Title
Methods for measurement of heterogeneous materials with laser-induced breakdown spectroscopy (LIBS)

Permalink
https://escholarship.org/uc/item/25t9947t

Author
Effenberger, Andrew Jay

Publication Date
2009

Peer reviewed|Thesis/dissertation
UNIVERSITY OF CALIFORNIA, SAN DIEGO

Methods for Measurement of Heterogeneous Materials with Laser-Induced Breakdown Spectroscopy (LIBS)

A dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy

in

Chemistry

by

Andrew Jay Effenberger Jr.

Committee in Charge:

Professor Douglas Magde, Chair
Professor Kimberly A. Prather, Co-Chair
Professor Steven Buckley
Professor Judy Kim
Professor Jerry Yang
Professor Paul K. L. Yu

2009
The Dissertation of Andrew Jay Effenberger Jr. is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Co-Chair

Chair

University of California, San Diego

2009
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signature Page</td>
<td>iii</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>iv</td>
</tr>
<tr>
<td>List of Figures and Tables</td>
<td>vi</td>
</tr>
<tr>
<td>List of Abbreviations</td>
<td>ix</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>x</td>
</tr>
<tr>
<td>Vita</td>
<td>xi</td>
</tr>
<tr>
<td>Abstract of the dissertation</td>
<td>xii</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 The Development of LIBS</td>
<td>2</td>
</tr>
<tr>
<td>1.2 Introduction LIBS remote applications</td>
<td>5</td>
</tr>
<tr>
<td>References</td>
<td>10</td>
</tr>
<tr>
<td>2. Background for Theory and Experiment</td>
<td>12</td>
</tr>
<tr>
<td>2.1 Fundamentals of LIBS</td>
<td>12</td>
</tr>
<tr>
<td>2.1.1 Plasma formation</td>
<td>14</td>
</tr>
<tr>
<td>2.1.2 Dual-Pulse LIBS</td>
<td>19</td>
</tr>
<tr>
<td>2.2 LIBS Instruments</td>
<td>23</td>
</tr>
<tr>
<td>2.2.1 Laser</td>
<td>23</td>
</tr>
<tr>
<td>2.2.2 Spectrometer</td>
<td>24</td>
</tr>
<tr>
<td>2.3 Scanning Mobility Particle Sizer Spectrometer</td>
<td>26</td>
</tr>
<tr>
<td>References</td>
<td>30</td>
</tr>
</tbody>
</table>
3. Dual-Pulse LIBS Signal Enhancement Correlated to Ablative Particle Production

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Abstract</td>
<td>33</td>
</tr>
<tr>
<td>3.2 Introduction</td>
<td>34</td>
</tr>
<tr>
<td>3.3 Experimental</td>
<td>36</td>
</tr>
<tr>
<td>3.4 Results and Discussion</td>
<td>40</td>
</tr>
<tr>
<td>3.4.1 DP-LIBS with variable inter-pulse delay</td>
<td>40</td>
</tr>
<tr>
<td>3.4.2 DP-LIBS with variable pre-pulse fluence</td>
<td>42</td>
</tr>
<tr>
<td>3.4.3 Single-pulse LIBS with variable ablation fluence</td>
<td>44</td>
</tr>
<tr>
<td>3.4.4 Correlation of intensity, temperature, and particle volume</td>
<td>44</td>
</tr>
<tr>
<td>3.5 Conclusion</td>
<td>49</td>
</tr>
<tr>
<td>References</td>
<td>79</td>
</tr>
</tbody>
</table>

4. Measurement of Common and Trace Elements in Molten Salts using LIBS...

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Abstract</td>
<td>81</td>
</tr>
<tr>
<td>4.2 Introduction</td>
<td>82</td>
</tr>
<tr>
<td>4.3 Experimental</td>
<td>84</td>
</tr>
<tr>
<td>4.4 Results</td>
<td>86</td>
</tr>
<tr>
<td>4.5 Discussion</td>
<td>89</td>
</tr>
<tr>
<td>References</td>
<td>107</td>
</tr>
</tbody>
</table>

5. Conclusion and Future Experiments

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>References</td>
<td>109</td>
</tr>
</tbody>
</table>
**LIST OF FIGURES AND TABLES**

Table: List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Illustration of plasma propagation</td>
<td>27</td>
</tr>
<tr>
<td>2.2</td>
<td>Average ablation rate versus laser fluence</td>
<td>28</td>
</tr>
<tr>
<td>2.3</td>
<td>TSI electrostatic classifier with long DMA</td>
<td>29</td>
</tr>
<tr>
<td>3.1</td>
<td>Experimental LIBS apparatus for DP-LIBS of brass</td>
<td>50</td>
</tr>
<tr>
<td>3.2</td>
<td>Comparison of DP-LIBS and single-pulse LIBS spectra</td>
<td>51</td>
</tr>
<tr>
<td>3.3</td>
<td>Comparison of DP-LIBS and single-pulse LIBS ablation</td>
<td>52</td>
</tr>
<tr>
<td>3.4</td>
<td>DP-LIBS of Cu intensity versus inter-pulse delay</td>
<td>53</td>
</tr>
<tr>
<td>3.5</td>
<td>DP-LIBS of Zn intensity versus inter-pulse delay</td>
<td>54</td>
</tr>
<tr>
<td>3.6</td>
<td>Ablation from DP-LIBS versus inter-pulse delay</td>
<td>55</td>
</tr>
<tr>
<td>3.7</td>
<td>Boltzmann plot of DP-LIBS plasma</td>
<td>56</td>
</tr>
<tr>
<td>3.8</td>
<td>Boltzmann temperature versus inter-pulse delay</td>
<td>57</td>
</tr>
<tr>
<td>3.9</td>
<td>DP-LIBS of Cu versus pre-ablative plasma fluence</td>
<td>58</td>
</tr>
<tr>
<td>3.10</td>
<td>DP-LIBS of Zn versus pre-ablative plasma fluence</td>
<td>59</td>
</tr>
<tr>
<td>3.11</td>
<td>Ablation from DP-LIBS versus pre-ablative fluence</td>
<td>60</td>
</tr>
<tr>
<td>3.12</td>
<td>Boltzmann temperature versus pre-ablative fluence</td>
<td>61</td>
</tr>
<tr>
<td>3.13</td>
<td>Single-pulse LIBS of Cu versus ablative plasma fluence</td>
<td>62</td>
</tr>
<tr>
<td>3.14</td>
<td>Single-pulse LIBS of Zn versus ablative plasma fluence</td>
<td>63</td>
</tr>
<tr>
<td>3.15</td>
<td>Ablation from single-pulse LIBS versus ablative plasma fluence</td>
<td>64</td>
</tr>
<tr>
<td>3.16</td>
<td>Boltzmann temperature versus ablation plasma fluence</td>
<td>65</td>
</tr>
<tr>
<td>3.17</td>
<td>Zn intensity (481 nm) versus plasma temperature dependence</td>
<td>66</td>
</tr>
</tbody>
</table>
Figure 3.18 Zn intensity (334.5 nm) versus plasma temperature dependence.....67
Figure 3.19 Cu intensity (521 nm) versus plasma temperature dependence…….68
Figure 3.20 Cu intensity (510 nm) versus plasma temperature dependence…….69
Figure 3.21 Zn intensity (481 nm) versus plasma temperature and particle volume
dependence........................................................................................................70
Figure 3.22 Zn intensity (334.5 nm) versus plasma temperature and particle volume
dependence........................................................................................................71
Figure 3.23 Cu intensity (521 nm) versus plasma temperature and particle volume
dependence........................................................................................................72
Figure 3.24 Cu intensity (510 nm) versus plasma temperature and particle volume
dependence........................................................................................................73
Figure 3.25 Zn intensity (481 nm) versus plasma particle volume dependence….74
Figure 3.26 Zn intensity (334.5 nm) versus plasma particle volume dependence..75
Figure 3.27 Cu intensity (521 nm) versus plasma particle volume dependence….76
Figure 3.28 Cu intensity (510 nm) versus plasma particle volume dependence….77
Table 3.1 Spectroscopic constants for Boltzmann temperature......................78
Figure 4.1 Electrorefiner setup..........................................................................93
Figure 4.2 Experimental setup of LIBS on molten salt....................................94
Figure 4.3 LIBS spectra comparing pure molten salt with Cr doped.................95
Figure 4.4 High resolution LIBS of Cr...............................................................96
Figure 4.5 LIBS of molten salt with Co and without.......................................97
Figure 4.6 LIBS of molten salt with Co and without zoomed in.......................98
Figure 4.7 LIBS calibration curve of Co using method one.........................99
Figure 4.8 LIBS calibration curve of Co using method two
Figure 4.9 LIBS of molten salt with Mn and without
Figure 4.10 LIBS of molten salt with Co and without zoomed in
Figure 4.11 LIBS calibration curve of Mn using method one
Figure 4.12 LIBS calibration curve of Mn using method two
Figure 4.13 Future LIBS molten salt setup
Table 4.1 Spectral lines of interest
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIBS</td>
<td>laser-induced breakdown spectroscopy</td>
</tr>
<tr>
<td>CCD</td>
<td>charge-coupled device</td>
</tr>
<tr>
<td>DP-LIBS</td>
<td>dual-pulse laser-induced breakdown spectroscopy</td>
</tr>
<tr>
<td>ICCD</td>
<td>intensified charge-coupled device</td>
</tr>
<tr>
<td>LSC</td>
<td>laser-supported combustion</td>
</tr>
<tr>
<td>LSD</td>
<td>laser-supported detonation</td>
</tr>
<tr>
<td>LSR</td>
<td>laser-supported radiation</td>
</tr>
<tr>
<td>SMPS</td>
<td>scanning mobility particle sizer spectrometer</td>
</tr>
<tr>
<td>CPC</td>
<td>condensation particle counter</td>
</tr>
<tr>
<td>DMA</td>
<td>differential mobility analyzer</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

I would like to acknowledge Professor Buckley for allowing me the opportunity to participate in the research in his laboratory.

I would also like to thank all of my committee members for their time in giving me guidance, not to mention a few beers at the pub.

I would also like to thank my family, my mother and my two sisters, Nicole and Michelle, who have always been dear to me, and wife’s family who accepted me as one of their own.

I’m most thankful to have such a wonderful wife, Aphone, who truly gives meaning to my life.

Chapter 3, in part is currently being prepared for submission for publication of the material. Effenberger Jr., Andrew J.; Buckley, Steven. The dissertation author was the primary investigator and author of this material.

Chapter 4, in part is currently being prepared for submission for publication of the material. Effenberger Jr., Andrew J.; Buckley, Steven. The dissertation author was the primary investigator and author of this material.
VITA

2002  Bachelor of Science, California State University, San Marcos

2002-2008  Teaching Assistant, Department of Chemistry and Biochemistry
            University of California, San Diego

2004  Master of Science, University of California, San Diego

2003-2009  Research Assistant, University of California, San Diego

2009  Doctor of Philosophy, University of California, San Diego

FIELDS OF STUDY

Major Field: Chemistry (Physical Chemistry)
Methods for Measurement of Heterogeneous Materials with Laser-Induced Breakdown Spectroscopy (LIBS)

by

Andrew Jay Effenberger Jr.

Doctor of Philosophy in Chemistry

University of California, San Diego, 2009

Professor Douglas Magde, Chair
Professor Kimberly A. Prather, Co-Chair

Laser-Induced Breakdown Spectroscopy (LIBS) is an analytical tool that can be used in a wide range of applications. By focusing a laser pulse onto a small area, material is ionized and heated to 10,000 to 20,000 K. As the plasma cools, atoms emit light. The light contains atomic information about the sample and is analyzed by a spectrometer. In this work, a fundamental study will examine the relationship between
ablation and LIBS enhancement in dual-pulse LIBS. Also, an application of LIBS to identify trace metals in molten salt will be presented.

The first experiment will look closely at how spectral enhancement of zinc and copper in brass is influenced by plasma temperature and ablation particles from a dual-pulse laser induced breakdown spectroscopy (DP-LIBS) compared with single-pulse LIBS. The work presented will look at a dual-pulse scheme using two pulsed Nd:YAG laser operating at a fundamental wavelength of 1064 nm. First, a pulse was focused parallel and above the surface forming a pre-ablative plasma in air. A second pulse is then fired to form an ablative (analytical) plasma on a surface while intersecting the volume of the pre-ablative plasma. Two parameters were studied in the DP-LIBS experiments, the inter-pulse delay and the pre-ablative flunce. Both these parameters have an effect on the emission intensity of zinc and copper and the ablation volume. Single-pulse experiments were also conducted by varying the fluence, which also has an effect on the emission intensity of zinc and copper and the ablation volume.

In experiments varying the inter-pulse delay, a 90 mJ pre-ablative laser pulse followed by a 30 mJ ablative (analytical) laser pulse were used. Using this scheme with an inter-pulse delay of 20 μs resulted in a 5 fold increase in intensity for Cu at 521 nm and a 7 fold increase in intensity for Zn at 481 nm compared to single-pulse LIBS. A thirty fold increase in ablation was observed in this DP-LIBS scheme compared to single-pulse LIBS at an inter-pulse delay of 20 μs. With a constant inter-pulse delay there is a mild increase in emission intensity for both zinc and copper with increasing pre-ablation fluence, however, a decrease in ablation volume is also observed with increasing fluence. The single-pulse experiments involved the use of
only the ablative analytical pulse. Emission intensity increased with increasing fluence for both Cu and Zn; however, there was a sharp decrease in ablation volume with increasing fluence. The electron temperature was calculated for all experiments using the Boltzmann plot. It was found that emission intensities of Cu and Zn correlated well with the electron temperature; however, considering ablation particle volume along with the electron temperature improved this correlation. The results of this experiment suggest that both particle volume and electron temperature play a significant role on the emission intensity.

