sectional average, a surface area average, or as the volumetric average. To define Stokes parameters and Reynolds numbers, the $D[1,0]$, or number weighted mean is ideal. For chemical kinetics or
evaporation which are rates related to the surface area, the surface area moment mean
is a better descriptor. In the case of mass, which is proportional to volume, the volume
moment mean is used. The most common means are expressed Table 3-1 with
numerical examples.

**Experimental Results and discussion**

The agreement of calculated diameters to the VOAG generated particle
diameters were studied using several sizing techniques. The vibrating orifice aerosol
generator is designed to produce monodisperse aerosols but will only do so under
certain conditions.\(^ {42}\) The system requires a stable liquid jet, dependent on a constant
back pressure of liquid. VOAGs also only produce monodisperse aerosols when
operated in certain frequency regimes. Particle diameters were initially calculated using
frequencies, flow rates, jet diameters, and solution concentrations in accordance with
equations 2-1 and 2-2. As a primary verification of the produced diameters, the aerosols
produced from these solutions were measured with a TSI 3603 PSA, which also allowed
for the frequency dependence to be determined and also the regimes which provided
either monodisperse, bimodal or continuous diameter distributions. It is notable, also,
that only uncharged aerosols were analyzed due to dramatics losses in transfer
efficiency of charged particles through the instrument. When charged were used no
instrument response was observed.

The TSI VOAG was coupled to the inlet of the aerosol analyzer adapter via 1”
reinforced vinyl tubing fitted with a “T” as an active bypass to the Aerosizer to eliminate
backpressure and to control the particle number density introduced into the instrument.
Dispersion gas, house nitrogen, is set to 2.0 LPM. Carrier gas, also house nitrogen, is
set to 8 LPM using KFR suspended float system rotameters. The nitrogen generated no
signal response from the instrument without active operation of the VOAG, indicating
that the particulate concentration in the filtered was negligible.

Solutions were introduced into the VOAG using a Harvard model digital syringe
pump at a flow rate of .239 mL/min using a 25mL disposable plastic syringe. The piezo
drive amplitude was 19 V\text{AC} at initial frequency of 60 kHz driven by a Tektronix arbitrary
function generator. The sine function was used. This arrangement has a calculated
liquid droplet diameter of 41.8 μm. DC charging was disabled as it was discovered that
the Aerosizer exhibited large losses when measuring highly charged aerosols.

Solutions containing 1.56, 4.89, and 12.42 g/250mL of calcium chloride
dissolved in 50/50 V/V isopropanol and HPLC grade water solutions were prepared in
volumetric glassware and then used to create the aerosols. The calculated \(d_p\) from the
solutions is 7.17, 9.55, and 14.3 μm respectively. After optimizing the frequency for
monodispersion and diameter, the measured volume weighted mean values were 7.2,
9.8, and 14.3 μm showing an excellent agreement with the calculated diameters. The
associated error in the 9.55 μm can be largely attributed to a change in piezo frequency
from 60 kHz to 55 Khz which caused \(d_d\) to increase from 41.7 μm to 51.6 μm. Correcting
the initial estimate for this demonstrates a perfect agreement with measurement. The
Aerosizer was disconnected and the VOAG connected to the EDB for particle
confinement. There was no further use for the PSA.

\textbf{Spring-point Measurements}

With the VOAG calibrated for particle diameter production and connected to the
EDB chamber, the stainless steel charging cap was reinstalled and a constant charging
voltage of 46.355 V was applied. The trap was energized with 1310 V\text{AC} at 60 Hz. No
bias voltage was applied. Particles were introduced into the chamber in approximately
500 ms bursts and the chamber resealed to eliminate external flows. After approximately 10 seconds the balance collected 10’s of particles and the system entered a steady state. The particles in the balance were selectively ejected until one remained. The remaining particle was balanced using the minimum DC voltage required to eliminate the violent vertical/diagonal oscillations to measure the spring-point.

Using identical parameters for particle production from calcium and magnesium solutions repeatedly showed decreased charging efficiency for the magnesium and is the reason the triple channel 10x amplifier was introduced into the system. Operating within the output range of ± 10 V DC from the SR-245 would not provide a sufficient mass to charge ratio to stabilize particles with diameters larger than 5 μm in the balance. With a lower effective limit of 4 μm, the range was simply unacceptable. Improvement was seen in trapping efficiency of the Mg containing particles when higher potentials were used but was still poor compared to Ca. It was decided that Ca would be the element of choice for the measurements.

**Illumination**

Small particles are inherently hard to see with the human eye under normal conditions. In order to view the particles entering balance chamber volume and confined in the trap’s fields, a Spectra-Physics model 117G argon ion laser was beam expanded and directed into the balance chamber. The laser was operated between 55 and 280 mW cw output based on the requirements to visualize the particles. The scatter image was recorded with a Supercircuits PC-23 Black and white CCTV camera and imaged using Labview. Particles in the a>5 micrometer size have large scatter cross sections and are easily visualized in this fashion. Particles below four microns were not capable of being imaged using this system.
With particles centered and balanced, a 10 mW HeNe laser was focused through an F/1 S1 fused silica lens and made to illuminate the particles in the absence of the argon ion area illumination. The beam is used to identify the precise alignment of the excitation laser for subsequent LIBS experiments.

The interference of electromagnetic radiation can be used to determine many parameters of a sample including diameter and refractive index. The HeNe which co-propagates with 1064nm Nd:YAG ablation laser provides a source of coherent radiation for interference measurements. Davis used light scattering measurements as early as the 1980’s in the electro dynamic balance to determine single suspended particle’s scattering profiles. These techniques also allow study of the VOAG’s operational parameters.

**Conclusions**

The TSI aerosizer demonstrated that the precise diameter of dried particles created from solutions could be calculated using equations 1-2 and 1-3 with minimal error. Also, since it has been reported that liquid droplets cause negative systematic errors in the terminal velocity measurement process, it can be inferred that either desolvation was completed during the transit time from the VOAG to the Aerosizer which is on the order of 10 seconds. A secondary demonstration of this is given by consistent measurement of the aerodynamic size. It was shown that the desolvation process is roughly linear with respect to $a^2$ and any deviations in measured size should be attributable to this trend as the transit time for the different size particles is very similar in the laminar flow, 8-10 s. For future particle diameters calculations the calculated value will be taken as the calibration value since there was no measurable discrepancy between the two.
The very small RSD in the spring point measurements allows a secondary verification of the results of the Aerosizer. The VOAG was run using parameters known to give a bimodal distribution as shown from the Aerosizer. The particles were trapped and their spring point measured. These calcium chloride particles, measuring 13.5 and 4.5μm D[4,3] showed two spring points of -5.2 and -8.9 indicating that the operation of the VOAG can be evaluated rapidly and *in situ* for normal operation. Furthermore, assuming consistent charging of the particles, which has been shown to be the case by Reischl, et al., we can consistently collect particles of precisely the same mass and reject any that deviate from the expectation voltage.$^{41}$ Thus the trap parameters define the diameters.

The difference in voltage required to effectively trap calcium chloride and magnesium nitrate particles demonstrate that the charging efficiency of the solutions of different materials may be substantially different. Both jets were inductively charged using the same 46.3 V$_{DC}$; yet the magnesium particles required an order of magnitude higher V$_{DC}$ offset voltage to reach the spring point. A higher V$_{DC}$ indicates that the mass to charge is an order of magnitude higher on the magnesium particles. High mass to charge ratios will provide higher inertial force to field force ratio and thus require elevated V$_{AC}$ to be applied to the ring electrodes to be confined. These were abandoned as an element for study because of the difficulty associated with trapping them.
Table 3-1. Relationships between different mean reportable values for particle distributions. Values provided are for the set of particles

<table>
<thead>
<tr>
<th>Descriptor</th>
<th>Representation</th>
<th>Equation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Numeric mean</td>
<td>D[1,0]</td>
<td>( D[1,0] = \sum_{i}^{n} \frac{D_i v_i}{1} )</td>
<td>3</td>
</tr>
<tr>
<td>Number volume mean</td>
<td>D[2,0]</td>
<td>( D[2,0] = \sum_{i}^{n} \frac{D_i^2 v_i}{1} )</td>
<td>3.1</td>
</tr>
<tr>
<td>Surface area moment mean</td>
<td>D[3,2]</td>
<td>( D[3,2] = \sum_{i}^{n} \frac{D_i^3 v_i}{D_i^2 v_i} )</td>
<td>3.2</td>
</tr>
<tr>
<td>Volume moment mean</td>
<td>D[4,3]</td>
<td>( D[4,3] = \sum_{i}^{n} \frac{D_i^4 v_i}{D_i^3 v_i} )</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 3-2. Parameters for monodisperse particles generated from the TSI 3050 VOAG and the associated error from the calculated diameters. The VOAG is in excellent agreement with the calculated particle diameters. * these are reported, yet not significant.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>( d_d ) (μm)</th>
<th>( d_p ) (μm)</th>
<th>Flow Rate (cc/min)</th>
<th>Piezo (kHz)</th>
<th>( D[4,3] ) ( d_d ) (μm)</th>
<th>( \Delta d_p ) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.56 g/250ml</td>
<td>41.8</td>
<td>7.17</td>
<td>.238</td>
<td>60.0</td>
<td>7.2</td>
<td>.03*</td>
</tr>
<tr>
<td>4.89 g/250ml</td>
<td>41.8</td>
<td>9.55</td>
<td>.238</td>
<td>55.0</td>
<td>9.8</td>
<td>.25</td>
</tr>
<tr>
<td>12.42 g/250ml</td>
<td>41.8</td>
<td>14.33</td>
<td>.238</td>
<td>60.0</td>
<td>14.3</td>
<td>.03*</td>
</tr>
</tbody>
</table>

Table 3-3. The measured particle diameters were trapped and the spring point was measured.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Trap Frequency</th>
<th>( V_{AC} ) trap (V)</th>
<th>( V_{charge} ) (V)</th>
<th>( V_{offset} ) (V)</th>
<th>( d_p ) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.56 g/250ml</td>
<td>60 Hz</td>
<td>1310</td>
<td>46.335</td>
<td>-.039</td>
<td>7.2</td>
</tr>
<tr>
<td>4.89 g/250ml</td>
<td>60 Hz</td>
<td>1310</td>
<td>46.335</td>
<td>-.400</td>
<td>9.8</td>
</tr>
<tr>
<td>12.42 g/250ml</td>
<td>60 Hz</td>
<td>1310</td>
<td>46.335</td>
<td>-.703</td>
<td>14.3</td>
</tr>
</tbody>
</table>
Figure 3-1. A sheath flow of carrier gas accelerates particles from the sensor flow. In standard PSA the particles acceleration is dependent on the flow within the nozzle. In Aerosizers the terminal velocity is measured and is acceleration independent. The total flow is equal to the sum of sensor and sheath flows.
Figure 3-2. Particles much smaller than the wavelength of incident light are described primarily by Rayleigh scattering where particles greater than about .1 micron are best described by Lorentz- Mie scattering. The intensity grows roughly as $a^2$. 
Figure 3-3. Light with wavelengths smaller than the radius of the particle have more complex interactions and cannot be fully described by Fresnel diffraction theory. Apart from Fresnel theory only being applicable in the small-angles regime, there are no considerations for internal reflection and absorption.
Figure 3-4. Depiction of Babinet’s principle. Adding the resultant electric fields produces the original electric field. $E_0 = E_a + E_b$. This principle is applied to measurements of the orifices used for the VOAG to ensure the consistency of the jet diameters after installation of new pinholes as well as spectrometer slit calibrations.
Figure 3-5. Tuning the frequency on the VOAG while maintaining a constant flow and solution concentration can fine tune the diameter of the particles produced. Changing the liquid flow rate can have similar effects.
Figure 3-6. Size distribution analysis for calcium chloride particles. Diameters were calculated using the above equations incorporating frequency and concentration. The parameters were fine-tuned using the TSI Aerosizer. Certain frequency ranges produce highly irregular distribution of diameters as can be seen in the upper right.
CHAPTER 4
THE LASER INDUCED PLASMA AND SINGLE PARTICLE LIBS

Introduction

The quadrupole electrodynamic balance is presented here as a tool for the analysis of direct laser-particle and plasma-particle interactions in the area of Laser-Induced Breakdown Spectroscopy (LIBS). This method provides a means to manipulate charged aerosols, measure particle diameters, and characterize constituent particles on an individual basis. An electrodynamic balance is assembled and characterized. The dielectric breakdown threshold is measured, providing the pulse energies for measurements below and above the threshold. Particle sizes are measured by aerodynamic sizing and monitoring the spring-point within the balance. Limitations of particle size for quantification by the LIBS method are discussed.