The second project involves the use of LIBS to analytically detect trace elements in a molten salt environment. Here an apparatus was built to simulate an electrorefiner and its enclosure. Electrorefiners are used to reprocess nuclear fuel for recycle through electrolysis in a molten salt bath. This is an important application that demonstrates ability of LIBS to analytically detect elements in hostile environments and on liquid surfaces. Chromium, cobalt, and manganese where measured in a eutectic potassium-lithium-chlorine molten salt mixture. Calibration curves were successfully constructed for cobalt (CoCl\(_3\)) and manganese (MnCl\(_3\)), while chromium (CrCl\(_3\)) was used to demonstrate the resolution of the spectrometer. Theoretical detection limits were determined to be 0.04, 0.5 and 0.3 percent mass for CrCl\(_3\), CoCl\(_3\) and MnCl\(_3\), respectively.
1. INTRODUCTION

Since the early 1980’s laser-induced breakdown spectroscopy (LIBS), also referred to as laser-induced plasma spectroscopy (LIPS), has evolved into a powerful analytical tool. The technique involves the focusing of a pulsed laser to ablate and/or vaporize and ionize a sample, creating a plasma. Light from this plasma contains atomic spectral information about the sample and can be analyzed using a spectrometer coupled to a camera. LIBS is an attractive analytical tool because little to no sample preparation is required, and it has the ability to give real-time elemental analysis. LIBS is well-suited for use in hostile environments where rapid data acquisition is needed (1), and is able to interrogate almost any substance whether solid, liquid, gas or aerosol. Of keen interest is the ability to analyze samples in places that are either too difficult or too dangerous to gain access. Long-focal-length lens or telescopic optical setups, like Gottfried used for standoff analysis over 20 meters (2), can be used to focus laser pulses into inaccessible locations and collect the emission from the plasma through the same optics from a safe location. If a location is optically-inaccessible, a laser pulse with sufficient energy can also be carried through fiber optics and the emission can then be carried back through the fiber optic for analyses (3,4).

In addition to the potential applications of LIBS, there are opportunities for improving spectral sensitivity and reproducibility. One way to improve sensitivity and reproducibility is to use a method referred to as dual-pulse LIBS or DP-LIBS. There are several competing mechanisms that are important in double-pulse LIBS and a better
understanding of key processes leading to signal enhancement could lead to development of other enhancement techniques.

1.1 The Development of LIBS

Theodore Maiman described the first operation of a laser in an essay “Stimulated optical radiation in ruby” (5). Soon after Maiman’s discovery, researchers realized that a pulsed laser could be used to produce a plasma for analytical uses. In a meeting in 1963, Brech and Cross were the first to describe the use of a laser plasma to stimulate excitation from a surface. Brech and Cross’s goal was to achieve a microexitation for analytical use; however, due to the lack of proven techniques for optical pumping they were left with a “semi micro optical excitation” (6). Debras-Guedon and Liodec were the first to publish work involving a laser-generated plasma for spectrochemical analysis on a surface (7). This was essentially the first documentation of laser-induced breakdown spectroscopy on a surface, which was soon followed by LIBS in gas by Maker in 1963 (8). Perhaps the most useful industrial application during the birth year of LIBS was work by Runge and co-workers. Using three steel samples with known amounts of chromium and nickel, they created calibration curves from laser induced plasma. With these calibration curves they were able to estimate the concentration of nickel and chromium within 5.3 percent and 3.8 percent accuracy, respectively (9).

The idea that LIBS could be used in hostile environments which would otherwise be very difficult to nearly impossible to analyze, was championed by Runge and co-workers in 1966 (10). Runge talked about the potential of LIBS and showed its
efficacy by detecting nickel and chromium in molten steel and compared them with LIBS spectra of the solid doped sample. Runge showed that even with thermal background from the furnace used to melt the samples, the spectra from the molten steel were discernable.

All of the early LIBS work was done without modern-day conveniences, such as high-repetition-rate lasers and spectrometers with intensified charge-coupled devices (ICCD). These advances have allowed for more dependable, rapid, and time-resolved data acquisition.

Laser-induced plasmas formed by pulsed lasers experience different emission stages during plasma formation and emission. Radiation from the plasma in its earlier stages is continuous. This continuum is due to recombination radiation and Bremsstrahlung radiation. The continuum contains little useful information for LIBS experiments and is avoided by delaying spectral acquisition to times shortly after the radiation from the continuum is minimal. Time-resolved LIBS has offered temporal control of the emission spectra collection. Early work by Radziemski and Loree in 1981 investigating time-resolved LIBS involved the use of a multichannel analyzer or a photomultiplier with a boxcar amplified apparatus (11). The multichannel analyzer offered the ability to survey the spectral range 350-800 nm; however, spectral resolution was poor due to cross talk and light spilling from nearby diodes. Once a spectral region of interest was identified, a higher resolution spectrum, theoretically 0.002 nm, was acquired by scanning the region with Czerny-Turner spectrometer coupled to a photomultiplier with a boxcar-detection apparatus. Using both the multichannel analyzer and the photomultiplier boxcar-amplified apparatus methods allows for a quick
initial large spectral range survey and a high resolution acquisition of interesting spectral regions. As technological advances were made, charge coupled devices (CCDs) replaced multichannel analyzers and echelle spectrometers became more common.

CCDs are still used today and the use of these devices with LIBS began in the early 1990s. CCDs differ from multichannel analyzer in that the CCD can store a charge in each device located beneath the light-sensitive layer. The CCD also allows for more rapid data acquisition than multichannels. Another useful attribute of a CCD is its ability to be arranged in two dimensions. Many researchers have been able to take advantage of the two-dimensional capabilities of the intensified CCD by spatially resolving plasmas in air. For example, in the work done by Vadillo, information about the distribution of atomic and ionic emission around the plasma plume was made possible using a two-dimensional intensified CCD (12). The result of this work yielded knowledge of the plasma morphology.

By the late 1990s and early 2000s, LIBS research started to shift towards more application-based experiments. Work was done using LIBS to monitor toxic metals such as cadmium, chromium, mercury and lead in incinerators. It was reported by Buckley and co-workers that detection of these toxic metals was in good agreement with traditional analytical methods, while offering real time-monitoring (13). Palanco and Laserna applied LIBS for quality assessment in steel factories (14). They showed that by using LIBS the assessment time is reduced by a factor of 25. The cost of pulsed lasers sufficient for plasma production and intensified charged coupled devices is decreasing, and as a result LIBS is becoming more popular as an analytical method.
1.2 Introduction of the LIBS remote applications

Laser-induced breakdown spectroscopy is an atomic spectroscopy and it is primarily useful in elemental analysis. There is a plethora of tools available for elemental analysis and determining which tool to use for elemental analysis depends on the application.

For elemental analyses atomic absorption spectroscopy is commonly used. Atomic absorption spectroscopy works by directing ultraviolet and visible radiation through an atomized flame, which contains the analyte. The analyte is prepared in an aqueous solution and is injected into the flame, while a spectrometer and a detector measure the amount of absorbed light from the ultraviolet and visible radiation. Atomic absorption spectroscopy is an excellent technique, but it does require sample preparation.

An alternative to atomic absorption spectroscopy is mass spectrometry. It offers even more capabilities, but also often requires sample preparation. In the case of inductively coupled plasma mass spectrometry, the sample is put into solution then nebulized. The plasma then ionizes the sample for the mass spectrometer. There are other ways to ionize a sample for mass spectrometry, but they may require some sort of sample preparation. An ablation laser can be used in conjunction with mass spectrometry. This technique will eliminate the need for pre-processing or sample preparation; however, it lacks the ability to make remote measurements. In surface analyses using LIBS, the ablative plasma, in a sense, prepares a sample by heating and vaporizing the surface. The vaporized material is further heated and ionized in the gas plasma which
forms above the surface. The resulting ionized atoms and electrons cool shortly after the initial laser pulse ends. During this cooling an electronic spectrum of the vaporized surface material is emitted.

Using LIBS to analyze hazardous radioactive material related to governmental and industrial nuclear research is a nearly perfect match. Many of the containment facilities offer no convenient way to gain access to the material of interest for traditional analytical methods. There are many examples where fiber optics have been integrated into LIBS instruments for remote LIBS. One place where LIBS can be useful is in the inspection of reactor components. In work done by Whitehouse and co-workers, LIBS was used to quantify the percent copper in bifurcation cracking tubes using a fiber optic to carry the laser pulse to the sample area and another one to carry the plasma emission to a spectrometer (16). It was known that bifurcation tubes cast with low creep ductility led to an increased risk of failure. It was also known that low creep ductility components contained higher concentration of copper. In this case LIBS was used in assessing the risk of component failure.

Using a method similar to the above, Noll and colleagues used LIBS to determine the chromium concentration in steel tubing used in sub-boiler annulus in a reactor (17). Noll’s work is significant because the level of chromium in the magnetite oxide layer of the sub-boiler tubes predicts the tube’s ability to resist erosion (18). Noll used a 30-meter protective umbilical tube to contain a fiber optic used to carry the laser pulse and light from the plasma emission. The LIBS focusing optics were contained in a protective probe, designed to attach to the sub-boiler tubes, at the end of the umbilical. An air line was also routed through the umbilical to provide air flow over the optics.
The umbilical leads to the rest of the instrument, which is outside of the sub-boiler annulus and includes the laser, spectrometer and electronics. After pre-conditioning the target site by firing 1600 laser pulses, LIBS spectra were collected from 100 shot accumulations. The detection limits for chromium were found to be 100 ppm while the precision of the measurement was better than 6%. The LIBS spectra of the sample were compared with iron chromium standards and after several days of repeat studies it was found that the accuracy was better than 15% (17).

Another way LIBS has been used remotely in a radioactive setting is by using a telescoping lens setup. In a case where various locations inside a hot cell needed to be analyzed chemically to find the source of contamination, a laser pulse was focused through a 1 meter thick lead-glass shield (17). A hot cell is an isolated structure where radioactive studies are performed as in spent fuel reprocessing. The lead-glass shield provides visual contact for operator outside to run robot arms and equipment inside the hot cell. The steel components inside the hot cell were positioned about 3 meters from the window while a 1064 nm laser pulse was focused onto it. Since the lead glass strongly absorbs light wavelengths shorter than 500 nm and most spectrometers are limited to wavelengths shorter than about 800 nm, only a narrow spectral range could be studied. Even with a narrow spectral range zirconium and molybdate contaminates were discovered, which allowed researchers to track the contamination source.

As a tool for elemental analysis, LIBS is an excellent fit if the application requires little to no sample preparation and/or rapid data acquisition. Because of these characteristics LIBS should be considered in applications where collecting a sample is either hazardous or too difficult. Any analytical chemist would appreciate better
sensitivity in their apparatus; with LIBS, improving the sensitivity can be done using a
dual-pulse configuration. Knowing what causes enhancement in DP-LIBS could lead to
further enhancement gains and some insight into this will be presented in chapter 3.

There are two excellent textbooks discussing LIBS, *Handbook of Laser-Induced
Breakdown Spectroscopy* by Cremers and Radziemski, and *Laser-induced Breakdown
Spectroscopy Fundamentals and Applications* by Miziolek, Palleschi and Schechter.
The first book contains information that would make for a great foundation in LIBS,
and would be well suited for a college lecture. It covers most of the important aspects of
LIBS, such as, LIBS plasma, apparatus fundamentals, analytical figures-of-merit, and
qualitative and quantitative analysis. It also discusses the use of LIBS in remote
application and covers several recent studies involving LIBS fundamentals and novel
applications. The second text is more of a compilation of several articles written by
influential authors. This text contains articles discussing subjects such as, the history of
LIBS, LIBS in gases, and LIBS on aerosols. More advanced topics include
fundamentals and application in short-pulsed LIBS, Resonance-enhanced LIBS, and
micro LIBS techniques. There is also discussion of applications for LIBS in biomedical,
pharmaceutical, and in environmental contamination studies. The texts complement
each other and should be considered required reading for anyone interested in LIBS
research.

Chapter 2 of this dissertation covers the fundamentals of LIBS. The first part of
Chapter 2 will serve as an introduction to laser induced plasma formation, emission, and
plasma temporal evolution. Dual-pulse LIBS will also be discussed in the first part of
Chapter 2. This section will discuss various DP-LIBS configurations with respect to
laser pulse width, ailment, and timing between pulses, while also discussing enhancements seen in spectral intensity from DP-LIBS. The first section of Chapter 2 is important because it helps in explaining phenomena observed in Chapter 3. The second part of Chapter 2 will discuss standard equipment used in LIBS experiments such as lasers, spectrometers, and charged-coupled devices. Though not a standard LIBS instrument, a scanning mobility particle sizer spectrometer (SMPS) will also be discussed in the last half of the chapter. Because Chapter 3 relies on data acquired from the SMPS, a discussion of its basic principles is pertinent.

Chapter 3 reports DP-LIBS and single-pulse LIBS performed on brass. The scope of Chapter 3 is to investigate the spectral enhancement seen in DP-LIBS. In this work, correlations were made between plasma temperature, ablation volume, and spectral emission of copper and zinc. Data presented show strong correlation among plasma temperature and emission from copper and zinc. To a lesser degree, ablation volume correlated with the emission intensity of copper and zinc. The most interesting development, from this chapter, is how well the emission intensity correlates with both plasma temperature and particle volume, when considered together.

The last portion of this dissertation, Chapter 4, will present a study evaluating the analytical merits of LIBS in a lithium potassium chloride molten salt environment. The lessons learned from this study could someday help in application of LIBS to measure trace elements in an electrorefiner used to purify uranium from nuclear waste products. In this study, theoretical detection limits for chromium, cobalt, and manganese, were determined to be 0.04, 0.5 and 0.3 percent mass, respectively. Also, calibration curves were created for both cobalt and manganese.
References


2. BACKGROUND FOR THEORY AND EXPERIMENT

2.1 Fundamentals of LIBS

Laser-induced breakdown spectroscopy is a type of atomic emission spectroscopy that utilizes a plasma as an excitation source for materials which can be initially gaseous, liquid, or solid. A laser focused in or on the medium ablates and/or vaporizes and excites the medium. The high laser intensity at the focal point is able to strip away electrons from the excited material, forming a plasma. As described below, LIBS measurements are most often made using a time-gated detector able to view the atomic emission during a specific window following plasma formation while gating out the earlier continuum emission. The composite atomic emission spectrum corresponds to an elemental analysis of the vaporized sample. Calibration curves can be determined based on the intensity of observed emission spectral peaks and known concentration of standards.

In LIBS, a laser pulse does the work of both material preparation through ablation/vaporization and subsequent excitation. A common LIBS setup involves using a pulsed laser, focusing optics, and a gated spectrometer. Generally the laser pulse length is on the order of nanoseconds but it can be much shorter. The LIBS laser pulse is focused through beam-shaping optics concentrating sufficient power, typically 0.1 to 10 GW/cm² for either nanosecond and picosecond pulsed laser (1,2), to vaporize and excite material on surfaces near the focal point. The plasma is commonly referred to as a dielectric breakdown. A laser plasma in the context of LIBS must have sufficient temperatures and degree of ionization to emit atomic radiation (3).
LIBS plasmas are generated with a pulsed laser, to deliver the required power to form a dielectric breakdown. Following the initial plasma kernel formation, the plasma goes through several stages of expansion and then decay. In the early stages of plasma, less than 1µs after laser pulse is initiated, continuum emission dominates the spectrum. The light from the continuum emission is a result of two phenomena, Bremsstrahlung interactions and recombination radiation. Bremsstrahlung radiation is the result of charged particles being accelerated in a Coulomb field. Electron-ion collisions play a major role in Bremsstrahlung emission and as a result much of the radiation spectrum is continuous because the initial and final states are continuous (3). In recombination radiation electrons in the continuum recombine with ions and because upper levels of these states are continuous therefore the radiation is continuous (3).

In the early stages of a laser plasma, the continuum dominates the spectra. For example in a time-resolved LIBS study by Harilal and co-workers (4), the continuum dominated the spectra during the first 60 ns of the plasma evolution. The use of a gated spectrometer allowed Harilal et al. to collect plasma emission at different times during the plasma evolution. Harilal et al. also found that soon after the continuum radiation was observed, ionic species appeared in the spectra, followed by excited atomic species beginning 200 ns after plasma initiation (4). The key for the spectroscopist is to take a snapshot of the plasma during the time when the max emission occurs from spectral lines of interest while minimizing unwanted emission. Utilizing a spectrometer that has time-gated abilities, like intensified CCDs, electron multiplying CCDs, or PMTs coupled with a boxcar integrator, does this snapshot.
2.1.1 Plasma formation

Photons are absorbed through two major processes, inverse Bremsstrahlung and photoionization. With inverse Bremsstrahlung absorption, electron kinetic energy is increased from the laser radiation electromagnetic field. This kinetic energy is then transferred, via collisions, to neutral and excited species leading to more collisions promoting ionization (1). Because inverse Bremsstrahlung absorption requires free electrons, it generally cannot initiate a plasma alone. If the laser frequency thus the photon energy is high enough photoionization can free electrons for inverse Bremsstrahlung absorption, either through single- or multi-photon processes (1). Plasma initiation by either single- or multi-photon processes was illustrated in a work done by Amoruso and co-workers (5) where it was shown that an UV laser operating at 355 nm (3.46 eV) ionizes an aluminum species through single photon ionization and a visible laser operating at 532 nm (2.32 eV) ionizes through multiphoton ionization. Amoruso et al. argued the potential energy between the aluminum first excited state of 3.14 eV and its ionization potential of 5.99 eV, is less than the energy of the UV laser. However, in the case of the visible laser at 532 nm (2.31 eV), the photon energy was less than the difference of the aluminum excited state and ionization potential. The insufficient energy of the visible laser requires two photons to ionize an aluminum atom (5).

Initially in nanosecond laser ablation, laser light heats the surface causing some material to melt and then vaporize. The approximate minimum laser power density $I_{\text{min}}$ needed to vaporize a surface can be found using equation 2.1 with $\rho$ being the surface
density, \( L_v \), the latent heat of vaporization, \( \kappa \) the thermal diffusivity, and \( \Delta t \) the laser pulse duration (31).

**Equation 2.1**

\[
I_{\text{min}} = \rho L_v \kappa^{1/2}/\Delta t^{1/2} \text{ (W/cm}^2\text{)}
\]

The latent heat of vaporization plays a major role in how much energy is required to vaporize mass from a surface. Because many surfaces in analytical studies are alloys, with two or more metals with different latent heat of vaporization, fractionation of ablation particles can occur. In work done by Liu and co-workers (6), particles from laser ablation of brass were analyzed using energy-dispersive X-ray analysis (EDAX). From this study it was found that zinc was concentrated in smaller particles while copper was concentrated in larger particles. Zinc has a lower latent heat of vaporization than copper, and because of this zinc particles primarily formed from nucleation of zinc vapor, resulting in smaller particles. Larger particles are simultaneously ejected from the surface as molten droplets containing higher concentrations of copper because the zinc vaporizes (6). Zinc vapor will also re-condense on the surface of particles resulting in smaller particles having enriched zinc concentration due to the high surface to volume ratio of smaller particles. Fractionation is important in laser ablation inductively-coupled mass spectrometry, however, its role in LIBS is unknown.

Once the plasma is initiated and begins to expand, its propagation can be described in three zones, the shock front, the absorption front, and the plasma front.
Figure 2.1 illustrates the propagation of the plasma as it expands toward the laser radiance. The plasma is led by the shock front, followed by the absorption front, then finally the plasma front. The expansion and propagation of a plasma can be explained by laser-supported combustion (LSC) or laser-supported detonation (LSD) (7,8). In the LSC model the energy from the shock and from plasma radiation drive the absorption front and is associated with lower laser intensities (7,8). Higher laser intensities favor the LSD model; here the shock is strong enough to cause breakdown of surrounding gases, which absorb the laser pulse (7,8). The shock wave is just in front of the absorption zone and both are in front of the plasma front. When the plasma energy is high enough the plasma becomes opaque to the laser light, which shields the surface from laser light. Absorption will occur if the plasma frequency becomes equal or less than the laser frequency. The plasma frequency is directly related to the electron density, and using equation 2.2 plasma frequency can be found from the electron density. In equation 2.2, $\omega_p$ is the plasma frequency, $n_e$ is the electron number density of the plasma, $e^2$ is the electron charge and $m_e$ is the electron mass (9)

\[
\omega_p = \left(\frac{n_e e^2}{\pi m_e}\right)^{1/2}
\]

Plasma shielding has a significant impact on the ablation of material. It was shown in work done by Vadillo and coworkers that ablation rates leveled off with increasing laser fluence (10). Vadillo et al. studied this by measuring the ablation rates of various metal foil samples from a focused 581 nm excimer pumped dye laser. The
rate of ablation was determined by monitoring the time it took to bore holes through Al, Cu, Mo, Ti, W, and Zn foil samples. In figure 2.2, from Vadillo et al., the laser fluence was varied from 1.3 to 16.7 J/cm². At lower fluences the average ablation rate (AAR) increased with increasing fluence, however, at higher fluences the average ablation rate reached a threshold after which an increase in fluence did not result in increased ablation (10).

The intensity of line emission from a plasma is influenced by the electron temperature and the number of atoms in the plasma. The number of atoms in a plasma is related to the level of ablation, which is also related to the amount of plasma shielding. To understand processes occurring in a plasma, such as dissociation, atomization, ionization, and excitation, it is essential to have knowledge of the electron temperature and electron density (11).

The electron density, used above in equation 2.2, can be estimated based on the Stark effect. Several other mechanisms, however, also contribute to spectral line broadening, such as Doppler effect, Van der Waals broadening, and resonance broadening. Stark broadening should only be of concern when estimating the electron density. Stark broadening is a result of collisions of electrons and ions. In a plasma electrons can perturb the energy level of an ion causing a broadening of the spectral line which relates to equation 2.3. In equation 2.3, $w$ is the electron impact parameter, $A$ is the ion–broadening parameter, $N_e$ is the electron density and $N_D$ is the number of particle in the Debye sphere. $\Delta \lambda_{1/2}$ is the full width at half-maximum (FWHM) of the peak. The first term in equation 2.3 estimates the electron broadening contribution, while the second term estimates the contribution from ion broadening. The contribution
of ion broadening is very low at typical plasma temperatures, less than 2% at 8000 K; as such the ion broadening contribution can be neglected reducing equation 2.3 to equation 2.4. To obtain the actual $\Delta \lambda_{1/2}$ the instrument broadening must be accounted for by using equation 2.5. One way to determine the instrument broadening is by observing the line width of a Hg line from low pressure Hg lamp, this value is typically on the order of 0.001 nm (12,13).

**Equation 2.3**

$$\Delta \lambda_{1/2} \text{(in Angstroms)} = 2w\left(\frac{N_e}{10^{16}}\right) + 3.54\left(\frac{N_e}{10^{16}}\right)^{1/4}[1-1.2N_D^{-1/3}]w\left(\frac{N_e}{10^{16}}\right)$$

**Equation 2.4**

$$\Delta \lambda_{1/2} \text{ (in Angstroms)} = 2w\left(\frac{N_e}{10^{16}}\right)$$

**Equation 2.5**

$$\Delta \lambda_{1/2} \text{(actually)} = \Delta \lambda_{1/2} \text{(observed)} - \Delta \lambda_{1/2} \text{(instrument)}$$

Another characteristic of interest is the electron temperature. Assuming the plasma has a local thermal equilibrium (LTE), the electron temperature can be determined by using the relative intensity of two spectral lines and equation 2.6. Equation 2.6, as written, relates the spectral intensity ($I_i$) the wavelength ($\lambda$), the statistical weight ($g_i$), the transition probability ($A_i$) and the energy of the excited state ($E_i$). Electron temperatures are typically between 6000K to 12000K (33,34).
2.1.2 Dual-Pulse LIBS

Dual-pulse LIBS, DP-LIBS, involves the use of two laser pulses to enhance the intensity of LIBS spectra (15). It is suggested by Scaffidi, Angel, and Cremers that there are three effects responsible for DP-LIBS enhancement: pulse-plasma coupling, sample heating and atmospheric effects (15). Pulse-plasma coupling occurs when the second laser pulse, the analytical pulse, is fired into the first plasma after it has weakened. If fired too soon the second plasma will be absorbed by the outer shell of the first plasma, but if the delay between the two pulses are optimized the second pulse will mostly be absorbed by the analyte rich core of the first plasma (16). There is some evidence that increased LIBS intensity can occur with sample heating, as seen in work by Su and co-workers on glass (17). Scaffidi, Angel, and Cremers argue that in DP-LIBS, the pre-pulse could locally heat the target (15). The final possible explanation for DP-LIBS enhancement involves the atmosphere above the target. Investigating the effect of inert gases on LIBS spectra, Matsuta and Wagatsuma, showed that spectral intensity was maximized at low pressures of Ar. For example, Cu I at 221.5 nm had the greatest intensity when the pressure was reduced to 1 Torr Ar, while Cu II at 224.7 had the greatest intensity at a reduced pressure of 3 to 4 Torr of Ar. In both examples the intensity steeply decreased with additional pressure reduction (12). With DP-LIBS the first plasma pulse briefly leaves behind a region that is hotter and of higher pressure

Equation 2.6

\[
\frac{I_1}{I_2} = \frac{g_1 A_1 / \lambda_2}{g_2 A_2 / \lambda_1} \exp[-E_1/(kT_e)] \exp[-E_2/(kT_e)]
\]
than ambient conditions; however, the number density of this region is greatly reduced. Scaffidi, Angel, and Cremers argue that enhancement may be due to the reduced number density, not necessarily the reduced pressure (15).

One way to configure a DP-LIBS experiment is to fire two collinear pulses at the same location along the same path. The delay between the two pulses is typically less than 100 μs apart. This is usually done with a q-switching laser capable of firing two laser pulses during each flash lamp excitation. In work done by Sattmann and co-workers, a laser able to fire consecutive pulses with variable pulse separation was used to compare collinear DP-LIBS with single-pulse LIBS on steel. The total energy of the two pulses in the DP-LIBS was equal to in the energy of the single-pulse. Spectral intensity in DP-LIBS was 7 times more intense with a 6 μs inter-pulse delay between pulses compared to single-pulse LIBS. In addition to enhanced spectra, fewer shots were needed to bore through a thin steel foil using DP-LIBS compared to single-pulse LIBS (18).

An orthogonal pulse configuration can also be used. Here, a pre-ablative laser pulse is focused parallel to and just above the surface while an ablative pulse is focused on the surface intersecting the parallel pulse orthogonally. When using nanosecond lasers in DP-LIBS the non-ablative pulse must precede the ablative (analytical) pulse, to enhance the spectral intensity.