Laser Plasmas

The plasma condition as is typically described requires that free electrons be formed from neutral species, and these free electrons and neutrals should exist in a quasi-static state and exhibit some collective behavior. Plasmas are readily formed from high temperatures, when \( k_B \cdot T \) is of the order of the ionization potential. They are also formed in the presence of high magnitude electric fields which cause a dielectric breakdown and from energetic collisions where the collider’s kinetic energy is sufficient for ionization. Lasers can create all of these conditions through a variety of energy transfer processes. The nature of the energy transfer process is dependent on the timescale and frequency of the laser excitation and the electrical properties of the media interacting with the pulse. Nanosecond timescale infrared radiation produced by the flashlamp pumped, pulsed laser such as the Nd:YAG has become a popular choice for
LIBS due to cost and simplicity. Extremely high electric field magnitudes can be produced by these lasers and used for triggering a dielectric breakdown in gasses and other non-absorbing media. The dielectric breakdown of purified, filtered air and subsequent plasma formation using a focused laser beam occurs in stages.

The first stage of plasma formation after focusing a several nanosecond long laser pulse into a medium involves single and multiphoton absorption processes which lead to the initial ionization or overcoming the dielectric breakdown threshold of the medium, both of which can produce free electrons. These initial processes are as much frequency dependent as they are timescale dependent. Following the creation of free electrons, inverse bremsstrahlung processes become the dominant energy transfer mechanism and lead to cascade collision ionization from highly energetic electrons. This causes a rapid growth in the free electron number density. This volume of free electrons’ absorption cross section rapidly increases and can effectively absorb the remainder of a laser pulse. This absorption of photons and intense electron heating causes the rapid expansion into the surrounding environment. What follows is the propagation of a shockwave and sonic expansion of the plasma volume creating a large pressure gradient inside and outside the shock front. This leads to a rarefication of the volume inside the shock front, helping to drive the expansion of the plasma volume. The plasma expands rapidly at first then assumes an almost constant volume, cools and rarifies, eventually recombining to form neutrals species. The recombination and cooling is later followed by aggregation and condensation. This is the life of a laser plasma created by typical nano-second pulses.
Thus the laser plasma formation is not simply a result of dielectric breakdown but is a cascade of events leading to a dense, hot plasma with typical temperatures on the order of $10^4$ K and electron number densities, $N_e$, of $10^{17}$-$10^{18}$ per cm$^3$ which eventually withers away. These processes require a higher fluence in pure gasses than the same laser focused into a volume of gas containing micro particles. The effects of wavelength and laser fluence required to consistently form a plasma in a particle containing atmosphere were studied by Pinnick et al. A general relationship of $1/\lambda$ was described with respect to J/cm$^2$ required for initiating the plasma event. This wavelength dependence was attributed to local field enhancements.

The primary reasons particles lower the threshold energy is the exhibition of higher extinction coefficients due to scattering phenomena which can be nonlinear or single photon processes. Simply put: the presence of particles makes it easier to deposit energy. This leads to heating of both the particle and the gas surrounding the particle. Energy transfer processes are enhanced and thus lower irradiance is required for plasma formation. These processes are discussed in greater detail in Appendix C. Resonances can occur with certain particle sizes when compared to the excitation wavelength further increasing the electric field magnitude and $Q_{ext}$. The presence of particles can lower the threshold at a given wavelength by up four orders of magnitude, from $10^{10}$ W/cm$^2$ to $10^6$ W/cm$^2$, depending on diameter and laser wavelength. As particle sizes grow past a certain size, it is reasonable to assume they might act as a bulk, continuous samples which are in fact nothing but very large particles.

**Particle LIBS**

Laser Induced Breakdown Spectroscopy, LIBS, has been used for compositional analysis in aerosol science dating to the early 1980’s with the study of seeded plasmas
by Radziemenski et al.\textsuperscript{58} Today the laser plasma is used to both produce aerosols and to evaluate their physical properties.\textsuperscript{4} In the case of the hyphenated LIBS technique, laser ablation-LIBS, the production and subsequent LIBS analysis of an aerosol from a matrix is used to decrease matrix effects found when directly sampling a solid.\textsuperscript{59} The analysis of aerosols presents with a unique set of challenges for the LIBS community. Hahn and Omenetto describe these at length in a recent review of LIBS in a section dedicated to aerosols and bioaerosols.\textsuperscript{2,3} Among the list of concerns are the intricacies of the related sampling statistics\textsuperscript{31} stemming from the discrete nature of the LIBS-aerosol measurement and the effects of maximum mass loading\textsuperscript{15} of a laser plasma by the aerosol.

Amodeo et al report a method for the analysis of aerosols composed of nanopicometer diameter sodium chloride and metal particles and indicate that at low mass loadings measurement times become a concern.\textsuperscript{60} Diwakar et al. describe both diffusion\textsuperscript{61} and the appropriate sampling statistics for the analysis of aerosols at length.\textsuperscript{9} In each of these studies the effects of particle-plasma interactions were investigated. It is noteworthy that previous reports on the limitations of size for quantitative analysis refer to particle size identification and not specifically for quantified compositional analysis of the aerosol. As alluded to earlier, all bulk samples are particles, though they may be quite large.

A topic receiving much less consideration recently has been the effects of the direct laser-particle interactions in the LIBS-aerosol system. A review of the laser matter interactions in which the energetic pathways are described was produced by Lushnikov and Negin.\textsuperscript{5} Theoretical modeling of field strengths and temperature gradients leading
to phase explosions within microspheres was considered by Belov before Radziemenski and Cremer’s work on the topic. The effects of resonance and refractive index were later calculated as well. Pinnick et al. showed experimentally the dependence on wavelength and particle diameter on the dielectric breakdown threshold.

The LIBS laser-particle interaction is an event that requires a focused, pulsed laser to be coincident with a particle whose cross sectional area is on the order of $10^{-12} \text{m}^2$, an event which, statistically, can occur in all LIBS aerosol measurements. One approach in the literature for this measurement which has gained traction is the falling droplet method. One produces a droplet at a known time and height and delays the firing of a laser to produce a coincidence. This method suffers from several drawbacks including the lower size limit for particle production and deviations from an ideal trajectory caused by Stokesian dynamics. Another consideration is the irradiance used for the aerosol measurements. The effects of seeding a plasma with particulate matter are well known and discussed at length by Radziemenski, Lushnikov and Pinnick and reported as early as 1982. With these effects in mind, laser-particle interactions should only be observed when operating at laser irradiances below that required for dielectric breakdown of the gaseous matrix. This type of measurement will be referred to as below the breakdown threshold, BBT, in this work with ABT representing irradiances above the dielectric breakdown threshold. The schematic and operational parameters of the quadrupole electrodynamic balance for application in LIBS aerosol analysis along with initial results were first presented in 2010 at the Winter Conference for Plasma Spectrochemistry. Recent LIBS-aerosol work by Dutouquet et al. use a balance operated in vacuum and at radio frequencies, both requirements for
confinement of charged aerosols and microparticles with large Stoksian drag parameters and low m/z.\textsuperscript{26}

It is the purpose of this work to provide and characterize a method of analysis to consistently study the laser particle interaction and the events leading to a robust laser plasma using a quadrupole, double ring electrodynamic balance.

**Experimental Details and Discussion**

With the particles and parameters of the VOAG characterized and the function of the trap demonstrated, an ablation laser and optical collection system was incorporated. It was necessary to fit the Balance chamber on an X-Y-Z stage to allow for fine adjustments. The balance chamber itself is constructed from a 2x2x2” 6-way hub to which a deceleration chamber and cap are attached in the top axial position. Three equatorial positions are fitted with S1 grade fused silica windows and the lower axial position has been fitted with a regulated gas inlet for trap flushing and gas replacement. The remaining equatorial position mounts the balance electrodes using a vacuum flange fitted with 2 BNC connectors for electrical connection.

**Optical Arrangement**

Three laser systems are used for the LIBS experiments. Two systems are used for illumination and positioning, and one for ablation. The ablation laser is a Q-switched Big Sky Ultra Nd:YAG operating at the fundamental and fired by remote trigger. The Nd:YAG is reflected off a dielectric mirror, which is transparent at 632 nm, prior to focusing into the chamber. The 1064 YAG pulse energy is measured using a Scientech model 200LA pyroelectric power meter and the beam waist by measuring the minimum hole diameter produced in a paper sample in the focal plane within the trap. This is also
calculated from the equations describing a diffraction limited beam. The calculation gives a resulting radius of 57.8 μm and a Rayleigh length of 2 mm.

\[
\omega_0 = \sqrt{\frac{2\lambda}{2\pi}} = 28.90 \mu m
\]  
\[Z_r = \frac{\pi \omega_0^2}{\lambda} = 1.97 mm\]  
\[\Theta_{dw} = \frac{Z_r \omega_0}{L_r} = 57.8 \mu m\]  
\[M^2 = \frac{2\pi \omega_0 D_0}{4f\lambda} = 3.864\]

A HeNe is made to co-propagate with the Nd:YAG by transmission through the dielectric mirror. The collimated HeNe scatter from the target particle is back-collected through the focal lens using a pierced mirror and its intensity observed with an Ocean Optics spectrometer. This allows the particle position to be optimized within the beam prior to ablation for each particle.

The Spectra-Physics model 117G argon ion laser was used for illumination through an Ocean Optics fiber-optic with a divergence of 25.4 degrees and core of 400 micrometers. This provided total chamber illumination. The setup is schematized in Figure 4-1 with individual optical elements described in Table 4-1.

**Breakdown Threshold measurements**

The dielectric breakdown threshold in the trap was measured by observing the pulse energy both before and after the trap. The front window remained and the electrode pack was removed for these measurements. The results are seen in Figure 4-2. At a setting of 5.5, which corresponds to 35 mJ, intermittent breakdown was observed which is regarded by Chen et al. to be the breakdown threshold for the gas. At a setting of 6.5 which corresponds to 40 mJ, an optically thick plasma was
consistently formed, absorbing a significant fraction of the incident radiation for all subsequent energy settings. Laser pulse energies below 35 mJ/pulse are used for studies below air breakdown threshold (ABT) and pulse energies above 65 mJ/pulse are used for above breakdown threshold measurements (ABT). It is a convenient fact that the air-breakdown threshold occurs at the midrange or the laser output energy.

An analogous measurement was performed in pure argon displacing laboratory air through the regulated gas inlet. Plasma images were taken while flushing the trap to demonstrate the effects of lasing in a seeded cavity when operating above the breakdown threshold for the pure gas. It can be seen that the plasmas formed are highly erratic spatially. If the laser fluence is great enough, ultimately these plasmas will expand, engulf each other and become one large elliptical plasma. The micro plasmas shown in Figure were generated with 85 mJ per pulse and are seeded in such a way that the fusion never occurs. Using this arrangement, the breakdown threshold for argon occurs at 80 mJ / pulse at the laser head, this value being greater than that measured in clean lab air. Figure 4-3 shows that as the trap is flushed the irregularities of plasma seeding disappear.

**Laser Pulse Shapes**

The laser profile was measured as well using a fast rise time photodiode whose rise time is <200 ps and a TDS-520D 500MHz 1Gs/s Oscilloscope externally triggered by the Q-switch sync output from the Big Sky Ultra. This trigger scheme is preferable to that of triggering by the pulse in that the pulse width and decay with respect to Q-switch trigger-in can be observed. Figure 4-4 shows the results of these measurements. The detector was tested for linearity using Thor-Labs .3 ND filter. The pulse energies were adjusted (increased) by changing the Q-switch delay time via the factory recommended
front panel control with arbitrary units ranging from 0-10 in increments of 0.5. Lasing output was not observed below a setting of 3.5. Maximum output is obtained with a flash lamp to Q-switch delay of 163 µs. As the Q-switch delay is increased, a decrease in laser output is observed along with pulse stretching. A minimum FWHM pulse width of 7.8 ns is obtained when the maximum energy and minimum Q-switch delay is used. A maximum FWHM pulse width of 55 ns is obtained at the maximum Q-switch delay.

**Time Integrated Measurements**

Measurements of spectral emission are typically collected as time integrated, spectrally resolved or as spectrally integrated temporally resolved signals. It has been shown by Carranza et. al. that while iCCD cameras provide significantly more gain on the signal, CCD detectors provided a greater signal to noise ratio. A system which uses a photomultiplier or any other continuous detector will be locked spectrally for each measurement, its spectral integration determined by the instrumental bandpass.

These measurements were carried out with an Ocean Optics LIBS 2000 spectrometer. The instrument incorporates seven broadband, high resolution spectrometers which provide a spectral resolution of .1 nm and a spectral range of 200-900 nm. All channels are triggered by the same clock and provide a spectrometer to spectrometer jitter of less than 20 ns. The system has a fixed integration time, $t_g$, of 1 ms and a variable delay time, $t_d$. This ensures that regardless of the $t_d$ value, the entirety of the emission signal will be integrated.