Using the pre-ablative pulse DP-LIBS method, enhancement was measured by Stratis and co-workers on glass samples doped with aluminum, titanium and iron. LIBS spectral lines of these metals were enhanced by 11 to 20 times over single-pulse. In addition to spectral enhancement, SEM images of the ablated surface indicated an
increase in ablation with DP-LIBS compared to single-pulse (19). In other work done by Angel, DP-LIBS using a pre-ablative pulse on pure samples was found to enhance intensity in copper by 11 times and lead by 35 times when compared with single-pulse. SEM examination of craters from 50 consecutive LIBS shots found that the craters left from DP-LIBS were larger than those from single-pulse LIBS (32).

Enhancement is also possible by using a re-heating configuration. This configuration involves the use of a femtosecond laser to serve as an initial ablative pulse followed by a non-ablative analytical pulse parallel to the target surface. The non-ablative pulse re-heats material ablated by the first pulse. Work done by Angel and Scaffidi investigated different configurations using nanosecond and femtosecond pulsed laser for DP-LIBS. All the experiments used one laser pulse fired orthogonally to the surface and the other laser pulse fired parallel to the surface. Of interest was the configuration that used a femtosecond orthogonally to the surface, to ablate the material, then a nanosecond pulse parallel to the surface to form the analytical pulse. This configuration yielded a spectral intensity 30 times greater than single-pulse LIBS on a copper target (20). Femtosecond lasers tend to ablate more material per unit of energy deposited than nanosecond pulse lasers, with less sample heating. This is likely why using a ablative femtosecond pulse first, followed by a nanosecond non-ablative analytical pulse yields significant enhancement (20). Liu and co-workers demonstrated how well a femtosecond laser ablates material, in respect to mass removal, compared to a nanosecond laser (21). Liu et al. showed that after 50 ablative pulses the femtosecond laser produced a crater 4 times deeper than the nanosecond laser. Another interesting observation in Liu’s study was how the nanosecond laser produced a rim of particles
and melted material around the ablation site, while the femtosecond laser drills straight holes with little to no melted material and particles around the rim. In other work involving femtosecond laser ablation, Koch and co-workers found that femtosecond laser ablation produces particles that more accurately represent the bulk material than particles from nanosecond laser ablation. Koch et al. also found the particles from femtosecond laser ablation was more mono-dispersed in size compared to particles from nanosecond laser ablation (22). During laser ablation energy is distributed into the lattice structure of the target through electron-phonon interactions. The time scale in which this distribution occurs is on the order of tens of picoseconds and is referred to as the electron-phonon couple time. In nanosecond laser ablation the pulse width is much longer than the electron-phonon couple time, which results in thermal equilibrium ablation. Femtosecond laser ablation is a nonequilibrium process because the pulse width is significantly less than the electron-phonon couple time (23). In other words, due to the short pulse width of a femtosecond laser, there is not enough time for energy to dissipate from the ablation site (24,25).

2.2 LIBS components and instruments

2.2.1 Laser

The laser is an integral component of any LIBS experiment. Generally, LIBS lasers are q-switched to provide high peak power, and operate from 1 to 20 Hz. The most common laser used is the Nd:YAG, which can typically have up to four harmonic frequencies, 1064nm, 532nm, 355nm, and 266nm, though many studies have been done using lasers capable of shorter or longer wavelengths. Depending on the optical setup,
laser pulse energy is generally in the range of 10 to 400 mJ. Though some groups have used lasers with picosecond and femtosecond pulse widths, until recently most research has been focused on the use of nanosecond pulse width lasers, in part driven by the much lower cost and availability of these lasers. Special care is needed to prevent laser light from being reflected back into the laser by the optics. Lenses with special dielectric coatings can be purchased to reduce this reflection, and optics can also be arranged to reflect light elsewhere.

2.2.2 Spectrometer

Depending on the configuration the spectrometers, analysis of emission spectra generally requires a prism or grating to disperse light onto a detecting element (26). Almost all spectrometers use a charged coupled device (CCD) as the sensing element. CCDs are generally two-dimensional devices and have found to be useful in spatially resolving a laser plasma while simultaneously analyzing the emission from the entire plasma and can be usefully in collecting data from more than one location simultaneously. Using a CCD can also improve gain by detecting narrow bands of light with multiple sensors. The two-dimensional configuration of a CCD is also well-suited for echelle spectrometers (described below), which require two-dimensional sensing.

The spectrograph portion of a spectrometer can have many different configurations to disperse light. The most common configuration is the Czerny-Turner, although, the echelle spectrograph is gaining popularity. In the Czerny-Turner type of spectrograph, light enters through entrance slit and encounters a mirror that collimates and directs the light to a grating. Depending on the wavelength, light is reflected at
different angles by the grating onto a second mirror. The second mirror then focuses the dispersed light through an exit slit and on to a detecting element, in the case of a monochromator, or the exit slit is discarded and the dispersed light is spatially-resolved on a CCD in the case of an imaging spectrograph (27). Gratings used in the Czerny-Turner spectrograph can have a range in the number of grooves/mm, with more grooves per mm resulting in higher resolution; however, increased resolution comes as a cost to spectral range on the detector element. When using a Czerny-Turner type spectrograph, a researcher may first use a grating with a lower number of grooves / mm to survey a larger spectral range. Once regions of interest are discovered, a higher-ruled grating can be used to resolve LIBS spectra.

The echelle spectrograph has the advantage over other spectrographs in that it has very high resolution while also having a large spectral range, 200nm to 780nm (28). The echelle spectrograph couples a grating element and a prism, the grating element has fewer grooves than gratings usually found in Czerny-Turner spectrographs. Light from the grating produces multiple orders of diffraction in a narrow range and results in a complex spectrum. The prism then sorts this complex spectrum on to a focal plane forming a two dimensional array of wavelengths (28). The echelle takes full advantage of the two dimensional structure of the CCD by projecting the wavelength array onto the CCD. Software then decodes the multiple spectral orders on the sensor and reconstructs the spectrum.

Most CCDs used for LIBS are intensified charged-couple devices or ICCD. The intensifier not only improves gain, it also allows for time resolved spectral acquisition. The intensifier is made of microchannel plates. At one end is a photocathode that
converts photons into electrons, and then electrons are multiplied by as much as 1000 times before hitting a luminescent phosphor screen. The luminescent phosphor screen converts the electrons to photons, which are then absorbed by the CCD. Adjusting the voltage between the photocathode and the luminescent phosphor screen controls the gain of the intensifier. Controlling when the voltage turns on and turns off serves as gate for the system and allows for time-resolved acquisition typically with gating resolution as fine as 10 ns or better (27). When performing time-resolved LIBS experiments, the spectrometer/ICCD is synchronized to the Q-switch of the laser through a pulse generator. The pulse generator receives a signal from the laser corresponding to the precise time the laser is firing. The signal leading to ICCD from the pulse generator can be timed accordingly.

2.3 Scanning Mobility Particle Sizer

During laser ablation, specifically LIBS on surfaces, particles are ejected from the ablation site. Researchers have studied the craters left after ablation, but little work has been done on analytically studying the distribution or the bulk mass of particles ejected during laser ablation. The Scanning Mobility Particle Sizer, SMPS, has the capability to scan and quantify a range of submicron particles. The following discussion references TSI supplied literature (29,30) which specifically applies to the TSI series 3080 electrostatic classifier and the TSI series 3010 particle counter. There are two main parts to an SMPS system, an electrostatic classifier and the condensation particle counter, CPC. The first part of the SMPS, the electrostatic classifier, is shown in Figure 2.3. Particles (or a polydisperse aerosol) are typically pulled through the electrostatic
classifier with a pump. Before the particles enter, an impactor removes particles too large for the system to handle. The polydisperse aerosol is then carried to a Kr-85 bipolar charger where they are exposed to high concentration of bipolar ions. In the bipolar charger the aerosol and ions reach a state of charge equilibrium. The equilibrium allows the aerosol to have a known bipolar distribution. The now charged aerosol enters the Differential Mobility Analyzer (DMA). The DMA is basically a long cylinder with a concentrically placed narrower cylinder inside. The outer cylinder is grounded while the inner cylinder, which is the collector rod, is negatively charged. The aerosol and sheath air enter through the top of the DMA and travel downward in a laminar stream between the two cylinders. There is no mixing in the DMA while the aerosol surrounds the inner core sheath air. As the charged particles and sheath air pass through the DMA the particles are affected by the electric field and traverse the DMA based on their electrical mobility. This electric field causes any positively charged particle to be attracted toward the center negatively charged cylinder. The electrical mobility of the particle determines where it impacts on the inner cylinder; higher electrical mobility particles impact on the upper region while lower electrical mobility particles impact in the lower region. A monodispersed flow of particles with a narrow range of electrical mobility exit the bottom of the DMA through a small slit. The rest of the particles in the flow are removed by way of the excess airflow. After exiting the DMA the particles pass into the CPC where they are counted. The CPC first condenses butanol onto the particles growing them into droplets, which make it easier for the optical particle detector to detect them.
Figure 2.1

Above is an illustration of the propagation of the plasma as it expands toward the laser radiance. The plasma is led by the shock front followed by the absorption front then finally the plasma front.
Figure 2.2

Above is from Vadillo et al. At lower fluences the average ablation rate (AAR) increased with increasing fluence, however, at higher fluences the average ablation rate reached a threshold after which an increase in fluence did not result in increased ablation (10).
Figure 2.3

The above is a diagram of a TSI electrostatic classifier with a long DMA (29).
References


30) Particle Instruments, series 3010 Condensation Particle Counter instruction manual P/N 1933010, Revision F. August 2002. TSI, Inc.


3. DUAL-PULSE LIBS SIGNAL ENHANCEMENT CORRELATED TO ABLATIVE PARTICLE PRODUCTION

3.1 Abstract

The signal enhancement from dual-pulse LIBS was investigated by correlating the nanoparticle production from the ablation of brass and the Boltzmann temperature in the ablation plasma. Several dual-pulse and single-pulse experiments were completed. In the dual-pulse experiments a pre-ablative plasma 0.5 - 1 mm above the surface was created from a laser pulse parallel to the target surface and an ablative plasma was created by focusing a laser pulse directly onto the target surface and intersecting the volume in the pre-ablative plasma. The timing between the two pulses and the power of the pre-ablative pulse were varied. Seven different emission lines from copper and zinc were integrated and averaged from four 100 shot spectra accumulations. Particle size distributions were measured using a scanning mobility particle sizer (SMPS) for each condition. Dramatic increases in mass ablation, up to 30 fold, were noted as a function of inter-pulse delay in the double-pulse experiments compared with the single-pulse experiments. These increases, along with the change in the Boltzmann temperature of the plasma, were correlated with signal enhancement of both Cu and Zn lines in double-pulse LIBS of brass. Compared to single, DP-LIBS enhancement was found to be 7 fold higher for Cu and 5 fold higher for Zn with a 90 mJ pre-ablative pulse followed by a 30 mJ ablative (analytical) 20 µs later. In general, the increase in LIBS signal is mostly due to the increase in plasma temperatures; however, an increase in ablation also
has a small effect. To explain the increased double-pulse signal enhancement, the combination of temperature and increased nanoparticle volume appear to work in tandem to provide enhanced signal. Continuing work related to nanoparticle size distribution from single- and double-pulse LIBS will be discussed.

3.2 Introduction

Laser induced breakdown spectroscopy (LIBS) is a technique that involves the use of optically focused high power laser to form a plasma in air, water, or on solids. The resulting emission spectra from the plasma can be analyzed to determine the atomic composition of an analyte. LIBS does not require sample preparation and can be used in environments that are not easily accessible, an example of which is shown in Chapter 4 of this thesis. LIBS can be useful in select applications; however, it is not as sensitive as some other spectroscopy techniques like inductively coupled plasma atomic emission spectroscopy (ICP-AES) (1-5). For example, it was found in research done by Cremers ICP-AES was 3 to 1000 times more sensitive than LIBS in detection of metals in aerosol (16).

One way to improve the sensitivity of LIBS is to employ a technique called dual-pulse laser-induced breakdown spectroscopy (DP-LIBS). This method uses two laser pulses with relatively short inter-pulse delays. It has been used in many applications to improve the reproducibility and increase the intensity of the emission spectra of the analyte (6). Dual-pulse LIBS can be implemented in a variety of configurations using both collinear and orthogonal beams. Collinear dual-pulse LIBS
employs two laser pulses aligned directly onto the target surface. Orthogonal dual-pulse LIBS involves the use of a non-ablative pulse parallel to the surface fired before or after the ablative pulse (7). Although the use of picosecond and femtosecond laser pulse lengths have been investigated in dual-pulse configurations (6), the robustness and availability of nanosecond pulse length lasers makes a nanosecond orthogonal configuration a fairly simple, inexpensive, and effective strategy for LIBS spectroscopy. Using a nanosecond orthogonal method with a pre-ablation laser plasma formed above a target surface has been shown to enhance spectral emission from LIBS more than 30 times and increase ablation, compared with single-pulse LIBS (7).

The mechanism of this enhancement is not fully understood. Most dual-pulse LIBS studies have focused on the enhancement of the emission spectra only while a few have also looked at the ablation craters left after repeated ablation at the same location (7, 8, 9). Ablation of a surface with shots accumulating at the same location affects the LIBS spectra. For example, it was found in research done by Corsi et al. (10) that LIBS is enhanced in shallow craters due to plasma confinement. Corsi also found that deeper craters have a negative effect on LIBS due to plasma cooling from the sidewalls of the crater (10). Consequently, examination of the crater size after ablation at the same location gives only a crude measure of how much material is removed during LIBS.

Emitted line intensity from a plasma is influenced by two factors, the density of atoms and the temperature (often assumed in equilibrium) of the plasma (11). With LIBS on surfaces, the increased ablation may result in an increase in analyte atomic density in the plasma. The relationship between ablated particle production and LIBS
spectra intensities is important for understanding the mechanism of enhancement in pre-ablative plasma dual-pulse LIBS. By coupling a scanning mobility particle sizer (SMPS) to a pre-ablative plasma dual-pulse LIBS experiment, correlation between spectral enhancement and particle production can be assessed. The dependence between inter-pulse delay and spectral intensity has been documented when using colinear DP-LIBS and orthogonal DP-LIBS using a femtosecond pulse and a nanosecond pulse (6,12). To date, no study has looked closely at how the inter-pulse delay affects the ablative particle production in orthogonal DP-LIBS using nanosecond laser pulses. The concentration of particles in the plasma volume and the plasma temperature are likely the two most important variables determining emission intensity. Using a rotating brass sample as a target, this chapter looks closely at ablative plasma temperatures and ablated particle production and their affect on spectral intensity enhancement.

3.3 Experimental

Figure 3.1 describes the experimental setup. Two Spectra-Physics Quanta-Ray Nd:YAG lasers operating at a fundamental wavelength of 1064 nm were used to create plasmas. The laser repetition rate and pulse width were 10 Hz and 8 ns, respectively, for both lasers. The first pre-ablative pulse was focused with a 200-mm focal length lens and positioned parallel and just above a rotating brass target. With this optical setup, a 90 mJ (3x10³ J/cm²) laser pulse was needed for sufficient breakdown in the air above the surface. The fluence (J/cm²) was calculated after determining the focused
laser beam spot size. Here the spot size is determined by diffraction of the laser beam using Equation 3.1. In Equation 3.1, $d_{\text{diff}}$ is the focused spot size diameter of the laser, $\lambda$ is the wavelength of the laser, $f$ is the focal point of the lens, and $d$ is the initial laser diameter.

\textbf{Equation 3.1} \quad d_{\text{diff}} = 2.4\lambda f / d \quad (7)

The edge of the pre-ablation plasma was between 0.5 mm and 1 mm above the surface. A pulse generator was triggered from the pre-ablative laser and controlled the delay between the pre-ablative pulse, the ablative pulse and the intensified echelle spectrometer. All of the instrument timing was monitored on an oscilloscope. The second laser pulse was focused using a 200-mm lens and aligned orthogonal to the surface, causing breakdown on the target surface. Emission from the ablative plasma was collected through the same 200-mm focal length focusing lens and then reflected by a pierced mirror and focused onto a fiber optic leading to a Catalina Scientific intensified echelle spectrometer model SE 200. Attached to the echelle spectrometer was a Princeton Institute Acton Pixis 1024 camera and a novel lens-coupled intensifier, which can be removed from the camera. The echelle spectrometer has the advantage of acquiring a very broad region in the ultraviolet and visible spectrum (200 nm to 800 nm) while having resolution of better than 0.1 nanometers. The echelle’s large range is useful for plasma temperature calculation since multiple emission lines can be analyzed simultaneously, and the relationship of multiple elements can be observed in
heterogeneous samples. The camera intensifier gate was delayed between 3 to 4 μs and had a width of 3 to 4 μs during the plasma formation, which allows collection of atomic emission while avoiding emission from the plasma continuum.

Particles were sampled 25 mm away from the ablation point, through a 2 mm orifice, and routed to a Scanning Mobility Particle Analyzer (SMPS) through electrically conductive tubing. The SMPS is made up of an Electrostatic Classifier, a condensation particle counter, and a vacuum pump by TSI. In the Electrostatic Classifier particles are charged to a known bipolar distribution by Kr-85 then carried down a Differential Mobility Analyzer (DMA). The DMA consists of an inner and an outer cylinder. Charged particles move through an electric field based on the electrostatic mobility. In the DMA the potential between the outer and inner cylinder creates an electric field that can be varied to sort charged particles as they flow axially through the instrument. The charge, aerodynamic drag, and mass of the particles combine to sort the particles by “electrical mobility diameter.” At given instrument conditions, a monodisperse aerosol exits through a small orifice at the end of the DMA and is routed to the condensation particle counter (CPC) where the concentrations of particles are measured. As the voltage is scanned in the DMA, the CPC measures a range of particle sizes (or electrical mobility diameters).

Brass samples containing approximately 5% zinc and 95% copper were affixed with two-sided tape to a rotating surface, thereby reducing the incidence of multiple shots on the same location. Spectra were generated using an accumulation of 100 shots of plasma emission. These were achieved by triggering the intensifier at 10 Hz,
allowing gated collection, while triggering the CCD once, and averaging 100 shots in 10 seconds. Spectra were thus accumulated on the CCD, minimizing read noise in the resulting spectra. The emission peak areas were calculated from four such averaged spectra for each data point, allowing for the calculation of a standard deviation for the emission peak area.

A total of seven spectra lines from both zinc and copper were used to calculate the Boltzmann temperatures of the laser plasma and were chosen based on the availability of fundamental spectroscopic constants (13,14). Table 3.1 contains the copper and zinc spectral constants. Using these spectral constants and integrated line intensities, the Boltzmann temperatures were calculated using Equation 3.2. Equation 3.2, as written, relates the spectral intensity \( I_i \) with the wavelength \( \lambda_i \), the statistical weight \( g_i \), the transition probability \( A_i \) and the energy of the excited state \( E_i \).

**Equation 3.2**  \[ I_i = g_i A_i / \lambda_i \exp[-E_i/(kT)] \]  (13, 14, 15)

In addition to a distribution of particle sizes in the range of 15 nm to 660 nm, the volume of ablated particles from the plasma can be determined by the SMPS. The standard deviation for the particle volume from the SMPS was not determined for each experiment; rather, it was determined for one DP-LIBS and one single-pulse LIBS experiment. In these experiments, the standard deviations were determined from the total volume of four SMPS collections, while keeping all laser variables constant.
These relative standard deviations were then assumed in all of the DP-LIBS and single-pulse LIBS experiments.

3.4 Results and discussion

3.4.1 DP-LIBS with variable inter-pulse delay

In the first experiment, a pre-ablative 90 mJ (3x10^3 J/cm²) laser pulse parallel to the target surface was employed to create plasma above the surface. An ablative laser pulse of 30 mJ (1x10^3 J/cm²) intersected the plasma zone of the pre-ablative pulse and was delayed from 10 μs to 130 μs after the pre-ablative pulse. The emission spectra from the ablative plasma pulse were collected simultaneously with the SMPS collection of ablated particles. The integration time and delay of the intensified echelle were 4 μs and 3 μs, respectively. Figure 3.2 compares single-pulse LIBS and dual-pulse LIBS with an inter-pulse delay of 21 μs while Figure 3.3 shows the corresponding SMPS plots. Although the echelle spectrometer acquires a large spectral range 200 nm to 800 nm, Figure 3.2 was truncated to better compare prominent Cu and Zn emission lines. There is obvious spectral enhancement with the dual-pulse spectra in Figure 3.2. Depending on the spectral wavelength and emission line, the emission intensity was enhanced by as much as 9 times when the delay between the pre-ablation plasma and the ablation plasma was 21 μs. The strongest emission lines from Cu at 521 nm and Zn at 481 nm were enhanced in figure 3.2 by factors of 5 and 7, respectively. The emission intensity reported in all plots was calculated by
integration of the peak area followed by a baseline subtraction. These intensities are plotted versus the inter-pulse delay (Figures 3.4 and 3.5). In Figures 3.4 and 3.5, the Cu emission peak at 521 nm and the Zn emission peak at 481, the emission peak intensity increases rapidly from inter-pulse delay times of 11 µs to 41 µs where the maximum intensity is observed. After reaching their maxima, the emission intensity of Cu and Zn decrease slowly with increasing inter-pulse delay. With an inter-pulse delay of 131 µs the emission intensity of Zn and Cu are only slightly stronger than intensities observed in a single-pulse LIBS experiment.

Figure 3.3 compares the ablation particle distribution of DP-LIBS and single-pulse LIBS from the SMPS. Interestingly, the ablation particle volume was 30 times greater in DP-LIBS with an inter-pulse delay of 21 µs than single-pulse LIBS and DP-LIBS with a long inter-pulse delay of 131 µs. It is also observed from Figure 3.3 that particles from DP-LIBS, with a inter-pulse delay of 21 µs, have a particle distribution centered near 200 nm particle size, while the single-pulse LIBS and DP-LIBS with a 131 µs delay have a distribution centered near 100 nm. An explanation for this difference in particle distribution is likely due to aggregation of particles. In a paper discussing the evolution of laser plasma on metals, Smirnov describes how ions condense forming particles 10 nm in size and as the particles continue to cool they form aggregates of micron size (16).

To better understand how the amount of ablated material will affect the emission of LIBS, the particle volumes were plotted versus inter-pulse delay in Figure 3.6. The SMPS software automatically calculates the total particle volume from the
area under the particle distribution plot. In Figure 3.6 this peak particle volume (mass) ablation occurs at an inter-pulse delay of 21 µs. In Figures 3.4 through 3.6, the peak particle ablation occurs at a shorter inter-pulse delay than the peak DP-LIBS emission. Due to the 20% error associated the SMPS data it is possible that the peak emission intensity and peak particle ablation occur at approximately the same inter-pulse delay in DP-LIBS. However, it is also possible that with delays shorter than 41 µs, the pre-ablation plasma shields the ablative pulse. The shielding deteriorates over time giving a maximum emission around 41 µs, while any positive effect on emission from the pre-ablative plasma diminishes after 41 µs.

The plasma temperature was calculated using Equation 3.2. A Boltzmann plot was generated, Figure 3.7, using the seven Cu and Zn peak areas and the corresponding spectral constants. The data plot in Figure 3.7 exhibited a fairly good fit with an R² of 0.89. From the slope of the Boltzmann plot and using Equation 3.2 the plasma temperature was calculated. This temperature is displayed versus the inter-pulse delay in Figure 3.8. The Boltzmann temperatures calculated from the measurements correspond well with the measurements of line emission intensity.

3.4.2 DP-LIBS with variable pre-pulse fluence

In a second experiment, spectral enhancement was investigated, by keeping the inter-pulse delay constant and varying the pre-ablation plasma energy. The pre-ablation laser fluence was varied from 100 mJ to 250 mJ (3.5x10³ J/cm² to 8.5x10³ J/cm²) while maintaining a constant inter-pulse delay of 21 µs and a 30 mJ (to 1x10³ J/cm²) ablative
plasma pulse. The integrated peak area from the copper line at 521 nm and zinc at 481 nm are plotted versus pre-ablation plasma pulse fluence in Figures 3.9 and 3.10. The emission intensity of the 521 nm peak had a modest increase of about 45% and the 481 nm had an increase of 200% for a pre-ablative pulse energy increase from $3.5 \times 10^3$ J/cm$^2$ to $8.5 \times 10^3$ J/cm$^2$. These plots also suggest that any pre-ablation fluence beyond $8.5 \times 10^3$ J/cm$^2$ provides no additional improvement in spectral enhancement. A possible explanation of this leveling off of enhancements is due to the pre-ablation plasma lifetime being long enough to interfere with the ablation pulse because of its higher laser fluence. This may suggest that with increasing pre-ablation fluence, the inter-pulse delay would have to be adjusted to optimize the emission from the ablation plasma.

The ablation particle volume is plotted versus pre-ablation plasma pulse fluence (Figure 3.11). It shows a gradual 40% decrease in ablative particle volume with increasing pre-ablative fluence.

In Figure 3.12, the Boltzmann temperature versus pre-ablation plasma pulse fluence showed an increase in temperature with increasing fluence until reaching a fluence of $8.5 \times 10^3$ J/cm$^2$, where the temperature is approximately 7100 K versus 6600 K at $3.5 \times 10^3$ J/cm$^2$. As shown in the previous experiment, the Boltzmann temperature paralleled well with the emission intensity of both Cu and Zn; however, that is not the case for particle volume in Figure 3.11. Again, much of this can be explained by recognizing that to some extent the pre-ablation plasma shields the ablation plasma. As the pre-ablation fluence increases it helps the ablation plasma heat up during its expansion; however, the pre-ablation plasma will shield more of the ablation laser pulse
preventing a portion of that pulse from reaching the surface. This will help in heating the plasma while inhibiting ablation.

3.4.3 Single-pulse LIBS with variable ablation fluence

Lastly, a single-pulse ablative plasma was examined to compare with the double pulse experiments. Copper and zinc peak areas were plotted versus ablation laser pulse fluence ranging from $2.0 \times 10^3$ J/cm$^2$ to $4.0 \times 10^3$ J/cm$^2$ (Figures 3.13 and 3.14). Over that range, the intensity of the copper line at 521 nm increased by 210% while the zinc line at 481 nm increased 300%. The ablation particle volume was also plotted versus ablation laser fluence in Figure 3.15. Figure 3.15 shows a significant decrease in particle volume with increasing fluence. Also, the Boltzmann temperature is plotted versus ablation laser fluence is plotted in Figure 3.16 and shows a rather modest increase in temperature with increasing ablation laser fluence. The observed decrease in ablation versus increasing fluence is a sign that the plasma is shielding the target surface. The plasma begins to expand more rapidly with increasing fluence and there by absorb a laser portion of the laser pulse, shielding the surface.