The plasma emission signal is back-collected using a pierced mirror. The plasma emission is collimated by the same lens used to focus the excitation laser and the pierced mirror projects it onto a heptafurcated fiberoptic cable coupled to the spectrometer module. The pierced mirror collects the emission from the direction of
beam propagation in order to collect consistent signals with small particle spacial fluctuations. Real time images and snapshots are acquired using a Supercircuits PC-243C CCD color video camera.

**Particle-Plasma Measurements**

Measurements for particle plasma interaction were conducted using a laser energy of 65mJ/pulse at the sample which corresponds to the maximum output of the Big Sky Ultra output. This provided 300 GW/cm² to the beam waist. Particles were suspended in the balance and aligned with the HeNe beam. Once the particle scatter signal was maximized by monitoring the output of the LIBS 2000 spectrometer, the Nd:YAG was triggered, creating a large luminous plasma in the vicinity of the particle. (Figure 4-5) A LIBS spectra was recorded for each laser shot. Every laser shot removed completely the particle in the balance. The process of particle capture, scatter signal maximization and signal acquisition was repeated for 50 particles per set. The V\text{DC} offset voltage was monitored for each particle ensuring similar m/z. The calcium chloride particles described and characterized in Table 3-2 were used for these measurements.

**Laser-Particle Measurements**

Measurements for the laser particle interaction were conducted using a laser pulse energy of 30 mJ/pulse. The procedure is the same as for the above breakdown threshold measurements with the exception of laser energy. While this energy is below the breakdown threshold of purified, filtered air, this energy provided sufficient fluence to initiate the LIP on the particle. Without a particle in the beam waste of the Nd:YAG there is no emission signal as there is no plasmas formed. The laser was free-run to ensure this condition prior to sampling. This effect can be seen in Figure 4-6. The calcium
chloride particles described and characterized in Table 3-2 were used for these measurements.

**Results and Conclusions**

In order to verify that the operational conditions provide a laser particle interaction between the particle and the excitation pulse, the chamber was flushed and a single 9.8 μm particle confined and desolvated through laser heating. The sample was moved 0.5 mm from the HeNe beam and the excitation laser fired. No luminous plasma was observed and no signal recorded on the spectrometer. The same particle was moved back into the HeNe and its scatter signal optimized. The particle was completely ablated upon triggering of the excitation beam. As seen in Figure 4-6, an intense LIBS emission signal representative of calcium chloride was recorded. Ensembles of 25 spectra were recorded and averaged for each particle diameter.

**Effects of the EMF in the Balance**

Particles and plasmas confined by a quadrupole experience many forces from external fields and from collisional interactions. The equations of motion described by Davis\(^{28}\) consider gravitational and electrical fields as well as Stoksian drag, which can be a restorative force in a particles EOM’s. Drag effects are reduced in reduced pressure. In the quadrupole field within the EDB or any quadrupole, there is no potential with respect to ground only at the centroid of the field. For all other space there exists a field gradient. As an extension of Gibb’s phase rule, one needs for each field present two state variables to describe the state of the system. Thus a plasma state may not be defined for a plasma in such a field using only pressure and temperature.

\[
F = C - P + 2
\]  

(4-5)
In the case of the EDB we may need the external electric and magnetic field magnitude. The associated torque on the plasma has been shown to significantly alter the emissions of some elements. The effects of the electric field were studied using a triggering mechanism which can consistently trigger the laser at any phase angle of the high voltage AC carrier designed through collaboration with electrical engineer, Steve Miles of the UF department of chemistry Electronics Shop. Signal to background ratios are taken and the argon ion line at 488 nm is observed for any change in intensity. There are no visible effects from this other external field on laser plasmas in the canter of the trap at any phase angle, though other positions were not tested.

**ABT v. BBT**

Representative spectra are presented in Figure 4-7 from the LIBS analysis of 9.8 μm CaCl₂ particles with the laser operated at 35mJ/pulse for set (a) and 85mJ for set (b). The spectra are presented sequentially in the order of ablation. Using the EDB we have a 100% direct particle hit rate, eliminating the need for complex sampling statistics or processing to discriminate hits and misses. ABT spectra are marked by a higher continuum contribution compared to BBT spectra as well as a higher variance in the emission signal from particle to particle. The higher continuum contribution is not unexpected at higher fluences as more radiation can be absorbed by the plasma after formation.

On initial observation of the data in Figure 4-7 showing the LIBS emission signal collected from 9.8 μm particles ABT and BBT, we see a larger continuum contribution and a significantly larger variance in the emission signals across the set of ABT measurements. The most dramatic noise is at the calcium emission lines. Causes of this variance cannot be completely attributable to the indiscriminate formation of a
plasma in the trap. As with BBT measurements, small variations in the position of the particle with respect to the plasma provide large fluctuations in the interaction of the particle and the LIP, but this position is highly controlled.

Apart from the high RSD in the calcium lines, another feature stands out. The hydrogen beta emission is consistently visible across all of the ABT measurements, and yet it stands out as a 36% RSD above the background in the BBT measurements. Our sample, CaCl₂, is used as a desiccant due to its hygroscopic nature. Desolvation of the CaCl₂ containing droplets will thermodynamically first produce CaCl₂•6H₂O.

**Particle Size Limits**

Analysis of the RSD per pixel for 14.3, 9.8 and 7.2 μm indicates that in the case of 7.2 μm operating at ABT conditions the entirety of the particle is included in the emissive volume. The RSD plots show that the noise in the signal is equivalent to the noise in the continuum. This indicates that there are no significant fluctuations in the calcium emission compared to that of the continuum. This trend results from complete incorporation by laser ablation and subsequent plasma formation. The same 7.2 micron particle ablated by a 35 mJ/pulse excitation show an increased RSD at calcium emission lines and hydrogen 656 showing the variation of signal associated with incomplete ablation processes. These effects only become more pronounced as particle diameters increase.

A classic calibration demonstrating this effect could not be constructed using the current experimental configuration. Trapping and visualizing particles below 6 μm becomes all but impossible due to field imperfections from the hand wrought electrodes. Aerodynamic drag forces begin to dominate the momentum terms in the EOM’s as well.
at low masses. A maximum frequency of 400 Hz and atmospheric pressure conditions are the limiting parameters.

**Limits of Laser-Particle Interactions**

For plasma particle interactions, Asgill showed that the particle size limits are diffusion and heat transfer processes limited.\(^{15}\) The plasma contains the energy absorbed from the pump source and transfers this into the particulate. There is no energy directly transferred into the particle from the laser source, with the exception of the occasional particle being in the beam waist which is a statistical occurrence. The laser-particle hits are attributed as a noise source by Hahn and Niemax.\(^{61}\) In the EDB we have direct laser absorption in the particle which we hoped would allow for complete ablation of larger masses, which would extend the dynamic range for quantification above those reported by Hahn and Omenetto.\(^3\)

Having been previously reported that an upper size limit for quantification exists from 2-7 μm, a similar limit was expected to be observed from our ABT measurements. The enthalpy of vaporization of is calculated from enthalpies of formation values tabulated in the Journal of Physical Chemistry Reference Data and found to be 1216 kJ/mol; thus a 6μm particle of CaCl2 should require only 22 μJ to vaporize and atomize.\(^{69}\) Our excitation pulse is 85mJ for the ABT measurements and 35 mJ for BBT, both a full three orders of magnitude greater that the required energy for complete vaporization and atomization.

As the mass of a spherical particle increases with the cube of the radius, a linear relationship should be observed when plotting signal intensity versus particle radius cubed. Non-normalized ensemble averages for sets of 20 particles of each diameter,
7.2, 9.8, and 14.3 µm, are presented in Figure 4-9 for laser energies BBT. It is readily observable that the expected cubic relationship in signal intensity and diameter does not exist for any calcium emission, indicating that a linear relationship between mass and signal intensity does not exist when operating below the breakdown threshold and supplying three orders of magnitude more energy than that required to potentially generate such a trend.

Closer examination of the nature of the laser particle interaction and its fundamental differences to that of the plasma particle interaction with respect to relationship between a large micro-particle and the bulk material offers a rationale behind this effect. The apparent energetic dilemma can be explained by following the energetic pathways as described by Lushnikov and Negin. The calculation for the enthalpy of vaporization does not incorporate the energy required for ionization or any energy losses to the surrounding in the form of convection, radiative losses, ionization of the surrounding gasses or transmission of the excitation pulse prior to dense plasma formation, nor does it consider the proportion of the beam which can interact with the particle. Consider that in these experiments, the beam diameter is up to 10 times that of the target. When within the Rayleigh length of the beam’s focus the quantity of energy directly deposited on the particle increases proportionally to the square of the particle radius, but the particle mass increases cubically, respectively. It follows that the photon to atom ratio, PAR, available for excitation decreases as particle diameters increase for any given pulse shape. (Figure 4-10) The photon atom ratio is a concept introduced by Stipe et al.
A second equally important consideration is that of the transition from absorption of laser energy from the particle to the inverse-Bremsstrahlung processes after the formation of optically thick plasma at the excitation wavelength. It is this decoupling process that terminates the laser material interaction in a traditional bulk sample, and it is this mechanism that limits the laser particle interaction time to the same timescale. The processes for plasma formation and propagation via a nanosecond pulse are absorption, heating, and cascade ionization rapidly followed a decoupling of the laser. These events can take place long before the pulse could traverse the particle’s position. While there is $10^3$ the energy required for full plasma incorporation, it simply cannot reach the sample to accomplish these processes. Thus all events which involve plasma formation from laser-particle interactions inherently undergo plasma-particle processes as well when the particle mass is not completely laser ablated by the laser.

Third, we consider the scatter cross section for a representative spherical particle and the air using Mie Theory and an algorithm developed by Laven$^{54}$ in order to determine the proportion of light which can be absorbed by varying diameter particles, $Q_{abs}(a)$. Using published values from CaF$_2$ as a surrogate for CaCl$_2$, which has limited information regarding the complex refractive index, the average absorption is found to be approximately 1.5% at 1.064 μm excitation. While the value is relative, the trend is consistent from one particle to another since in the Mie regime the scatter cross section increases with the square of the radius. Figure 4-11 offers an optimistic maximum value of 7% by $Q_{abs}$. The same calculation was done for a sphere of superheated air at 5000K
and plotted along side $Q_{\text{abs}}$ for the particle. It is concluded that absorption by air offers an insignificant contribution to the heat transferred to the particle for plasma formation.

The fourth and likely the most critical consideration regarding the laser particle interaction and its differences from the plasma particle interaction involves the breakdown threshold and the irradiance (W/cm$^2$) required. We consider a pulse with a 4 ns FWHM as shown in Figure 14 with an irradiance just below the dielectric breakdown in air. Knowing the square dependence of the extinction coefficient with radius, the results presented by Weyl$^{57}$ and the threshold measurements by Pinnick$^{55}$ and the absorption trends shown by Chen et al.$^{71}$ can be combined into Figure 4-12.

For this pulse, the amount of time during which the laser can interact directly with the particle is limited by the characteristic time it takes to achieve the critical irradiance, form an optically dense plasma, and change the scattering scenario from that of particle dominated scattering to that of plasma dominated scattering mechanisms. After this time only photons not scattered by the plasma can reach the particle. It is this decoupling of the laser from the particle surface which limits the laser interaction and the mass ablated via the interaction. After the absorption processes are dominated by inverse Bremsstrahlung processes. The rapid, the fluid dynamic expansion of the vaporized mass decays to an equilibrium state and further mass removal should be considered by diffusion models as per Asgill and Hahn.$^{61}$ A direct result of this characteristic time is that in order to extend the linear dynamic range of aerosol analysis into larger particle sizes, it is not necessarily more energy we require, but more time for deposition of the energy from the laser pulse. Longer pulses with lower peak power will provide greater mass action.
A second consequence of this critical time is that every laser-particle interaction which forms a plasma must then be a plasma-particle interaction, creating two clear regimes for the processes which dominate. We are lead to revisit and clarify the terms ABT and BBT and the conditions that follow from each. Clearly, if a plasma is to be formed, the dielectric breakdown threshold must be breached. Energies ABT will form a plasma with or without the presence of a particle while BBT will not. In both cases, the energies are above the dielectric breakdown threshold for the particle/air system. In both ABT and BBT measurements we always have a direct particle hit, i.e. a laser interaction followed by plasma interaction. Thus, the primary difference is the ratio of energy absorbed by the particle to energy absorbed by the plasma, and the energetics can then be defined by plasma dominated events or by particle dominated events. Long pulses offer a greater amount of time for the laser to interact with the particle directly.

The last consideration on the limits of particle size involves the excitation wavelength. Infrared excitation at 1064 nm has, as a consequence of its frequency, some of the least desirable effects when applied to LIBS laser-particle analysis. The frequency has a poor absorption cross section for the analyte and a very high absorption cross section for the plasma. In fact, examination of collider resonance conditions shows that the higher is the excitation frequency, the lower the plasma absorption cross section will be.

**Partial Particle Ablation**

When performing BBT measurements on 14.3 μm particles as well as other diameters, it was necessary to position the particle exactly in the center of the 1064 nm beam. In one study the particles were placed on the beam edge to investigate the resulting effects. When this was done, the particle could be partially ablated in a way
that gave a LIBS signal and left part of the particle remaining in the trap. Since a luminous plasma would form indicating particle contact and the LIBS signal showed the presence of calcium, as expected it must be inferred that it was a “direct” laser interaction and that mass was removed in order to provide the calcium signal. What was unexpected was the resulting behavior of the particle. It remained vertically centered in the balance indicating that the mass to charge ratio remains constant after partial ablation with 1064 radiation.

As a rule: the volume of a sphere is reduced cubically with respect to the radius \( a \). The charge on these particles was assumed to reside entirely on the surface which would decrease quadratically with respect to \( a \), which is not expected. One explanation is that of a uniform charge distribution throughout the particles. Conductive spheres produced from the conductive solution should have a uniformly distributed electrical charge. Even dielectric spheres of CaCl\(_2\) should provide relatively smooth distributions. Another possible explanation is that the 1064 radiation induces a local dipole in the charge sphere causing the local charge on the particle to be lower in the vicinity of the ablated material. This measurement was repeated several times and recorded in live video.

**Micro-particle Generation**

Following ablation of all particles, a flow of particles is observed traversing the \( z \)-direction on either side of the balance rings after approximately 420 ms and rapidly moving. The motion of these particles is unperturbed by the electric field on the rings indicating that they are electrically neutral. These observations were made using the CC-TV camera originally intended for alignment purposes.
Table 4-1. Description of optics used for alignment, ablation, and signal collection to be used in conjunction with Figure 4-1.

<table>
<thead>
<tr>
<th>Optical Element</th>
<th>Description</th>
<th>Diameter (Φ, mm)</th>
<th>Focal Length (F#)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>BCV Lens</td>
<td>50</td>
<td>50 (1.0)</td>
<td>S1 Fused Silica</td>
</tr>
<tr>
<td>L2</td>
<td>PCV Lens</td>
<td>50</td>
<td>120 (2.4)</td>
<td>S1 Fused Silica</td>
</tr>
<tr>
<td>L3</td>
<td>PCV Lens</td>
<td>25</td>
<td>80 (3.2)</td>
<td>UV/AR Quartz</td>
</tr>
<tr>
<td>L4</td>
<td>PCV Lens</td>
<td>25</td>
<td>120 (4.8)</td>
<td>UV/AR Quartz</td>
</tr>
<tr>
<td>L5</td>
<td>BCV Lens</td>
<td>25</td>
<td>110 (4.4)</td>
<td>S1 Fused Silica</td>
</tr>
<tr>
<td>M1 / M4</td>
<td>Mirror</td>
<td>50</td>
<td>N/A</td>
<td>Coated Aluminum</td>
</tr>
<tr>
<td>M2</td>
<td>Dielectric Mirror</td>
<td>25</td>
<td>N/A</td>
<td>Coated BK7</td>
</tr>
<tr>
<td>M3</td>
<td>Pierced Mirror</td>
<td>300 x 300</td>
<td>N/A</td>
<td>Coated Aluminum</td>
</tr>
<tr>
<td>P1</td>
<td>Dove Prism</td>
<td>30</td>
<td>N/A</td>
<td>BK7</td>
</tr>
<tr>
<td>F1</td>
<td>Fiber Optic</td>
<td>1.00</td>
<td>(0.22)</td>
<td>UV-Vis XSR</td>
</tr>
<tr>
<td>F2</td>
<td>Fiber Optic</td>
<td>0.400</td>
<td>(0.22)</td>
<td>UV-Vis highOH</td>
</tr>
</tbody>
</table>
Figure 4-1. Optical setup for LIBS signal collection. Laser paths are shown with red arrows. Signal paths are shown with blue. 632 and 1064 nm laser beams are made to co-propagate on the primary optical axis and focused on the sample volume. Collimated plasma emission is back-collected with the pierced mirror and F-matched to an optical fiber and spectrometer.
Figure 4-2. Measurement of the breakdown threshold in laboratory air is shown. Unfiltered Lab air was measured to ensure that chamber seeding would not cause spurious plasmas to be formed when performing BBT measurements.
Figure 4-3. Laser Pulse Shapes. Changing the pulse energy by controlling the flash lamp to Q-switch delay causes both pulse stretching and increased the time from Q-switch trigger to pulse output. FWHM values range from 7.8 – 55 ns. The observed undershoot is due to operation of the detector in photovoltaic mode v. operation with a forward bias.
Figure 4-4. As argon flushed the cell the effects of chamber seeding diminish, eventually allowing the formation of a single plasma. The 488 nm emission line on argon is shown here centered as a spectral image. The scale is approximately two centimeters from top to bottom.
Figure 4-5. The HeNe signal used for targeting is shown here. In the bottom trace, the only signal recorded is from the Fresnel reflection from the front window on the balance chamber. Upon illumination of an incident particle centered in the balance the signal reaches a maximum. This condition is repeated for each particle.
Figure 4-6. Signals here result from below breakdown threshold measurements using a broadband spectrometer. In the absence of a particle, no plasma is formed and no signal is generated. Using identical conditions with the introduction of a particle in the laser focus yields a luminous plasma formed from the interaction of the laser with the particle.
Figure 4-7. Representative spectra for BBT (a) and ABT (b) LIBS measurements on 9.8 μm particles. The two general trends observed from ABT and BBT measurements for all particle diameters are that pixel by pixel RSD increases as laser energy decreases and as particle size decreases.
Figure 4.8. Demonstrating the significant differences in %RSD and noise trends in measurements made ABT and BBT. ABT spectra generally show a greater variation in the calcium emission signal with respect to the background. There appears to be a significant variation in the hydrogen emission in BBT interactions. The exception to the rule is 6 ABT.
Figure 4-9. Here the ensemble averaged spectra for nominal 7.4 (a), 9.8 (b), and 14.3 (c) μm particles are shown. Considering any line one could choose from the emission of calcium, there is no visible trend suggesting a relationship between mass and signal intensity.
Figure 4-10. As the particle diameter increases, the mass increases cubically (dash) while the cross section in the excitation beam increases quadratically (solid). Volume and cross section comparisons are made to a 2.1μm particle.
Figure 4-11. Plotting $Q_{\text{abs}}$ v. particle size parameter shows that the extinction coefficient for differing particles of identical composition can be substantially different. Ablation processes decrease the particle diameter making the interaction uniquely dynamic.
Figure 4-12. Comparing the irradiance of a pulse to the threshold for plasma formation provides a characteristic time, $\tau_{\text{crit}}$, which defines the termination of the direct laser-particle interaction.
CHAPTER 5
STATISTICAL CONSIDERATIONS FOR LASER-PARTICLE AND PLASMA-PARTICLE INTERACTIONS

Introduction

Each LIBS spectrum collected from a sample is taken from a unique experiment conducted with one unique sample interface configuration and one laser pulse. The inherent noise in the spectral data and the way in which that noise propagates into the uncertainties for absolute sample quantification is one of the primary reasons LIBS is not yet widely accepted as a quantitative analytical technique. Samples are most often collected by averaging an ensemble of spectra collected through repeated experiments.\textsuperscript{72} The ability to accurately represent information about sample compositions is limited by an analysis of the noise composition of different signal components either by the variance in normally distributed data, comparison of relative standard deviations or by inferences from a calibration graph.\textsuperscript{73} Work by Michel and Chave show explicitly that the assumptions of normality are not always applicable.\textsuperscript{74}

Attempts to correct for shot to shot fluctuations in signal and background intensity have been made by considering the signal to background ratios, multivariate analysis, and even acoustics considerations.\textsuperscript{75,76,77} Each of these methods is a normalization process. Poussel and Mermet note that for low concentrations, using a peak to background ration appears to lower the LOD.\textsuperscript{78} The P/B method as well as S/N and averaging were compared for gaseous and particulate systems by Alvarez et al.\textsuperscript{79} Ingle and Crouch offer an extensive treatment of statistical considerations for spectroscopic analyses.\textsuperscript{80}

LIBS nowadays vary from the analysis of soils, complex organics, recyclable materials and other materials which are highly amorphous and/or do not have matrix
matched standards available.\textsuperscript{81,82} LIBS is even being applied to molecular systems such as explosives and bio-weapons.\textsuperscript{83,84} Researchers are depending on more rigorous chemometric methods which combine multivariate normalization and techniques such as principal component analysis or singular value decomposition to pull important information out of the seemingly noisy mess that the ensembles of spectra can produce.\textsuperscript{85,86} These methods are often effective because, while not immediately obvious in the spectral data to the casual observer, each spectral component has an intrinsic interdependence on another.

Just as the spectral features are intertwined, so must be the processes that govern both plasma particle and laser particle interactions. When laser plasmas are formed in air we should expect to see emission from nitrogen and oxygen, the primary components of our atmosphere. In Florida and other damp environments it is common to see a significant contribution from water vapor as well. Trace elements can also appear such as carbon from CO$_2$.\textsuperscript{87} When laser plasmas are formed on or adjacent to bulk samples we expect to see emission from the representative constituents in that particular sample as well as the surrounding environment. The net signal will contain some combination of sample and environment. This emission intensity interdependence is highly correlated to where and how one focuses the laser on the sample.

It is common practice to have a bulk sample positioned such that it lies on a plane some few millimeters before the actual focal length of the lens used for the excitation pulse. It has been noted that the sound of the shockwave from the LIBS event can be directly related to the emission.\textsuperscript{88,76} LIBS operators are likely familiar with the dramatic audible changes which occur from slight changes in sample depth. If a laser is
operated at pulse energies that breakdown air at the focus, it makes sense by our last conclusions that one should have the sample in a location which the plasma is formed only by interaction with the sample and not the atmosphere. Due to the transition of energy deposition mechanism at the onset of an optically dense plasma and the orders of magnitude differences in the critical irradiance required to initiate dielectric breakdown on differing media, the total energy of the plasma-analyte system can be greatly affected by very small fluctuations in space or peak pulse power.

With particles, the sample depth as well as the radial positions within the beam can create signal variances. An extreme case of position sensitivity is the hit no-hit comparison in exemplified in work by Carranza et al. for on online particle monitoring.\textsuperscript{31} No particle returns no signal. In the present work, this issue has been all but eliminated by the sampling methods, but large signal variances are still present despite the careful positional control. In plasma systems we have at least two processes occurring either simultaneously or sequentially. A plasma must be formed, clearly, but whether the plasma is formed in air simultaneously with the plasma formation from the particulate matter is an interesting consideration. For both ABT and BBT the processes were originally considered as being coincident.