3.4.4 Correlation of intensity, temperature and particle volume

To better understand the relationship that ablation particles and plasma temperature have on the emission intensity for LIBS, data from all three experiments were fitted into one plot. First, only the plasma temperature was considered. This was done by plotting the intensity for Zn at 481 nm and 334.5 nm, Cu at 521 nm and 510
nm versus the right half of equation 3.2 using the respective constants and Boltzmann temperatures (Figures 3.17, 3.18, 3.19, and 3.20). The better the data fits linearly, the more the spectral intensity is dependent on plasma temperature. The $R^2$ values for zinc in these plots were 0.90 for Zn at 481 nm and 0.94 for Zn at 334.5 nm. For copper at 521 nm and 510 nm, the $R^2$ values were 0.76 and 0.79, respectively. The data for zinc has a much better linear fit than the copper data, and this may be due to the fact that copper makes up 95% of the sample material leading to some self-absorption in emission spectra.

The plasma temperature obviously plays a major role in determining the spectral intensity, as observed in Figures 3.17 – 3.20; however, including the volume of particles from ablation into these plots can greatly improve the linear fit. The inclusion of particle volume was done in a similar way as in Figures 3.17, 3.18, 3.19, and 3.20, with the addition of multiplying equation 3.2 by the natural log of the quotient of particle volume and a constant. The constant is necessary because the particle volume measured represents the volume of particles per unit volume and since the plasma volume is not known, the measured particle volume only gives a relative indication of the particle volume in the plasma. The same constant was used in all of the analysis and was found empirically by trial and error to maximize the linear fit (Figures 3.21, 3.22, 3.23, and 3.24).

The data in Figures 3.21 – 3.24 fits significantly better than the correlation with temperature alone. The $R^2$ values for zinc in these plots were 0.97 and 0.95 for Zn at 481 nm and 334.5 nm, respectively. For copper, the $R^2$ values were 0.92 and 0.97 for
Cu at 521 nm and 510 nm, respectively. The use of the natural log for the particle volume was found intuitively, based on observing how the intensity increases with respect to the particle production. For example, in Figure 3.5 the intensity increased by a factor of 5.4 in comparing single-pulse LIBS and a DP-LIBS at 21 µs and the particle volume increased by a factor of 38 while the temperature only increased by around 6%. Thus, increasing particle volume increases the amount of analyte in the plasma; however, this increase comes at a cost to the plasma temperature since more of the laser energy is employed in heating and vaporizing the analyte.

In a final analysis of data only the particle volumes were correlated with the spectra intensities. In Figures 3.25, 3.26, 3.27, and 3.28 the intensities were plotted versus the natural log of the quotient of particle volume and a constant. The $R^2$ values for zinc in these plots were 0.68 and 0.52 for Zn at 481 nm and 334.5 nm, respectively. For copper the $R^2$ values were 0.83 and 0.84 for Cu at 521 nm and 510 nm, respectively. As expected, these results are much worse than the correlation including temperature and particle volume together, highlighting the importance of both ablation and temperature in the efficacy of double-pulse LIBS.

It is demonstrated above that both ablated particles and plasma temperature play a role in dual-pulse LIBS enhancement. In explaining the large enhanced particle production, it could be argued that the pre-ablative plasma somehow prepares the surface for ablation by charging or heating the ablation target region (17,12). The pre-ablative pulse is very close to the surface, without causing any ablation, but close enough to supply energy to the surface. With shorter inter-pulse delays (less than 10 µs)
there is little ablation, lower plasma temperature, and little to no spectra enhancement compared with longer delay times. These observations are likely a result of the pre-ablation pulse shielding the surface from the second ablative pulse (15). Increasing the inter-pulse delay gives time for most of the electrons and charged ions to move out of the region where the second pulse will pass.

Using interferograms of laser induced plasmas, Najmabadi calculated a shockwave velocity of $5 \times 10^6$ cm/s (18). Shock waves from pre-ablative plasmas traveling at this velocity will reach a surface 1 mm away in approximately 10 nanoseconds. The shock has a high concentration of electrons, which was also observed by Najmabadi (18). Electrons from the pre-ablation plasma shockwave may prepare the surface for the ablation pulse, allowing for better laser absorption. In the work presented, DP-LIBS experiments with an inter-pulse delay of 20 to 40 μs, the electron density in the path of the second pulse is low enough for shielding to be relatively negligible while the surface receives a sufficient exposure of electrons to help facilitate ablation. When looking at the plots of enhancement versus inter-pulse delay (Figures 3.4 and 3.5) and ablation particle concentration versus inter-pulse delay (Figure 3.6) it is observed that a small increase in inter-pulse delay has a big effect on enhancement and particle production at shorter inter-pulse delays. As soon as the enhancement and particle production reach a maximum, between 20 μs and 40 μs, it slowly drops off. It is possible that electrons originating from the pre-ablation plasma charge
the surface locally around the ablative target zone. This would agree well with the data presented.

When the ablative plasma is produced it expands into a less dense atmosphere due to a rarefaction from the pre-ablative pulse this maybe advantageous. The low-density region from the pre-ablation pulse is probably like LIBS done at lower pressures, which yields an enhancement close to that of dual-pulse LIBS (19). It has been argued by Scaffidi et al. that the condition after the pre-ablative pulse, in DP-LIBS, is similar to the condition of single-pulse LIBS at reduced pressures. With a less dense region to expand into, the ablation plasma will have a less dense electron shock wave. This reduction in electron density will lead to a plasma with reduced plasma shielding, thus allowing more photons to reach the ablation site.

When the pre-ablation pulse energy is varied while maintaining a constant delay the spectral intensities increase 45% for Cu at 521 nm and 200% for Zn at 481 nm with increasing fluence (Figures 3.9 and 3.10); however, the particle production decreases (Figure 3.11). This is likely due to the fact that maximum particle production enhancement occurs at an inter-pulse delay of 21 μs (Figure 3.5), while the spectral enhancement is optimized at a 41 μs delay (Figures 3.3 and 3.4). When the pre-ablation pulse energy is increased, the lifetime of the resulting plasma increases. Since the inter-pulse delay was optimized for a pre-pulse energy of 90mJ (3.5x10^3 J/cm^2), the inter-pulse delay time likely needs to be widened to accommodate for the higher energy pre-pulse.
3.5 Conclusion

The work presented here is novel because it offers a way to predict intensity based on a combination of particle volume produced during ablation and plasma temperature on brass samples. The temperature alone yields a moderately good prediction for the intensity of zinc and copper in brass; however, accounting for the particle production greatly increases the precision. Even though many parameters were adjusted, such as ablation fluence, pre-ablation fluence, inter-pulse delay, single-pulse or dual-pulse, all of the measured LIBS spectral intensities could be fit with a high level of linearity when both plasma temperature and ablation particle production were used to correlate double-pulse LIBS emission intensities. The above results suggest that LIBS spectral intensity is strongly influenced by plasma temperature and ablation particle volume. Accounting for both plasma temperature and ablation may allow for calibrations to be universally applied to other materials. This assumes that the density of ablation particles is very similar to the ablation target. If a truly universal calibration proves to be too ambitious, it would still be useful to require only standardization of confirmation at a single point or a few single points of material composition, rather than have to make extensive calibration curves for all concentration of each material component. Future studies will involve applying calibration made in material to other materials.

Chapter 3, in part is currently being prepared for submission for publication of the material. Effenberger Jr., Andrew J.; Buckley, Steven. The dissertation author was the primary investigator and author of this material.
Figure 3.1

Experimental setup. Two Spectra-Physics lasers were used to create a pre-ablative plasma and an ablative plasma. Plasma emission was collected and routed to an echelle spectrometer, and particles from the ablation process were collected and analyzed by the SMPS.
Figure 3.2

Comparing dual-pulse with single-pulse. The top spectrum utilizes a pre-ablative parallel pulse of 90 mJ (3x10^5 J/cm^2 fluence) followed by a 30 mJ (1x10^5 J/cm^2) ablative pulse with 21μs delay. Bottom spectrum is a single 1x10^5 J/cm^2 ablative pulse
Figure 3.3

Comparing dual-pulse with single-pulse. The top spectrum utilizes a pre-ablative parallel pulse of 90mJ (3x10^5 J/cm^2 fluence) followed by a 30 mJ (1x10^5 J/cm^2) ablative pulse with 21µs delay. Bottom spectrum is a single 1x10^5 J/cm^2 ablative pulse.
Figure 3.4

Emission intensity from DP-LIBS of Cu line (521 nm) plotted versus inter-pulse delay using a 90 mJ (3x10^5 J/cm^2 fluence) orthogonal pre-ablative pulse followed by a 30 mJ (1x10^5 J/cm^2) ablative pulse.
Figure 3.5

Emission intensity from DP-LIBS of Zn line (481 nm) plotted versus inter-pulse delay using a 90 mJ (3x10^5 J/cm^2 fluence) orthogonal pre-ablative pulse followed by a 30 mJ (1x10^5 J/cm^2) ablative pulse.
Figure 3.6

Ablation particle volume from dual-pulse LIBS versus inter-pulse delay using a 90 mJ (3x10^5 J/cm^2 fluence) orthogonal pre-ablative pulse followed by a 30 mJ (1x10^5 J/cm^2) ablative pulse.
Figure 3.7

Boltzmann plot from a dual-pulse LIBS spectra with a 41 μs inter-pulse delay using a 90mJ (3x10⁵ J/cm² fluence) orthogonal pre-ablative pulse followed by a 30mJ (1x10⁵ J/cm²) ablative pulse.
Figure 3.8

Boltzmann temperature versus inter-pulse delay using a 90 mJ (3x10^5 J/cm^2 fluence) orthogonal pre-ablative pulse followed by a 30 mJ (1x10^5 J/cm^2) ablative pulse.
Figure 3.9

Emission intensity of Cu line (521 nm) plotted versus pre-ablative pulse fluence. The pre-ablative orthogonal pulse energy was varied while the ablative pulse was held constant at 30 mJ (1x10^5 J/cm^2). The inter-pulse delay was 21 µs.
Figure 3.10

Emission intensity of Zn line (481 nm) plotted versus pre-ablative pulse fluence.
Figure 3.11

Ablation particle volume from DP-LIBS versus pre-ablation pulse fluence.
Figure 3.12

Boltzmann temperature of DP-LIBS versus pre-ablation pulse fluence.
Figure 3.13

Emission intensity of Cu line at 521nm from single-pulse LIBS versus ablative pulse fluence.
Figure 3.14

Emission intensity of Zn line at 481nm from single-pulse LIBS versus ablative pulse fluence.
Ablation particle volume versus ablation fluence

Figure 3.15

Ablation particle volume from single-pulse LIBS versus ablation pulse fluence.
Figure 3.16

Boltzmann temperature from single-pulse LIBS versus ablation pulse fluence.
Zn intensity (481 nm) versus plasma temperature dependence

Figure 3.17

Zn intensity at 481 nm versus equation 3.2. Spectral constants for the 481 Zn line were used in equation 3.2. The $R^2$ value for the linear line is 0.90.
Figure 3.18

Zn intensity at 334.5 nm versus equation 3.2. Spectral constants for the 334.5 nm Zn line were used in equation 3.2. The $R^2$ value for the linear line is 0.94.
Cu intensity (521 nm) versus plasma temperature dependence

Figure 3.19

Cu intensity at 521 nm versus equation 3.2. Spectral constants for the 521 nm Cu line were used in equation 3.2. The $R^2$ value for the linear line is 0.76.
Figure 3.20

Cu intensity at 510 nm versus equation 3.2. Spectral constants for the 510 nm Cu line were used in equation 3.2. The $R^2$ value for the linear line is 0.79.
Figure 3.21

Zn intensity at 481 nm versus the product of equation 3.2 multiplied by the natural log of the quotient of particle volume and a constant. Spectral constants for the 481 nm Zn line were used in equation 3.2. The $R^2$ value for the linear line is 0.97.
Zn intensity (334.5 nm) versus plasma temperature and particle volume dependence

Figure 3.22

Zn intensity at 334.5 nm versus the product of equation 3.2 multiplied by the natural log of the quotient of particle volume and a constant. Spectral constants for the 334.5 nm Zn line were used in equation 3.2. The $R^2$ value for the linear line is 0.95.
Cu intensity (521 nm) versus plasma temperature and particle volume dependence

Figure 3.23

Cu intensity at 521 nm versus the product of equation 3.2 multiplied by the natural log of the quotient of particle volume and a constant. Spectral constants for the 521 nm Cu line were used in equation 3.2. The $R^2$ value for the linear line is 0.92.
Cu intensity (510 nm) versus plasma temperature and particle volume dependence

Figure 3.24

Cu intensity at 510 nm versus the product of equation 3.2 multiplied by the natural log of the quotient of particle volume and a constant. Spectral constants for the 510 nm Cu line were used in equation 3.2. The $R^2$ value for the linear line is 0.97.
Figure 3.25

Zn intensity at 481 nm versus the natural log of the quotient of particle volume and a constant. Spectral constants for the 481 nm Zn line were used in equation 3.2. The R$^2$ value for the linear line is 0.67.
Zn intensity at 334.5 nm versus the natural log of the quotient of particle volume and a constant. Spectral constants for the 334.5 nm Zn line were used in equation 3.2. The $R^2$ value for the linear line is 0.52.
Cu intensity (521 nm) versus particle volume dependence

Figure 3.27

Cu intensity at 521 nm versus the natural log of the quotient of particle volume and a constant. Spectral constants for the 521 nm Cu line were used in equation 3.2. The $R^2$ value for the linear line is 0.83.
Figure 3.28