In order to determine the interdependence of the events we use several statistical approaches originally presented in an unpublished work by Omenetto and in the theses presented by Heh Young Moon.\textsuperscript{89} The considerations compare how the noise in the signal and the noise in the background are related in order to make inferences about the spectral information and vice versa.
Theory

Noise in any measured value is comprised of separate components or types having definite origins. An instrument has a certain level of signal fluctuation even in the absence of any signal input. This type of fluctuation is specifically referred to as dark noise. Adding an input signal may or may not affect the dark noise. If the signal does not affect the dark noise we say that the two types of noise are uncorrelated. A signal itself may have a component such that there is a system response in the absence of an actual signal. This type of response is known as the background. Each type of response can have its own associated noise and may be correlated or uncorrelated. The effects of this can be seen from the definition of error and the rules for propagation of error. The error in an arbitrary response function composed of only signal noise and background noise is found by differentiation and application of the chain rule and given by Eqns. 5-(1-3):

\[ R(S, B) = S + B \]  

\[ \varepsilon_R^2 = \left( \frac{\partial R}{\partial B} \right)^2 \varepsilon_B^2 + \left( \frac{\partial R}{\partial S} \right)^2 \varepsilon_S^2 + 2 \left( \frac{\partial R}{\partial B} \right) \left( \frac{\partial R}{\partial S} \right) \varepsilon_S \varepsilon_B \]  

\[ \varepsilon_R^2 = \left( \frac{\partial R}{\partial B} \right)^2 \varepsilon_B^2 + \left( \frac{\partial R}{\partial S} \right)^2 \varepsilon_S^2 + 2 \theta \left( \frac{\partial R}{\partial B} \right) \left( \frac{\partial R}{\partial S} \right) \varepsilon_S \varepsilon_B \]  

Correlation

Theta, \( \theta \), is defined here as the correlation coefficient and has a range of -1 to 1. When \( \theta \) is zero we say that the errors are uncorrelated and the errors can be calculated simply as the RMS noise and will be considered from here out as SD. RSD are calculated by the wavelength to wavelength (pixel to pixel) ratio of the SD to the mean.
Without some assumptions or *a priori* knowledge, the correlation coefficient shown in Eq. 5-3 is unsolvable as we cannot directly measure the noise in the background under a peak. For LIBS measurements it is accepted to take the off peak continuum intensity as the background intensity for the line and the associated noise. When considering two or more events occurring either simultaneously or independently we can consider the dependence of one event on the other by calculating the correlation coefficient between the two events, in particular the Pearson Product Moment Mean, $\rho(X, Y)$ since the definitions are equivalent.

$$
\rho(X, Y) = \frac{\text{Cov}(x, y)}{\sigma_x \sigma_y} = \frac{\sigma_{xy}}{\sigma_x \sigma_y} = \theta
$$

**Methods**

The correlation coefficient, $\theta$, is calculated using two approaches in order to determine the relationships between signal and background and represented in Figures 5-1 and 5-2. Data sets are comprised of 25 samples covering 14400 individual $\Delta\lambda$ intervals which include both S and B. The maximum $\Delta\lambda$ is determined by careful observation of the LIBS data and with exception of H($\alpha$), is determined to be 16 pixels. A signal array, $X_i$, is defined at pixel one and a background reference array, $Y_i$, at $X_i + 16\Delta\lambda$ so that $Y_i = X_{i+16}$. $\rho(X, Y)$ was then plotted with respect to wavelength. In the second $\theta$ approach four lines corresponding Ca I, Ca II, N I, N II and H($\alpha$) are defined as X and $\theta$ calculated with respect to each $Y_i(\lambda)$. This approach gives the $\rho(S, \lambda)$ between the emission of each signal to each $\Delta\lambda$ whether S or B. This was performed for each dataset ABT(6,9,12), BBT(6,9,12). The average spectral intensity, SD, and RSD of each set is also calculated in a similar fashion.
Results and Discussion

The lines that were chosen for correlation analysis are of interest as they represent species that all show strong emission from the plasma and which must have different origins. In filtered laboratory air it was observed that nitrogen is present but not calcium. Any calcium emission observed is representative of the particulate loading and nitrogen emission is representative of the air plasma. The following trends are observed.

- Ca(I) : \( Y_i \) Sample : sample / plasma
- Ca(II): \( Y_i \) Sample : sample / Plasma
- N(I) : \( Y_i \) Plasma : sample
- N(II) : \( Y_i \) Plasma : sample
- H(α) : \( Y_i \) Moisture : sample/plasma

Several themes are observed from the statistical analysis which produce SD and RSD plots. First, the RSD plots for BBT show smaller variance in emission lines than those RSD plots for ABT. (Figure 5-3) In ABT, RSD measurements are typically higher than that of the continuum, while BBT shows positive and negative deviations with respect to the background. Second, the standard deviation of pixels corresponding to emission lines is always greater than that of those containing only continuum.

Plots of \( \rho(X, Y) \) show excellent correlation between background noises from the blue up to 630 nm though a different trend is observed in the red to NIR. This proved to be a good proof of concept for the correlation algorithm used. These data also indicate
an increasing correlation of (S+B):B as the photon to atom ratio increases. That is to say that, as the pulse energy increases, there is an increasing relationship between the emission of calcium from the particles, the nitrogen from the plasma and the hydrogen which can originate from both vapor laden air and the particles.

The correlation of N(I) to each Δλ is considered in Figure 5-4. The spectral window shown contains background continuum, calcium I, hydrogen α, nitrogen and oxygen. Looking at 656.3 H(α) in the ABT cases (black) the increase in correlation in from N(I): The increase of correlation in the H(α) noise is clearly visible as particle size decreases. In the case of BBT measurement the Noise correlation remains relatively constant and exhibits a high θ of ≈0.9 in the vicinity of H(α). The range of 642 nm to 650 nm contains several emission lines of calcium. The FWHM of the noise bandwidth associated with the calcium lines decreases and the correlation of those emission lines to the nitrogen emission and the continuum increases as particles get smaller.

In Figure 5-5 the noise in the hydrogen emission signal is compared to the spectral window containing N(II), Ca(I), and plasma continuum. The data indicate that ABT, the larger the photon to atom ratio, PAR, the higher the correlation between H(α) emission noise and N(II) emission noise at 500 nm. In the ABT measurements, there is also a monotonic increase in the correlation between H(α) and the continuum emission. BBT measurements show a consistently high correlation between all emissions. Two considerations can explain the processes at hand. First, in the plasmas that are formed, the free electrons which contribute to the continuum can come from either the ionization of the surrounding gas or from the ionization of the target particle. Secondly, the hydrogen can come either from the hydrated calcium chloride crystal or from the vapor
laden surroundings. In the BBT case, we know that the peak laser power is insufficient to cause a dielectric breakdown only in the surrounding gas; this is an experimental requirement. It follows that the free electron contribution as well as the hydrogen should come from the CaCl₂. This produces a high correlation between both the noises in the H(α) and the continuum regardless of the extent of ablation of the particle.

For the ABT, application of the same logic tells us that a plasma can be formed in the absence of the particle. A large robust plasma is formed from a laser pulse whose beam waist is an order of magnitude larger than the particle. The proportion of energy which is deposited in the particle to that deposited into the air-plasma by the pulse is very small. The plasma is dominated by laser-plasma and plasma-particle interactions and incorporates a significantly higher fraction of the free electron contribution from the surrounding gases. This is clearly seen in the ABT 9 and 12 data. If the water comes from the particle but the electron density comes from the surroundings, a low correlation between the noises in the two would be expected. Variations in particle water content will cause uncorrelated noise compared to the independently varying gas plasma.

The calcium neutral correlation to the continuum background, N(II) and other Ca(I) lines is shown in Figure 5-6 for 14.3, 9.8 and 7.2 μm particles using 35 and 80 mJ per pulse of excitation energy. We see a monotonic increase in the correlation to the signal and background noise for ABT conditions. The correlation plots indicate that when ablating 7.2 μm that signal (S+B) fluctuations in the signal are dependent on plasma processes (B). That is to say: when the continuum increases, the signal increases. The noise in the calcium lines is consistent with respect to the background
and a S/B plot would improve the S/N compared to the average alone. In cases of larger particles this would not hold true.

Comparison of the noise in the Ca(I) to N(II) for ABT shows anti-correlation. An increase in calcium neutral emission is accompanied by a decrease in the emission intensity of the nitrogen ion. This is explicable by considering the signal sources, as we did for hydrogen. Both hydrogen and calcium come from the ablation and incorporation of the particle in the laser plasma. Conservation rules dictate that an increase in energy deposition to the particle necessitates a decrease in energy to the plasma.

Conclusions

Noise correlation plots provide a means to interpret the interrelated processes involved in both laser-particle and plasma particle interactions. Plasma-particle noises appear to be uncorrelated while laser-particle noises appear highly correlated or anti-correlated. When working with aerosols whose mass is too great to be fully ablated, the continuum noise (plasma background) and the noise from particle emission is enhanced by operating the laser BBT. This is the same situation observed when dealing with solid samples. You focus the laser into the sample at a depth before the focal plane. The spot size on the sample increases compared to being exactly at the focus. The Irradiance drops, and the plasma formed has the highest laser-sample interaction possible prior to laser sample separation and laser-plasma dominated energy transfer mechanisms. As is the case for 7.2 μm particles, when the particle is completely ablated by the energy deposition, correlation is improved by increasing the amount of total energy in the system.

Along with noise correlation, it is also important to consider the signal to noise. Figure 5-7 shows signal to background ratios for calcium neutral and ion lines and the
corresponding noise. Better precision is observed for BBT as particle size decreases while the reverse is observed for ABT. The calcium ion to neutral ration is shown in Figure 5-8 and indicates decreasing temperatures as particle size increases. These results are a topic for further consideration.
Figure 5-1. The first method for calculation of the correlation providing $\rho(S, B)$
Figure 5-2. The second method for calculation of the correlation providing $\rho(S, \lambda)$.
Figure 5-3. Demonstrating the significant differences in %RSD and noise trends in measurements made ABT and BBT. ABT spectra generally show a greater variation in the calcium emission signal with respect to the background.
Figure 5-4. From top to bottom, the plots show the correlation of N(I) emission at 744.2 nm for 7.2, 9.8 and 14.3 μm particles. ABT are shown in black and BBT in blue.
Figure 5-5. From top to bottom the plots show the correlation of H(α) at 656.3nm for 7.2, 9.8 and 14.3 μm particles. ABT are shown in black and BBT in blue.
Figure 5-6. From top to bottom, the plots show the correlation of Ca(I) at 633.9nm for 7.2, 9.8 and 14.3 µm particles. ABT are shown in black and BBT in blue.
Figure 5-7. Signal to background plots for two major calcium neutral and ion lines.
Figure 5-8. Calcium ion to neutral trends for ABT and BBT measurements.
CHAPTER 6
SIMULTANEOUS MULTI-ELEMENT ANALYSIS

Introduction

The introduction of the gated CCD and iCCD camera systems as an effective and efficient optical transducer has allowed the LIBS community and other optical spectroscopies to perform many types of measurement with an ease and speed previously unattainable with earlier detector types. The CCD and iCCD camera systems signal to noise was considered by Mueller et al.\textsuperscript{90} and Carranza et al.\textsuperscript{67} for steels with differing results. Mueller reports that the S/N is the same or better for a CCD while Carranza et al. show improvement for the iCCD. Granted, Mueller et al. worked on large bulk materials and Carranza et al. with aerosol laden air. Considerations for the measurements include an optimization of delay and integration times for signal collection of a calcium line. These optimizations would not be possible without time resolution.

Commonly reported in the LIBS literature by individuals using iCCD systems, the detectors are triggered at time, $t_d$, after laser pulse initiation and the charge collected and integrated from the iCCD over a gate width, $t_g$. When used with a suitable spectrometer current iCCD array systems can provide either imaging or rapid broadband detection at a particular time referenced to plasma initiation, $t_0$. Whether operating for imaging or spectral measurement, all space or time dimensions are recorded simultaneously. These qualities can be analytically advantageous and simultaneously quantitatively an Achilles heel to any application which measures a dynamic process like the laser induced plasma as iCCD and CCD systems record the
same interval for each spectral line that may or may not produce the optimal S/N for that particular species.

Each LIBS experiment is an entity unto itself. Each laser pulse is unique; each laser pulse perturbs the sample causing the interaction to be unique. The community has approached this issue statistically, relying primarily on S/N enhancement through signal averaging through enumeration of data from many excitation pulses or by single shot normalization methods. While this is an effective approach for homogenous samples for which there are sufficient material and time required for acquisition, there exist many applications which this is not the case. Inhomogeneity in the form of inclusions or as layers can also cause significant signal variance when sampling across them, causing misidentification. In certain cases, most notably LIBS for aerosols, the sample is simply not massive enough for averaging multiple shots. A CCD system simply cannot provide a complete representation of any event for any given plasma for two reasons. Firstly, time is treated as a scalar and secondly the measurement is only defined for predetermined gate.

LIBS signals are also transient by nature and present limitations to the inferences which can be made about any single measurement from time integrated detectors. Also, situations exist in which this traditional sampling method is impractical or simply impossible. In the cases of LIBS methods for single particles, in aerosol analysis, or for industrial production lines, the sample exists in a different state immediately after measurement rendering ensemble averaging impossible. Carranza and Hahn, Gornushkin et al. and Radziemski et al. report in separate accounts that for diagnostic purposes it is often beneficial to record information about the plasma by
sampling using time resolved measurements and in the case of single shot measurements time resolution is imperative for the improvement of sampling statistics. The physics of the laser plasma and experimental evidence both tell us that the average temperature and density of the plasma decrease over time. While the conditions in the very earliest times of plasma formation are often assumed, extensive work has been done to identify the populations and densities of ions and neutrals within and around the plasma. In doing so, it has been observed through several studies that delay times can be optimized for different species in order to optimize S/N and sensitivity.

Fisher analyzed the emission signal decay of hazardous metals in order to optimize the signal to noise of their emission signals. Their results indicate the time delay selected for signal integration is species dependent. Hohreiter and Hahn describe a technique which uses time resolved measurements to investigate the relationship between single and double pulse LIBS measurements as a tool to investigate “laser coupling” mechanisms while in the related plasma spectroscopy field of ICP-MS Groh et. al show using dual monochromators coupled to time resolved detectors that the transient response signal of aerosolized matter entering the ICP plasma could be monitored. Individual processes such as vaporization and ionization were characterized from the particle injection into an ICP flame by Neimax, et. al.

The experimental requirements of multiple monochromators and multiple iCCD imaging systems, while effective, greatly increase the overhead of the measurement in both time and cost. This work demonstrates that analogous measurements can be accomplished by coupling multiple PMT’s to a polychromator. In this way one can simultaneously observe many species throughout the persistence of the plasma event.
and optimize each analysis for each species within a single shot event. Other methods are available. Polychromators fitted with PMTS or (i)CCD’s can provide rapid, simultaneous measurement of multiple emission lines. Variants such as these have been reported recently for alloy discrimination. 41,100

A Paschen-Runge polychromator fitted with 32 PMT detectors is used to simultaneously collect the persistence profiles of six elemental species in a laser induced plasma on pelletized samples and considered for use in the analysis of aerosols. Calibration plots are generated and statistically analyzed to determine the optimal delay times and integration times for collection. Fitness and instrumental sensitivity are compared at varying delay times to demonstrate the independence of each signal’s persistence in the plasma emission. It is shown that, by carefully selecting delay times and integration gates when collecting time resolved measurements, that one can limit nonlinear effects on calibration curves such as self-absorption and self-reversal when dealing with frequency dependent optically opaque plasmas.

**Experimental Considerations**

Two laser systems are used for the LIBS experiments. One system is used for illumination and positioning, and one for ablation. The ablation laser is a Q-switched Big Sky Ultra Nd:YAG operating at the fundamental frequency and fired by remote trigger. The Nd:YAG is reflected off a dielectric mirror, which is transparent at 632 nm, prior to focusing into the sample with an F/1 suprasil lens. The plasma emission is back-collected and collimated using the F/1 focusing lens, reflected on a front surface U/V enhanced pierced aluminum mirror and condensed onto an Ocean Optics p-1000-2-UV-VIS optical fiber with a 50ax120mm suprasil lens. A two lens system is used at the fiber output to create a region of collimation and create an f-matched input for a
polychromator. When needed, filters are always installed in the collimated region. This collection method reduces effects signal variance due to spatial variances by effectively collecting emission from the entire plasma. The general arrangement is shown in Figure 6-1.

In order to perform the simultaneous time resolved analyses a Leco, Paschen-Runge polychromator fitted with 32 photomultiplier tubes (PMT), originally from a Leco glow discharge SA-2000, was converted from continuous to pulsed operation and retrofitted for use with NIM HV power supplies. The 32 PMT correspond to 32 wavelengths for elemental detection. Wavelength assignments can be found in Table 6-1. A selection of 6 common elements was chosen. The elemental and pertinent spectroscopic data is presented in Table 6-2.

The Rowland Circle’s fixed entrance slit width was measured using diffraction and found to be 12.5 um. The grating was reported by the manufacturer as 2400 groove/mm and the spectral bandpass of .025-.040 nm through fixed exit slits. The bandpass variance is a product of dispersion and uniform-width exit slits. Six individual HV power supplies are used to control each channel separately for gain control. The spectrometer uses R300 tubes below 300 nm and R-306 tubes above. Both Hamamatsu R-300 and R306-m PMT’s are terminated at 1kΩ and read by a Tektronix TDS 520-D 2 channel and a HP54542-C 4 channel, 500 MHz oscilloscopes. Signal disambiguation and tuning was performed using both multi-element and single element hollow cathode lamps coupled through the same fiber optic used for plasma sampling. The Q-switch synchronization output from the Big Sky is used to trigger both oscilloscopes for acquisition.
Individual samples of the pure elements corresponding to the PMT response desired were used to tune and verify the response of the spectrometer. The signals from all 6 pure substances are compared in Figure 6-2. The Paschen Runge has an entrance slit mounted on an adjustable translation stage to traverse tangent to the Rowland circle. Moving the entrance slit across the Rowland circle simultaneously tunes or detunes all spectral lines on the exit arc within the spectrometer. It was demonstrated that tuning one line simultaneously tunes all lines as shown in Figure 6-3.

A series of ½" pellets were pressed from a graphite and sodium chloride matrix containing increasing mass fractions of six elements whose compositions can be found in Tables 6-3 and 6-4. A method blank was prepared from each using pure graphite and pure sodium chloride, respectively. Reagent grade powered samples from Alpha Aesar and Fisher Scientific were massed on an analytical balance, combined and homogenized by milling. The pellets were easily made by compression of the homogenized powders for forty-five seconds in a 1/2" die at 12000 psi.

**Results and Discussion**

Time response curves from the PMT’s were integrated using various $t_g$ and $t_d$ values and plotted to generate compositional calibration curves for each element from each sample. (Figure 6-4) Both pellet sets, the graphite and sodium chloride, displayed significant self-absorption at higher concentrations with the emission of zinc I and silicon I showing self-absorption as concentrations of 1% by mass. In the case of zinc emission from NaCl matrices, the resonant transition at 213.9 nm, the signal has completely diminished within the first few microseconds.

The general trend observed with respect to the calibration curves generated from the two sample sets is that of significantly higher non-linear effects from the sodium
chloride matrix when compared to the graphite at the same concentration. Assuming LTE and a Boltzmann distribution of populations across a density of states which is similar for the neutral emitters, there should not be a significantly higher population of one state when comparing two plasmas with similar parameters. In the case of the sodium chloride matrix a condition must exist which selectively increases these populations compared with the graphite plasma. This is, in fact, a matrix effect.

It is expected that at earlier times in the plasma the population of ions will be at a maximum and the neutrals at a minimum since the temperatures are highest at these early times. However, the slopes of the calibration curves decrease monotonically over time indicating a continuous reduction of emitters. With regard to instrument sensitivity and accuracy, early times in the plasma emission provide the steepest calibration curves and instrumental sensitivity, but the optimum time to collect data for calibration varies from 1.5 to 5.25 microseconds and is element dependent. This trend is shown explicitly in Figure 6-5.

A novel depth profile optimization was used to determine the optimal focal plane in the sample. Ranges of ±2 mm were scanned while the emission signals were collected. The ratios of two time resolved emission signal were taken. As the signals are transient and decaying, at late times when the signals become background noise limited the ratio will fluctuate rapidly on the order of the noise frequency. This is an indication of the relative total plasma emissivity. Figure 6-6 illustrates that a depth of -.2 mm (focal flane within the sample) provides the longest lived signal persistence and the best laser sample energy coupling.
Conclusions

The Paschen Runge polychromator collects many wavelengths, representing many possible sample constituents. By simultaneously collecting the time resolved signals from multiple elements within the laser plasma one can discern plasma to plasma fluctuations as well as element to element trends. This allows for the integration optimization of each elemental emission signal from a single laser-sample interaction which is not possible with iCCD or CCD camera systems coupled to echelle or other grating spectrometers.

This particular polychromator suffers from two major design issues. Leco designed this particular instrument to be used for DC signal collection. The PMT bases were determined by Hamamatsu to be capable of pulsed operation, but significant noise exists in the signal outputs. Also, the exit slits in the instrument are fixed. The selection of only resonant lines by Leco means that self-absorption will be a persistent problem from plasma emission collection.

In order to improve the S/N on the PMT outputs many spectra were averaged. Ten sets of 32 spectra after several cleaning shots were required to get presentable results. Repetitive sets were taken lieu of one, 320 shot sequence due the variance in the signal observed after a few decades of ablation. Finding a new sample spot on the pellet is not an issue, but this is unacceptable for individual aerosol. Different PMT bases may fix this problem. Even if the S/N for the device is improved, the issue of line selection still exists.

In the case of studying particle interactions the Paschen Runge could be an invaluable tool for analysis since not only is each shot a new experiment because of the nature of the generic LIBS experiment, but there is an entirely new sample as well.
Incorporating this type of detector as the collection device for particle interactions could provide volumes of information unattainable from an iCCD system.
Table 6-1. Resonant atomic emission lines detected by the Leco Paschen-Runge polychromator. Aluminum, copper, iron, magnesium, silicon and zinc were selected for isolated, non-interfered lines.

<table>
<thead>
<tr>
<th>Element</th>
<th>Channel #</th>
<th>Wavelength</th>
<th>Interferances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N)</td>
<td>1</td>
<td>149.262</td>
<td></td>
</tr>
<tr>
<td>Carbon (C)</td>
<td>2</td>
<td>165.701</td>
<td>Ar</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td>3</td>
<td>174.272</td>
<td>Fe</td>
</tr>
<tr>
<td>Phosphorus (P)</td>
<td>4</td>
<td>177.499</td>
<td>Cu</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>5</td>
<td>180.731</td>
<td>Mo, Ti</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>6</td>
<td>189.042</td>
<td></td>
</tr>
<tr>
<td>Boron (B-2)</td>
<td>7</td>
<td>208.959</td>
<td>W, Mo</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>8</td>
<td>213.856</td>
<td>Co</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>9</td>
<td>219.226</td>
<td></td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>10</td>
<td>220.353</td>
<td>Co</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>11</td>
<td>225.386</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>12</td>
<td>260.572</td>
<td></td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>13</td>
<td>267.716</td>
<td>W</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>14</td>
<td>288.158</td>
<td>Mo, Zr, W</td>
</tr>
<tr>
<td>Niobium (Nb)</td>
<td>15</td>
<td>316.34</td>
<td>Ce, W</td>
</tr>
<tr>
<td>Tin (Sn-2)</td>
<td>16</td>
<td>317.505</td>
<td></td>
</tr>
<tr>
<td>Copper (Cu-2)</td>
<td>17</td>
<td>327.396</td>
<td>Ar</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>18</td>
<td>330.294</td>
<td>Ce</td>
</tr>
<tr>
<td>Zirconium (Zr)</td>
<td>19</td>
<td>339.198</td>
<td>Mo, Ar</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>20</td>
<td>345.351</td>
<td>Cr, Ni</td>
</tr>
<tr>
<td>Nickel (Ni-2)</td>
<td>21</td>
<td>349.296</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>22</td>
<td>365.35</td>
<td>Mo</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>23</td>
<td>371.994</td>
<td>Cu, Ar</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>24</td>
<td>383.829</td>
<td></td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>25</td>
<td>386.411</td>
<td>Zr</td>
</tr>
<tr>
<td>Aluminum (Al)</td>
<td>26</td>
<td>396.152</td>
<td>Ni, Nb, Zr, Ar</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>27</td>
<td>403.449</td>
<td>Nb, Cr, Ni</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>28</td>
<td>411.179</td>
<td>Ar, Cr, Mo, W</td>
</tr>
<tr>
<td>Cerium (Ce)</td>
<td>29</td>
<td>413.765</td>
<td></td>
</tr>
<tr>
<td>Chromium (Cr-2)</td>
<td>30</td>
<td>425.433</td>
<td>Nb</td>
</tr>
<tr>
<td>Tungsten</td>
<td>31</td>
<td>429.461</td>
<td></td>
</tr>
</tbody>
</table>
### Table 6-2. Transition probabilities and energy levels for corresponding transitions of the six elements monitored with the polychromator

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>(A_{ki}) (hz)</th>
<th>(E_i) (cm(^{-1}))</th>
<th>(E_k) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>213.856</td>
<td>7.09e+08</td>
<td>0</td>
<td>46745</td>
</tr>
<tr>
<td>Si</td>
<td>288.157</td>
<td>2.17e+08</td>
<td>6 299</td>
<td>40 992</td>
</tr>
<tr>
<td>Cu</td>
<td>327.396</td>
<td>1.37e+08</td>
<td>0</td>
<td>30535</td>
</tr>
<tr>
<td>Fe</td>
<td>371.993</td>
<td>1.62e+07</td>
<td>0</td>
<td>26 874</td>
</tr>
<tr>
<td>Mg</td>
<td>383.829</td>
<td>1.61e+08</td>
<td>21 911</td>
<td>47 957</td>
</tr>
<tr>
<td>Al</td>
<td>396.152</td>
<td>9.8e+07</td>
<td>112.061</td>
<td>25 347</td>
</tr>
</tbody>
</table>

### Table 6-3. Sodium chloride pellet composition. Pellets 1 through 5 were initially made and tested. Pellets 1b through 4b were made to supplement the linear portions of the response region.