Cu intensity at 510 nm versus the natural log of the quotient of particle volume and a constant. Spectral constants for the 510 nm Cu line were used in equation 3.2. The $R^2$ value for the linear line is 0.67.
Table 3.1

<table>
<thead>
<tr>
<th>Wavelength $\lambda$ (nm)</th>
<th>Energy of the upper level $E_k$ (cm$^{-1}$)</th>
<th>Statistical weight $g_k$</th>
<th>Transition probability $A$(s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>334.5</td>
<td>62776.95</td>
<td>5</td>
<td>$15.0 \times 10^7$</td>
</tr>
<tr>
<td>472.2</td>
<td>53672.24</td>
<td>3</td>
<td>$4.58 \times 10^7$</td>
</tr>
<tr>
<td>481.0</td>
<td>53672.24</td>
<td>5</td>
<td>$7.00 \times 10^7$</td>
</tr>
<tr>
<td>636.2</td>
<td>62458.51</td>
<td>3</td>
<td>$4.65 \times 10^7$</td>
</tr>
<tr>
<td>510</td>
<td>30783.69</td>
<td>4</td>
<td>$0.20 \times 10^7$</td>
</tr>
<tr>
<td>515</td>
<td>49935.2</td>
<td>4</td>
<td>$6.02 \times 10^7$</td>
</tr>
<tr>
<td>521</td>
<td>49942.06</td>
<td>6</td>
<td>$7.59 \times 10^7$</td>
</tr>
</tbody>
</table>

Spectroscopic constants used in Boltzmann temperature calculations (4,5,7)
References


4. MEASUREMENT OF COMMON AND TRACE ELEMENTS IN MOLTEN SALTS USING LIBS

4.1 Abstract

Among the advantages of Laser-Induced Breakdown Spectroscopy (LIBS) is the ability to make measurements remotely and with little or no sample preparation. In this work LIBS has been used to detect and quantify trace metals in a system intended to simulate a molten salt electrorefiner. An electrorefiner recycles spent nuclear fuel through electrolysis. The molten salt dissolves nuclear fuel and attached metal components while also acting as an electrolyte. It is desirable to obtain atomic information about the molten salt so the recycling process can be optimized. Due to the danger of radiation exposure and the slow lead times of traditional analytical methods, LIBS is being investigated as a possible real-time analytical tool for monitoring the electrorefining process. It was determined that LIBS can effectively detect and quantify trace metals such as chromium, cobalt and manganese in molten lithium chloride-potassium chloride salt. Calibration curves were constructed for cobalt (CoCl$_3$) and manganese (MnCl$_3$), while chromium (CrCl$_3$) was used to demonstrate the resolution of the spectrometer. Detection limits for CrCl$_3$, CoCl$_3$ and MnCl$_3$ were determined to be 0.04, 0.5 and 0.3 percent mass, respectively.
4.2 Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) involves the use of a focused, high-power laser pulse to create a plasma. The plasma can be formed in liquid, air, or on the surface of interest. During the formation of the plasma, the analyte is vaporized and excited. The emission spectra from this plasma can be analyzed, yielding valuable atomic information about the analyte, surface or target. The main advantages of LIBS over other analytical techniques are that it requires no sample preparation, has rapid data acquisition and can interrogate samples in hostile environments from afar (12,13).

LIBS has been successfully used in many molten metal applications (1-5) and has also been used to detect analytes in aqueous liquids (8, 9). If the liquid is transparent to the laser light then spectra can be acquired from the liquid surface or within the bulk. If the liquid is not transparent then measurements can only be acquired at the surface. Novel configurations have used fluid mechanics and fiber optics to control the laser interaction with the sample and to make measurements in difficult places. For example, Aragon and co-workers used an argon jet to remove material from the surface during LIBS on molten steel (10). The removal of the top layer was necessary because the surface composition differed from the bulk due to lighter components migrating to the surface. Singh and colleagues designed a probe to administer the laser pulse and collect the LIBS spectra through a single fiber optic. Their probe used a continuous flow of nitrogen to protect and cool the optics from the aluminum melt during LIBS (7).
For transparent liquids, there are caveats to either choosing to acquire LIBS from the surface or the bulk. If the LIBS plasma is formed on the surface then the shock wave from the plasma will cause splashing on the surface. On the other hand, if the laser is focused into the bulk LIBS will be suppressed due to lower temperature plasma formation (9).

Idaho National Laboratory is currently involved in the reprocessing of nuclear material from decommissioned nuclear reactors. An integral piece of this reprocessing is an electrorefiner. A schematic of the electrorefiner can be seen in Figure 4.1. The refiner has a pair of electrodes that lead to the cathode and the anode which are submerged in a molten salt bath. The molten salt is a eutectic mixture of lithium chloride-potassium chloride, which enables the electrorefiner to operate at temperatures sufficient to dissolve the material to be reprocessed. Attached to the anode is a dissolution basket where the nuclear material is placed. As the nuclear material dissolves into the molten salt mixture and a potential is placed on the electrodes, pure uranium is deposited on the cathode. During this process transuranic actinide impurities enter the molten salt and eventually migrate to a cadmium bath at the bottom of the electrorefiner. In order to optimize and fully understand the electrorefining process, information about the concentrations of these impurities in the molten salt is essential.

Due to the potentially lethal radioactivity of the nuclear material, the reprocessing must be done in a radioactive-proof room called a hot cell. Human-controlled robotic arms do all the work inside the hot cell, which makes the collection of analytical samples from the electrorefiner a challenge. Due to the risk of radioactive
exposure and long time scale for collecting a sample, an in situ LIBS system would be ideal for monitoring the progress of the electrorefining process. To date, no studies have been published regarding the detection of trace metals in a molten salt environment similar to an electrorefiner.

To explore the possibility of using LIBS to monitor the electrorefining process, a basic electrorefiner mock-up was fabricated. The mock-up was contained in an acrylic enclosure and consisted of an Inconel crucible, a heating apparatus and the necessary power supply and controller. The optics necessary for performing LIBS were integrated into the acrylic enclosure allowing a laser pulse to be carried into the enclosure and emission from the plasma to be collected outside the enclosure. Rare earth metals such as chromium chloride, cobalt chloride and manganese chloride were added to the molten salt at increasing concentration. LIBS spectra of the molten salt with increasing cobalt and manganese concentrations were used for calibration, while chromium was used to demonstrate the resolution of the spectrometer.

4.3 Experimental

The experimental setup is shown in Figure 4.2. A purge box was fabricated from acrylic sheets and was designed to integrate LIBS optics and a molten salt heating apparatus under an argon purge. The heating apparatus was a ceramic fiber infrared heating element, custom fabricated by Watlow to fit a 500 ml capacity Inconel crucible. Inconel is an iron-nickel alloy with a very high melting point and excellent resistance to corrosion. An electronic controller monitored the temperature of the crucible with a
thermocouple while controlling the power supply leading to the heater. The heater was monitored and controlled with a Watlow 93 series controller and a Watlow Din-a-mite power supply. Also, a thermocouple with a protective stainless steel sheath was attached directly to the crucible.

The molten salt mixture was made up of 250 g of eutectic lithium chloride-potassium chloride (LiCl/KCl) salt with the temperature maintained at approximately 530 °C. A 50 mm diameter lens with a 500 mm focal length was fixed to the top of the acrylic box to focus the laser pulse at the molten salt surface. The laser plasma was formed on the surface of the molten salt and the plasma emission was collected back through the same 500 mm lens, reflected by a pierced mirror, and then coupled to a fiber optic leading to an Acton 2300i Czerny-Turner spectrometer and a Princeton Instruments ICCD. To prevent the precipitation of salt particles on the lens, a small transparent housing was affixed over the focusing lens. Argon was introduced to the main enclosure through the lens housing, which had a 50 mm hole entering the main enclosure and through which the laser was also focused. This housing allowed for a constant flow of argon gas to travel away from the focusing optic reducing particle precipitation on the optics.

A 100 mJ laser pulse from a Nd:YAG Spectra-Physics laser operating at 1064 nm and 10 Hz formed the plasma. The ICCD/Czerny-Turner spectrometer was triggered from the Q-switch on the laser. The ICCD was delayed 1 μs from the Q-switch and had an integration time of 2 μs. A 600-groove grating was chosen to monitor the manganese and cobalt lines. This grating allows for a wide spectral range to be monitored at once, 450 nm to 540 nm for manganese and 305 nm to 395 nm for
cobalt. Having a wide spectral range makes it possible to compare the manganese line and the cobalt line with either the lithium or the potassium lines or both. Since lithium and potassium are two of the main components of the molten salt, the other being chlorine, their emission intensities should not change much as small amounts of manganese and cobalt are added. Calibration curves were constructed using two different methods. The first method plots the ratio of intensity from analyte and lithium versus concentration while the second method plots the ratio of intensity of the analyte and the total spectrum versus the concentration. A 2400-groove grating was used for higher resolution spectra of chromium.

The error in massing the analyte was 0.01 grams. This error was propagated into each increasing concentration because the analyte was added in succession between experiments. The error in spectral intensity was estimated from several spectra and assumed throughout the experiment. All spectra were created from 100 shot accumulations.

### 4.4 Results

A LIBS spectrum of pure molten LiCl/KCl was compared with molten LiCl/KCl doped with 0.3% CrCl₃ (Figure 4.3). Chromium triplet lines are observed near 360 nm and 427 nm. A potassium line is observed at 405 nm and the peak centered near 413 nm consists of many lithium and potassium spectral lines. A high-resolution spectrum was taken of the doped molten LiCl/KCl to demonstrate the resolution of the spectrometer (Figure 4.4). As seen in Figure 4.4, the high-resolution spectrum easily resolves peaks that are 1 nm apart. The ability to discern emission peaks close to each other can be
useful since many radioactive elements have emissions within a few nanometers of each other (11).

Cobalt was also detected in the molten salt using LIBS. Figure 4.5 compares molten salt with 1.7 percent cobalt and without cobalt. In Figure 4.5, cobalt emission dominates in the spectral region between 340 nm and 400 nm. There is a slight offset in the wavelength between the two overlaid spectra due to drift in the calibration of the spectrometer; this is also seen in the following spectra. Figure 4.6 is a zoomed-in image of Figure 4.5. Since the concentration of lithium is relatively constant, the ratio of the spectra emission intensity of interest and the lithium emission intensity can be plotted versus percent concentration for calibration curves. Using the first method, a calibration curve for cobalt on constructed by plotting the ratio of the spectrum emission intensities for cobalt at 340 nm and the spectra emission intensities for lithium at 323 nm versus the concentration of CoCl₃ in the molten LiCl/KCl (Figure 4.7). The emission peaks were chosen because of the lack of peak overlap hampering most of the spectra in Figure 4.5. Table 4.1 summarizes emission lines seen in all spectra. A linear trend line was fitted to the plot with fair agreement, yielding a R² value of 0.90. Using the second calibration method, a curve was created by taking the ratio of the Co (340 nm) intensity and the entire spectral intensity, between 310 nm and 395 nm, plotted versus the Co concentration. This method resulted in an improved calibration curve with an R² of 0.93 (Figure 4.8).

In addition to cobalt, manganese was also successfully detected. Figure 4.9 compares LIBS spectra of molten LiCl/KCl with 1.3 percent manganese and without manganese. The largest feature in Figure 4.9 near 460 nm is from both lithium and
potassium. There are also many manganese emission lines between 470 nm to 482 nm. Figure 4.10 is a zoomed in image of Figure 4.9. The manganese emission intensity at 482 nm was chosen for the calibration curve because there is no overlap with the other spectra. Also, the emission peak near 497 nm consists of emission lines from both lithium and potassium. As noted above, the concentration of lithium and potassium change only slightly with increasing manganese concentration, so the ratio of the area from the 482 nm manganese emission intensity and the lithium potassium emission intensity at 497 nm can be used for the calibration curve. Figure 4.11 shows the result of plotting the ratios of the emission intensities of manganese at 482 nm and lithium-potassium at 497 nm versus MnCl₃ in the molten LiCl/KCl. This plot yields a best-fit trend line with a R² of 0.96. The emission intensity is calculated by simply integrating the peak and subtracting the continuum background. This method, while simple, does not correct at all for emission fluctuations that may be due, for example, to changing laser or plasma conditions. To address this, a calibration curve was also constructed by taking the ratio of the Mn peak intensity to the integration of the entire spectrum between 445 nm and 540 nm. When plotted versus the concentration, this normalized emission results in an improved R² of 0.99 (Figure 4.12). In this case, the integral of the entire spectrum captures the continuum emission that is indicative of the strength of the plasma, and thus provides a first-order correction for laser plasma fluctuations and matrix effects.
4.5 Discussion

In this initial study calibration curves were successfully created from LIBS spectra for CoCl₃ and MnCl₃ in a molten eutectic LiCl/KCl salt using two different methods. The first method used the ratio of the analyte emission intensity to the emission intensity of Li versus analyte concentration, while the second method used the ratio of the analyte emission intensity to the total spectrum intensity versus the analyte concentration. The calibration curves for the second method fit a linear trend line better than the first method. Using the first method for Co calibration resulted in a linear trend line with an $R^2$ of 0.90 while use of the second method resulted in an $R^2$ of 0.93. For Mn calibration, the first method resulted in a linear trend line with an $R^2$ of 0.96, while use of the second method resulted in an $R^2$ of 0.99. The reason taking the ratio of the analyte intensity and the total spectrum intensity resulted in a slightly better calibration is possibly because the ratio is less susceptible to plasma temperature changes compared to the ratio of analyte intensity and the Li intensity. It was also demonstrated that the spectral resolution of LIBS spectra from molten salt surfaces is no worse than 1 nm for the chromium triplet near 360 nm, when using a Czerny-Turner spectrometer with a 2400-groove grating. The 600-groove grating was used for the calibration because a wider spectral range was needed to simultaneously acquire cobalt peaks with lithium peaks and manganese peaks with lithium/potassium peaks.

Experimental detection limits were not studied here, but as little as 0.3 percent by mass of CrCl₃ was detected in the molten LiCl/KCl salt. Also, 0.5 percent of CoCl₃ and MnCl₃ were detected in the molten LiCl/KCl salt. The theoretical detection limits can be determined using Equation 4.1, where Std is the background standard deviation.
near peaks of interest, \( C_0 \) is a known peak concentration, and \( I_0 \) is the peak intensity. This equation follows the IUPAC convention of defining the detection limit as 3x the noise. Here, the detection limits were determined by first calculating the integral of the noise in the LIBS spectra of pure molten salt near 360 nm for chromium, 482 nm for manganese and 340 nm for cobalt, over a width equivalent to a LIBS spectral peak. These values were multiplied by three and then compared with peak areas of known concentrations of chromium, manganese and cobalt. Using this method and Equation 4.1, the theoretical detection limits for CrCl₃, CoCl₃ and MnCl₃ were found to be 0.04, 0.5 and 0.3 percent mass, respectively.

**Equation 4.1**  
\[
D.L. \text{ (percent mass)} = 3 \times \text{Std} \times \frac{C_0}{I_0}
\]

Because the error in massing was 0.1 g, error associated with each data point is on the order of 10 percent. Also, there may be some error associated with the dosing and mixing of the analyte into the molten salt and the amount of error is assumed to be minimal. The homogeneity of the molten salt was not determined; however, the molten salt was mixed after each dose of analyte.

There was some difficulty in protecting the focusing lens from salt precipitation but this problem was alleviated when the argon flow was increased. The setup has room for improvement and by modifying the optic housing further it may be possible to eliminate any salt precipitation on the optics.

Dosing of the analyte was done through a side door on the purge box. This temporarily introduced outside air into the purge box, which may slightly affect the
plasma due to the change of the argon atmosphere. Ideally, an airtight enclosure made of heat and corrosion resistant material should be used in place of an acrylic enclosure. Also, a more convenient method of dosing the molten salt while reducing the introduction of outside air should be developed.

One major difficulty in the experimental setup was arranging the optics up, over, and into the very large acrylic enclosure. The acrylic enclosure was oversized so that it would not be too close to the intense heat of the molten salt and heater. Having a smaller enclosure would reduce the distance the laser pulse would have to travel before arriving at the molten salt surface. Emission from LIBS would also travel a shorter distance before arriving to the spectrometer.

Generally, the heating setup worked well for approximately the first 15 hours of work. Eventually the thermocouple corroded and the heating was no longer under control. Also, the Inconel crucible suffered corrosion during the course of these experiments although there was no evidence of contamination of the molten salt from the crucible. It is possible that since the enclosure was not completely airtight and outside air was introduced each time analyte was added, the lifetime of the equipment was shortened. Future studies should involve probing the volume to determine the composition below the surface, perhaps using a submersible lance equipped with laser optics as Peter and co-workers did in work involving LIBS of molten steel (12). Studies should also involve the use of a hollow fiber optic to carry the laser pulse to a surface contained in a remote chamber, such as a heat-resistant purge box. Another hollow fiber optic could then be used to route the resulting plasma emission to the spectrometer. This could be done similarly to the work done by Dumitrescu and co-
workers, where a hollow fiber integrated into an optical setup to perform LIBS inside a stainless steel cylinder (13).

A potential setup for such future experiments is illustrated in Figure 4.13. Here, a hollow fiber is used to carry a laser pulse into the molten salt enclosure. This laser pulse is then focused onto the surface of the molten salt forming a plasma. Another set of optics and hollow fiber would collect the plasma emission and carry it to a spectrometer outside the enclosure. The hollow fiber is a thin tube with a silver coating inside; however, the hollow fiber carrying the laser pulse has an added dielectric layer. The dielectric thickness is optimized for high transmittance of the wavelength of the laser light (14).

Chapter 4, in part is currently being prepared for submission for publication of the material. Effenberger Jr., Andrew J.; Buckley, Steven. The dissertation author was the primary investigator and author of this material.
Figure 4.1

Electrorefiner from Idaho National Laboratory. Fuel to be recycled is placed in the fuel dissolution basket. Pure uranium is precipitated on the cathode. Contaminants accumulate in the cadmium bath below the molten salt. Figure courtesy of Idaho National Laboratory.
Figure 4.2

Experimental setup. An Inconel crucible has a ceramic heating element and is controlled with a Watlow power supply and controller. The molten salt setup was kept under Argon in an acrylic enclosure. The lens used to focus the laser pulse was encased in a small enclosure that had an outward argon flow into the larger enclosure to prevent precipitation of salt on the lens.
Figure 4.3

Comparison of LIBS spectra of pure LiCl/KCl and LiCl/KCl with chromium (0.3% CrCl$_3$).
Figure 4.4

Higher resolution, 2400-groove grating, LIBS spectrum of chromium (0.3% CrCl₃) in LiCl/KCl.
Figure 4.5

Comparison of LIBS spectra of LiCl/KCl without and with cobalt (1.7% CoCl$_3$).
Figure 4.6

Zoomed-in comparison of LIBS spectra LiCl/KCl without and with cobalt (1.7% CoCl$_3$).
Figure 4.7

The ratio of spectra emission intensities from cobalt (340 nm) and lithium (323 nm) plotted versus percent of cobalt by mass.
Figure 4.8

The ratio of spectra emission intensities from cobalt (340 nm) and the entire spectrum (310-395 nm) plotted versus percent of cobalt by mass.
Figure 4.9
Comparison of LIBS spectra of LiCl/KCl without and with manganese (1.3% MnCl₃).
Figure 4.10

Zoomed in comparison of LIBS spectra of LiCl/KCl without and with manganese (1.3% MnCl₃).
Figure 4.11

The ratios of spectra emission intensities from manganese (482 nm) and lithium (497 nm) plotted versus percent of manganese.
Figure 4.12

The ratios of spectra emission intensities from manganese (482 nm) and the entire spectrum (445-540 nm) plotted versus percent of manganese.
Figure 4.13

Proposed future molten salt LIBS experiment. Here, hollow fiber optics carry the laser pulse and plasma spectral emission to and from the enclosure.
<table>
<thead>
<tr>
<th>Co (nm)</th>
<th>Mn (nm)</th>
<th>Cr (nm)</th>
<th>K (nm)</th>
<th>Li (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>340.5</td>
<td>450.2</td>
<td>357.8</td>
<td>344.6</td>
<td>323.2</td>
</tr>
<tr>
<td>340.9</td>
<td>470.9</td>
<td>359.3</td>
<td>344.7</td>
<td>348.8</td>
</tr>
<tr>
<td>341.2</td>
<td>472.7</td>
<td>360.5</td>
<td>364.8</td>
<td>357.9</td>
</tr>
<tr>
<td>343.3</td>
<td>473.9</td>
<td>391.9</td>
<td>364.8</td>
<td>361.8</td>
</tr>
<tr>
<td>344.3</td>
<td>475.4</td>
<td>396.3</td>
<td>404.4</td>
<td>366.2</td>
</tr>
<tr>
<td>344.9</td>
<td>476.1</td>
<td>396.9</td>
<td>404.7</td>
<td>371.8</td>
</tr>
<tr>
<td>345.3</td>
<td>476.2</td>
<td>397.6</td>
<td>404.4</td>
<td>379.4</td>
</tr>
<tr>
<td>346.2</td>
<td>476.5</td>
<td>425.4</td>
<td>404.7</td>
<td>391.5</td>
</tr>
<tr>
<td>346.5</td>
<td>476.6</td>
<td>427.4</td>
<td>460.2</td>
<td>391.5</td>
</tr>
<tr>
<td>347.4</td>
<td>478.3</td>
<td>428.9</td>
<td>460.2</td>
<td>398.5</td>
</tr>
<tr>
<td>348.9</td>
<td>482.3</td>
<td>433.9</td>
<td>460.2</td>
<td>398.5</td>
</tr>
<tr>
<td>350.2</td>
<td>534.1</td>
<td>434.4</td>
<td>476.0</td>
<td>413.2</td>
</tr>
<tr>
<td>350.6</td>
<td>435.1</td>
<td>497.1</td>
<td>413.2</td>
<td></td>
</tr>
<tr>
<td>351.2</td>
<td></td>
<td>497.1</td>
<td>413.2</td>
<td></td>
</tr>
<tr>
<td>351.8</td>
<td></td>
<td>527.1</td>
<td>427.3</td>
<td></td>
</tr>
<tr>
<td>352.6</td>
<td></td>
<td>531.5</td>
<td>427.3</td>
<td></td>
</tr>
<tr>
<td>352.9</td>
<td></td>
<td>539.5</td>
<td>460.2</td>
<td></td>
</tr>
<tr>
<td>356.9</td>
<td></td>
<td>460.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>358.7</td>
<td></td>
<td>460.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>384.5</td>
<td></td>
<td>476.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>387.3</td>
<td></td>
<td>497.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>389.4</td>
<td></td>
<td>497.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>399.5</td>
<td></td>
<td>527.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Spectral lines of interest from NIST.
References


5. CONCLUSION AND FUTURE EXPERIMENTS

As discussed in this dissertation, spectral intensity of zinc and copper in brass was influenced by plasma temperature and ablation particles in dual-pulse LIBS and single-pulse LIBS. The work presented looked at a dual-pulse scheme using two pulsed Nd:YAG laser operating at a fundamental wavelength of 1064 nm. First, a pulse was focused parallel and above the surface forming a pre-ablative plasma in air. A second pulse is then fired to form an ablative (analytical) plasma on a surface while intersecting the volume of the pre-ablative plasma. Two parameters were studied in the DP-LIBS experiments, the inter-pulse delay and the pre-ablative fluence. Both these parameters have an effect on the emission intensity of zinc and copper and the ablation volume. Single-pulse experiments where also conducted by varying the fluence, which also has an effect on the emission intensity of zinc and copper and the ablation volume.

In experiments varying the inter-pulse delay, a 90 mJ pre-ablative laser pulse followed by a 30 mJ ablative (analytical) laser pulse were used. Using this scheme with an inter-pulse delay of 20 µs resulted in a 5 fold increase in intensity for Cu at 521 nm and a 7 fold increase in intensity for Zn at 481 nm compared to single-pulse LIBS. A thirty fold increase in ablation was observed in this DP-LIBS scheme compared to single-pulse LIBS at an inter-pulse delay of 20 µs. With a constant inter-pulse delay there was a mild increase in emission intensity for both zinc and copper with increasing pre-ablation fluence, however, a decrease in ablation volume is also observed with increasing fluence. The single-pulse experiments involved the use of only the ablative analytical pulse. Emission intensity increased with increasing fluence for both Cu and
Zn; however, there was a sharp decrease in ablation volume with increasing fluence.
The electron temperature was calculated for all experiments using the Boltzmann plot.
It was found that emission intensities of Cu and Zn correlated well with the electron
temperature; however, considering ablation particle volume along with the electron
temperature improved this correlation. The results of this experiment suggest that both
particle volume and electron temperature play a significant role on the emission
intensity.

The above may have an interesting application in areas where calibrations from
one material can be used to make measurements in other materials. An interesting
experiment would involve making calibration for zinc in NIST standard brass then
applying this calibration to other alloys. Results from this dissertation suggest that
spectral intensity is strongly influenced by both plasma temperature and particle
ablation, so accounting for these components could allow for calibration curves to be
universal applied to other materials. This idea hinges on the assumption that the ablation
particle density is similar to that of the ablation target. This may be a reasonable
assumption when dealing with similar materials, like bronze, brass, or other alloys.
Future studies should also be conducted to determine whether calibrations made in one
environment could be applied to other environments, for example, ambient conditions
compared to low-pressure conditions.

This dissertation also discussed the use of LIBS to analytically detect trace
elements in a molten salt environment. Here an apparatus was built to simulate an
electrorefiner and its enclosure. Electrorefiners are used to reprocess nuclear fuel for
recycle through electrolysis in a molten salt bath. This is an important application that
demonstrates ability of LIBS to analytically detect elements in hostile environments and on liquid surfaces. Chromium, cobalt, and manganese where measured in a eutectic potassium-lithium-chlorine molten salt mixture. Calibration curves were successfully constructed for cobalt (CoCl$_3$) and manganese (MnCl$_3$), while chromium (CrCl$_3$) was used to demonstrate the resolution of the spectrometer. Theoretical detection limits were determined to be 0.04, 0.5 and 0.3 percent mass for CrCl$_3$, CoCl$_3$ and MnCl$_3$, respectively.

Future molten salt experiments should involve the use of a fiber optic to carry the laser pulse to the electrorefiner while also using the fiber optic to carry light from the LIBS plasma to a spectrometer. The Idaho National Laboratory Fuel and Conditioning Facility, which contains the electrorefiner, can only be accessed through small ports leading from a safe location. Though not mentioned in the dissertation, preliminary results showed that LIBS can be done on a metal sample using a 1 meter hollow glass fiber. The next step would be to repeat the molten salt experiment discussed in this dissertation using a fiber optic to carry the laser pulse and plasma light.