<table>
<thead>
<tr>
<th>Element</th>
<th>Blank</th>
<th>Pellet 1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>1b</th>
<th>2b</th>
<th>3b</th>
<th>4b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.000</td>
<td>1.034</td>
<td>0.640</td>
<td>0.379</td>
<td>0.159</td>
<td>1.656</td>
<td>0.768</td>
<td>0.456</td>
<td>0.296</td>
<td>0.141</td>
</tr>
<tr>
<td>Cu</td>
<td>0.000</td>
<td>3.870</td>
<td>2.440</td>
<td>1.432</td>
<td>0.602</td>
<td>6.243</td>
<td>0.602</td>
<td>5.927</td>
<td>0.305</td>
<td>0.483</td>
</tr>
<tr>
<td>Fe</td>
<td>0.000</td>
<td>4.024</td>
<td>2.890</td>
<td>1.201</td>
<td>0.640</td>
<td>6.259</td>
<td>0.656</td>
<td>0.383</td>
<td>0.280</td>
<td>0.218</td>
</tr>
<tr>
<td>Mg</td>
<td>0.000</td>
<td>0.778</td>
<td>0.458</td>
<td>0.242</td>
<td>0.122</td>
<td>1.264</td>
<td>0.605</td>
<td>0.412</td>
<td>0.289</td>
<td>0.149</td>
</tr>
<tr>
<td>Zn</td>
<td>0.000</td>
<td>3.110</td>
<td>1.720</td>
<td>0.928</td>
<td>0.503</td>
<td>5.029</td>
<td>0.735</td>
<td>0.426</td>
<td>0.317</td>
<td>0.167</td>
</tr>
<tr>
<td>Si</td>
<td>0.000</td>
<td>1.791</td>
<td>1.041</td>
<td>0.561</td>
<td>0.288</td>
<td>2.940</td>
<td>0.692</td>
<td>0.429</td>
<td>0.464</td>
<td>0.197</td>
</tr>
</tbody>
</table>
Table 6-4. Graphite pallet composition

<table>
<thead>
<tr>
<th>element</th>
<th>Mass %</th>
<th>Blank</th>
<th>Pellet 1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.00</td>
<td>0.8867</td>
<td>1.1197</td>
<td>0.6921</td>
<td>0.5672</td>
<td>0.4467</td>
<td>0.2586</td>
<td>1.9219</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.00</td>
<td>1.7902</td>
<td>2.2605</td>
<td>1.3972</td>
<td>1.1451</td>
<td>0.9018</td>
<td>0.5222</td>
<td>3.8800</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.00</td>
<td>0.7773</td>
<td>0.9815</td>
<td>0.6066</td>
<td>0.4972</td>
<td>0.3915</td>
<td>0.2267</td>
<td>1.6846</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.00</td>
<td>0.1515</td>
<td>0.1913</td>
<td>0.1183</td>
<td>0.0969</td>
<td>0.0763</td>
<td>0.0442</td>
<td>0.3284</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.00</td>
<td>0.8493</td>
<td>1.0724</td>
<td>0.6629</td>
<td>0.5433</td>
<td>0.4278</td>
<td>0.2477</td>
<td>1.8407</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.00</td>
<td>0.8900</td>
<td>1.1238</td>
<td>0.6946</td>
<td>0.5693</td>
<td>0.4483</td>
<td>0.2596</td>
<td>1.9290</td>
<td></td>
</tr>
</tbody>
</table>

Table 6-5. Neutral resonant lines monitored with six channels of the Paschen-Runge polychromator. Aluminum, iron and copper all have similar upper energy levels as do zinc, silicon, and magnesium.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>A_ki (Hz)</th>
<th>E_i (cm^{-1})</th>
<th>E_k (cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>213.856</td>
<td>7.09e+08</td>
<td>0</td>
<td>46745</td>
</tr>
<tr>
<td>Si</td>
<td>288.157</td>
<td>2.17e+08</td>
<td>6 299</td>
<td>40 992</td>
</tr>
<tr>
<td>Cu</td>
<td>327.396</td>
<td>1.37e+08</td>
<td>0</td>
<td>30535</td>
</tr>
<tr>
<td>Fe</td>
<td>371.993</td>
<td>1.62e+07</td>
<td>0</td>
<td>26 874</td>
</tr>
<tr>
<td>Mg</td>
<td>383.829</td>
<td>1.61e+08</td>
<td>21 911</td>
<td>47 957</td>
</tr>
<tr>
<td>Al</td>
<td>396.152</td>
<td>9.8e+07</td>
<td>112.061</td>
<td>25 347</td>
</tr>
</tbody>
</table>
Figure 6-1. Optical setup for simultaneous multi-element analysis. The Rowland circle contains 32 fast rise time “peanut” photomultiplier tubes at fixed wavelengths, recording up to 30 elements. 6 channels are used. Collection of back collected signal eliminates spatial fluctuations by optical integration.
Figure 6-2. Emission traces generated from 6 samples of pure substances corresponding to the detectors response. Different species exhibit different behavior. From the trace, it is possible that the iron detector is on the line wing.

Mg and Fe persistence follows markedly different trend than Al and Cu. Line wing?
Figure 6-3. Demonstration of the tuning ability for the Paschen-Runge spectrometer. Moving the entrance slit across the Rowland circle simultaneously tunes or detunes all spectral lines on the exit arc within the spectrometer. Tuning one line simultaneously tunes all lines.
Figure 6-4. Calibration curves using various integration times. The curves are generated from sodium chloride pellets containing various concentrations of the elements of interest. Trends are shown as simple connected points.
Figure 6-5. Early times in the plasma emission provide the steepest calibration curves and instrumental sensitivity, but the optimum time to collect data for calibration varies from 1.5 to 5.25 microseconds.
Figure 6-6. Ratios of emission signals were used to determine the optimal focal depth in the sample. If one signal tends to zero, the ratio goes to infinity or zero causing large fluctuations. A variation of only four millimeters causes significant change in the persistence of the emission.
Applying a potential of the form:

- Yields a potential of the form:
  - In a quadrupole
- Finding a stable trajectory:

Solve the EOM
- Introduce parameters:

\[
\begin{align*}
\alpha_x &= \alpha_y = \frac{-4QU_0}{M \omega^2 \Omega^2} \\
\alpha_z &= \frac{8QU_0}{M \omega^2 \Omega^2} \\
\beta_x &= \beta_y = \frac{2QV_0}{M \omega^2 \Omega^2} \\
\beta_z &= \frac{-4QV_0}{M \omega^2 \Omega^2} \\
\gamma &= \frac{1}{2} - \Omega t
\end{align*}
\]

- Substitution of parameters yields:
  - Homogeneous Mathieu
- Solutions are:
- Implications:

\[
\begin{align*}
\frac{d^2}{dt^2} \mu_j + \left( \alpha_j - 2Qy_j \cos(2\gamma) \right) \mu_j &= 0 \\
\mu_j &= \alpha + i\beta \\
\omega_1(\tau) &= e^{i\mu \tau} \Omega(\tau) \\
\omega_2(\tau) &= e^{-i\mu \tau} \Omega(-\tau)
\end{align*}
\]

\[
\begin{align*}
a_x &= \frac{8QU_0}{M \omega^2 \Omega^2} \\
q_x &= \frac{-4QV_0}{M \omega^2 \Omega^2}
\end{align*}
\]

Stability is solely dependent on \(a\) and \(q\)
APPENDIX B
SAMPLE PARTICLE SIZE CALCULATIONS FOR THE VOAG

\[ C_1 := 2.92 \times 10^{-3} \]
\[ C_2 := 6.91 \times 10^{-3} \]
\[ C_3 := 2.33 \times 10^{-2} \]

\[ Q := .238 \times 10^{-6} \text{ m}^3/\text{min} \]

\[ f_1 := 60000 \frac{1}{\text{s}} \cdot 60 \frac{\text{s}}{\text{min}} \]

\[ d_d := \left( \frac{6 \cdot Q}{\pi \cdot f_1} \right)^{\frac{1}{3}} \]

\[ d_d \cdot C_1^3 = 7.17 \times 10^{-6} \text{ m} \]
\[ d_d \cdot C_2^3 = 9.55 \times 10^{-6} \text{ m} \]
\[ d_d \cdot C_3^3 = 1.43 \times 10^{-5} \text{ m} \]

V/V concentrations used for making solutions in the 50/50 isopropanol/water solution

Liquid Flow rate in ml/min

Frequency of the piezo in oscillations per min

Definition of droplet diameter.

Dried particle size from solution with \( C = C(1) \)

Dried particle size from solution with \( C = C(2) \)

Dried particle size from solution with \( C = C(3) \)
APPENDIX C
SEMANTIC CONSIDERATIONS FOR LASER-SAMPLE COUPLING IN LASER INDUCED BREAKDOWN SPECTROSCOPY

Introduction

As science expands our understanding of processes and phenomena occurring naturally around us, we develop new theories and techniques, and as a consequence, we have created and adopted new terminologies to describe the newly illuminated physical processes and methodologies. This natural neology has occurred in the field of laser induced breakdown beginning with the simplest convention, the name. Laser Induced Plasma Spectroscopy was considered, though the acronym makes a humorous reference. LIBS, or Laser induced breakthrough spectroscopy, came out as a popular favorite for the field. Throughout the LIBS literature, scientists work to explain extremely complex and interconnected events that are involved with the inception, evolution and termination of the plasma state, which can be quite complex. Energy transfer processes in the laser plasma and laser matter interactions have been discussed at length by several authors in the field\textsuperscript{2,3} and are incorporated into several recent reviews.\textsuperscript{59,102}

Among the language used to describe the processes involved in laser sample interactions throughout the literature is a term which has become popularized through use, but has not been given a clear and concise definition. In fact, I would argue that the term "couple" has found its place as an umbrella, and actually serves to shadow our potentially clear reports with the haze of uncertain denotation. To couple systems has an intuitive meaning for this author of joining, intertwining or combining. Merriam-Webster’s dictionary states, in a definition which seems most applicable to our situation, that the meaning may be "to connect for consideration together" or "to join for combined effect".\textsuperscript{102} This particular set of definitions does not seem directly applicable to photon-
matter interactions and certainly does not cover the interactions with a depth of understanding necessary at the level of peer review. So, we begin with the question: “What does it mean to couple a laser pulse to a sample or any other material?”

A perusal of some recent literature hints at several colloquial definitions. Windom et al. refer to laser sample coupling mechanisms between a laser and a solid and differentiates laser-sample coupling and effects of hydrodynamics. Michel and Chave indicate there is a difference in laser-material coupling and laser pulse-plasma interactions. Gunther and Hattendorf imply that coupling is affected by absorption only in certain samples. In other articles, lasers are coupled to fibers, implying transmission. Lasers are coupled to samples, lasers to plasmas, plumes and samples, plasmas to samples. LIBS seems very coupled and the literature does not immediately offer much in the way of explicitly describing the coupling processes.

Within the literature, attempts have already been made to clarify this in tables, plots and graphs but fall short of a unified explanation. A review by Winefordner et al. of atomic emission techniques presents a table, “Summary of laser-matter interaction and LIP evolution” which could potentially be used to explain coupling. The authors divide samples first by phases and then the solid phase by bandgap. Each of the five sub-categories has its plasma formation characterized by description of free electron formation pathways. While this description improves the view of what may be meant by laser sample coupling by introducing the idea of a bandgap, the processes are unclear and the categories which are described are overlapping.

A better metric for categorization of the interactions is needed, and to rediscover this metric we only need to consider the fundamentals of the interaction pathways.
Presented here is a synopsis of the events occurring in the laser-bulk and laser-plasma interactions from the perspective of fundamental mass and force carrier interactions. Three systematic approaches are used to determine, perhaps, a better choice of diction which can clarify our intent and enhance our communication regarding these laser and plasma processes.

**Laser-Material Interactions**

In LIBS we have two distinct types of interaction which derive from one fundamental relation. They are the laser-analyte and the plasma-analyte processes. One could say they are *coupled*. We have a mass (the analyte) and a force carrier (the photon). The interpretations considered here are the network analogy, Maxwell’s description of electric fields and Mie’s and Lorentz’s solutions to those equations. These considerations along with basic thermodynamic heat transfer considerations can describe all the events leading up to plasma initiation and the energetic consequences of that plasma formation.

**The Network Analogy**

Considering the highly interconnected nature of the laser material processes we first look at the system as a two-port network representing input and output transmission and reflection in order to identify the nature of *coupling*. Four matrices can be generated to describe all possible interactions in the 2-port system. The physical analogy of the multi-port network for designing impedance matched electrical circuits is not new and is applicable to our question of laser-sample coupling. In the schematic of the two-port network shown, \( P_1 \) and \( P_2 \) are the input and output. \( S_{12} \) and \( S_{11} \) represent input transmission and reflection, and \( S_{21} \) and \( S_{22} \) represent output reflection and
transmission. In theory, one could define a higher order multi-port scenario which combines all possibilities of the energetic pathways discussed by Lushnikov and Negin\textsuperscript{1} for all time dependent frequencies and impedances for each of the processes. Defining the complex impedance functions of a material has been the subject of solid state physics and plasmonics for decades. Resonators (antennas) have been developed which are said to enhance certain techniques such as SERS. These antenna tricks are used across the physics, chemistry and medical communities, and the applications can be seen in techniques like EPR, NMR, ECT, “microwave enhanced” LIBS and many others. Each technique relies on absorption or scattering from the equivalent of an embedded antenna. The system response provides information about resonant conditions and is translated into physical descriptions of interactions.

All matter can be described by its frequency and power dependent impedance. Consider the following depiction of dipoles. A material with a frequency dependent permittivity is embedded in a media with a different dielectric function. This case presents the option to select frequencies which resonate with either material or possibly both, depending on the nature of the dielectric functions. The dipoles can represent either an EM transverse wave in a vacuum or the dipoles of a media like a fiber optic cable. This schematic depicts a sample as an embedded antenna and is immediately recognized as describing a particle embedded in a plasma as well. This analogy can also represent a plasma in air or any two boundary model, and is mathematically
equivalent to the network diagram. Impedance matching of the local oscillator and antenna allows for the greatest amount of power throughput, with the least loss in the system.

Maxwell

The interactions of the electric field with matter have been extensively studied and generally described by J.C. Maxwell through a set of classical equations known colloquially as Maxwell’s equations. The state of a transverse wave across two media with different electrical properties can be found by solving Maxwell’s equations for the system. Of great importance when calculating these fields are the electrical properties of the domain the transverse wave occupies and the electrical properties of the wave itself. Rigorous mathematics aside, there are a finite set of outcomes for a wave interacting with a boundary of two materials as a consequence of the continuity and curl requirements for the field. The accepted interpretations of these outcomes are as follows. The wave can be unchanged across the boundary via undisturbed transmission. The wave can be sent back to the source through reflection. The wave can be elastically or inelastically scattered by an interface. The wave can be absorbed through interference and inelastic collisions. Strictly speaking these are all scattering events.
Following conservation laws, the sum of all of the associated energies for each process must total that of the incident wave. Since Maxwell’s equations limit the interactions and since these processes are understood, coupling as referred to in the LIBS literature must be described by one or all of these terms.\textsuperscript{11}

\[ E_{\text{total}} = E_{\text{trans}} + E_{\text{refl}} + E_{\text{scat}} + E_{\text{abs}} \]

The two distinct interactions in LIBS aforementioned are simultaneously described as follows:

(i) The pulsed laser produces intense, coherent electromagnetic transverse waves which oscillate at a given frequency within a given media. All components of the field can be quantified;

(ii) Matter is composed of atoms and ions which are themselves composed of positively and negatively charged particles.

As a result of (ii), all matter can be polarized to some extent through interactions with external forces. While most matter does not exist with permanent electric dipoles, an external electric field can induce such a dipole.

The ability for an EMF to induce a dipole or polarize a material is parameterized by the materials polarizability, \( \alpha \). Polarization of atoms, molecules or any substance requires energy. The energy deposited is stored as a charge separation as in a capacitor. This extent of this is charge separation is the polarization density, \( \mathbf{P} \), and describes the average dipole. For any material we can use the relationships between polarizability and susceptibility along with the drive and receiver oscillator frequencies to evaluate the dynamics of the electric field at any point. The relations are presented without derivation below. From these relationships we determine frequency dependent
dispersion properties for a given material. These dispersion relationships define how EM waves propagate in and around the material, e.g. a laser and a particle or bulk.\textsuperscript{104}

\[
P = E \ast \chi_e \varepsilon_0 \quad P = \varepsilon_0 (\varepsilon_r - 1)
\]

\[
\varepsilon_r = 1 + \chi_e \quad \bar{\varepsilon} = \varepsilon_1 + i\varepsilon_2
\]

It follows that a review of the general dielectric properties of solids liquids and gasses provides a better categorization than previously offered by Winefordner et al. because the electric susceptibility, polarizability and permittivity are fundamental observables which define the dielectric function for a material regardless of phase. The ranges are shown in a power scale below and demonstrates why there is overlap in the descriptions provided by the aforementioned table; there is overlap in susceptibility.

Calculating the electric field magnitude at any point in space around an object as a function of time will provide the portions of energy transmitted, scattered, absorbed and reflected from the impinging field. In the case of laser-plasma initiation, the contributions to energy deposition from reflection and general elastic scattering are null by definition. This leaves inelastic scattering and absorption processes as the sources for depositing the remaining energy.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{susceptibility.png}
\end{figure}

\textbf{Mie}

A comprehensive theory describing all of these energetic pathways for spherical objects with diameters greater than those of the Rayleigh-Gans regime was developed
by Gustav Mie and Lorentz and is known generally as Lorentz-Mie theory or simply Mie theory. The derivations and descriptions are beyond the scope of this work but presented in Van de Hulst’s, “Light Scattering by Small Particles”. Mie scattering theory can be used to determine the magnitudes of each effect through the determination of three matrices: \( Q_{\text{ex}} \), \( Q_{\text{abs}} \), and \( Q_{\text{sca}} \). \( Q_{\text{abs}} \) is simply the difference in \( Q_{\text{ex}} \) and \( Q_{\text{sca}} \). These solutions are well known and similar solutions exist for cylinders, sheets, and other geometric entities. Thus we can completely describe the interaction of a laser beam with a given sample. Coupling was not discussed by Maxwell or Mie, though other physical processes were. Several computer algorithms have been written to solve these equations and can be found free of charge and in open source format.

\[
Q_{\text{ext}} = \frac{2}{x^2} \sum_{i=1}^{N} (2i + 1) \cdot \Re(a_i + b_i)
\]

\[
Q_{\text{sca}} = \frac{2}{x^2} \sum_{n=1}^{N} (2n + 1) \left[ (|a_n|^2 + |b_n|^2) \right]
\]

\[
Q_{\text{abs}} = \frac{2}{x^2} \sum_{i=1}^{N} (2i + 1) \cdot \Re(a_i + b_i) - \frac{2}{x^2} \sum_{n=1}^{N} (2n + 1) \left[ (|a_n|^2 + |b_n|^2) \right]
\]

An alternative approach to finding rigorous solutions to Maxwell’s equations is to consider attenuation by k losses from a plane wave which may be applicable to large particles or bulks. In this approach we take a complex plane wave and consider losses due to a complex component of the refractive index as follows.

\[
E(z, t) = \Re(e^{i(kz - \omega t)})
\]

\[
E(z, t) = \Re(e^{i(2\pi(\eta - i\kappa)z - \omega t)})
\]

\[
E(z, t) = e^{-\frac{2\pi\kappa z}{\lambda_0}} \Re(e^{i(kz - \omega t)})
\]
This analysis leads us back to Beer’s and Lambert’s famous relationship describing the absorption of light by a material with a complex refractive index. Both of these approaches imply that the phenomena of laser-coupling as described by many authors is perhaps a more familiar relationship when dealing with the interactions of a laser and a sample.

One more approach will be considered to directly compare the relations shown for absorption by solids, liquids and gasses to that of the remaining 99.9% of the known universe which exists in the plasma state.

### Laser-Plasma Interactions

The two most important parameters for the laser plasma are arguably the electron number density and the temperature. In the absence of external fields, these two state variables can define the plasma state. Hence, these are the two plasma parameters listed most often in the literature for laser plasma diagnostics and are often calculated from the Saha-Boltzmann or from scattering techniques. Both are optical methods relying on UV-Vis range signals and require careful spectrometric calibration and highly sensitive and elaborate optical setups which negate two of the most appealing aspects of laser plasma spectroscopy: its low cost and experimental simplicity.

The typical laser plasma is a temporal event resultant from the dielectric breakdown of vaporized samples or from a gaseous medium. These plasmas exist on the timescale of microseconds to milliseconds. Determining the plasma state at any given time for these transient plasmas has often relied on the application of pLTE statistical mechanics after having the condition verified or simply assumed to exist in some cases. Previous works show that laser plasmas range in temperature from 10000-
18000 K and have variations in electron number density at least spanning $10^{14}$ – $10^{18}$ per cc.$^{4}$ These temperature and density ranges often occur in a single plasma event as a function of time. High temperatures and pressures exist at early times in the plasma and both decrease as plasma expansion and cooling occurs.

Once dielectric breakdown occurs and free electrons are formed the dependence on sample electric permittivity becomes less important and the predominant consideration is that of highest frequency collider frequencies.$^{56}$ In neutral plasmas this will be that of the electron collision frequency which is also known as the fundamental plasma frequency, $\omega_0$. Generally speaking when the drive frequency is much lower than the plasma frequency the wave is reflected. When the frequencies are resonant the wave is absorbed. When the drive frequency is much greater than the plasma frequency the wave is transmitted unchanged. This can be seen by consideration of the dispersion relationships in the laser induced plasma.

For an ideal, collisional plasma the polarization density is determined by the electron number density, electron mass, and the deviation from resonance of the oscillator as follows. Rearrangement and simple substitution gives the frequency dependent relative permittivity of the plasma.$^{105}$ Using this information we know the frequency dependent extinction coefficient. When the frequencies match, the plasma absorbs energy. When the frequencies mismatch the plasma energy absorption suffers.

$$P = \frac{ne^2}{\varepsilon_0(\omega_0^2 - \omega^2)} * E$$

$$\varepsilon = 1 + \frac{ne^2}{m_\varepsilon\varepsilon_0(\omega_0^2 - \omega^2)}$$

$$\omega_0 = \frac{ne^2}{m_\varepsilon\varepsilon_0}$$

$$\varepsilon = 1 - \frac{\omega_0^2}{\omega^2}$$
The case of the ideal plasma discussed here is qualitatively little different than a conductor with free electrons in the conduction band. The electrons on the surface have a given frequency and will reflect, transmit or absorb in the same manner as our plasma. After all, a mirror reflects light for a reason. This provides the final nail in the coffin for “coupling” as we have defined all processes that can occur using classical electrodynamics and terminology.

**Summary**

In order to effectively discuss LIBS processes we, as a community, should be as clear and consistent in our communication as possible. There are enough ambiguities in these complex processes that we should not exacerbate the situation with a poor choice of descriptors. Coupling as an “umbrella” term should be avoided and the direct processes referred to. Absorption, either single or two photon, always play a role, both in plasma formation and plasma excitation. The absorption process can be optimized by selection of an appropriate excitation frequency. Energy not absorbed by the system cannot be used for development of a plasma or excitation of the sample. These processes can be optimized by matching the excitation frequency to the given sample.

When choosing a sample-laser combination we need to consider the complex permittivity of the material and the frequency of the laser. These cases are described as follows:

(i) Band gap = 0. Free electrons are present, the susceptibility is unity, and the plasmon frequency determines absorption and energetic losses as described by the dispersion relationships.
(ii) Band gap > 0. The absorption spectrum, dictated by $\chi(\nu)$ will provide all relevant energy transfer information up to the point ionization occurs.

(iii) Plasma state. At the time of free electron formation in the gas phase, the absorption coefficients for both the plasma and the sample need to be considered. If the excitation source is not completely absorbed, energy can be simultaneously deposited into both the sample and the plasma.

Excitation of electrons from the valence band to the conduction band in case (ii) creates case (i). Ionization of (i) or (ii) creates case (iii). Each of these interactions and the procession form one to the other are predictable based on the susceptibility and ionization potential of the material. The interactions of laser radiation with the plasma which is formed can be described by Maxwell and if a spherical plasma is created, by Mie.

Instead of using coupled to describe these processes we can consider:

(i) Sample/plasma absorption
   a. Energy available to the system

(ii) Sample/plasma transmission
    a. Energy not available to the system

(iii) Sample/plasma reflection/scattering
    a. Energy not available to the system
LIST OF REFERENCES


54. Laven, P. Mie Plot. (accessed September 1).


63. Belov, N. N., SIMILARITY OF OPTICAL-FIELDS IN LOW-ABSORBING PARTICLES. *Optika I Spektroskopiya* 1988, 64 (6).


BIOGRAPHICAL SKETCH

Andy Warren received his Bachelor of Science degree in Chemistry from Georgia College & State University in 2007 where he was named the Top Graduating Senior for the Department of Chemistry and Physics. As an undergraduate, Andy maintained GC/MS and FTIR instrumentation for the department of chemistry. He worked as an electrical and HVAC/R contractor, welder and consultant for his company, Designed Mechanics, throughout his undergraduate tenure.

After graduating, he joined the doctoral program at The University of Florida where Andy has been the recipient of numerous honors and awards, including the University of Florida graduate teaching award and a Grinter Fellowship.

While at UF, Andy became a member of the research group of Nicolò Omenetto and began his research in laser induced plasma spectroscopy. His research was centered on single-particle LIBS, for which he designed novel instrumentation. His research has been presented at several international conference meetings.

Andy is now pursuing a commercial-industrial role in instrument design and development.