Laser Induced Breakdown Spectroscopy For Detection Of Organic Residues Impact Of Ambient Atmosphere And Laser Parameters

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LASER INDUCED BREAKDOWN SPECTROSCOPY FOR
DETECTION OF ORGANIC RESIDUES:
IMPACT OF AMBIENT ATMOSPHERE AND LASER PARAMETERS

by

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ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) is showing great potential as an atomic analytical technique. With its ability to rapidly analyze all forms of matter, with little-to-no sample preparation, LIBS has many advantages over conventional atomic emission spectroscopy techniques. With the maturation of the technologies that make LIBS possible, there has been a growing movement to implement LIBS in portable analyzers for field applications. In particular, LIBS has long been considered the front-runner in the drive for stand-off detection of trace deposits of explosives. Thus there is a need for a better understanding of the relevant processes that are responsible for the LIBS signature and their relationships to the different system parameters that are helping to improve LIBS as a sensing technology.

This study explores the use of LIBS as a method to detect random trace amounts of specific organic materials deposited on organic or non-metallic surfaces. This requirement forces the limitation of single-shot signal analysis. This study is both experimental and theoretical, with a sizeable component addressing data analysis using principal components analysis to reduce the dimensionality of the data, and quadratic discriminant analysis to classify the data. In addition, the alternative approach of ‘target factor analysis’ was employed to improve detection of organic residues on organic substrates.

Finally, a new method of characterizing the laser-induced plasma of organics, which should lead to improved data collection and analysis, is introduced. The comparison between modeled and experimental measurements of plasma temperatures and electronic density is discussed in order to improve the present models of low-temperature laser induced plasmas.
To my family...
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LIST OF ABBREVIATIONS

CBRNE – Chemical, Biological, Radiological, Nuclear, or Explosive

IEDs – Improvised Explosive Devices

TNT – Trinitrotoluene

ANFD – Ammonium Nitrate combined with Fuel Oil

THz – Terahertz

AFP – Amplifying Fluorescence Polymers

AAS – Atomic Absorption Spectrometry

AES – Atomic Emission Spectrometry

AFS – Atomic Fluorescence Spectrometry

DC – Direct Current Arc

AC – Alternating Current Arc

ICP – Inductively Coupled Plasmas

DCP – Direct Current Plasmas

MIP – Microwave Induced Plasmas

LIP – Laser Induced Plasmas

Ns – Nanosecond

Fs - Femtosecond

LIBS – Laser Induced Breakdown Spectroscopy

TFA – Target Factor Analysis
LTE – Local Thermodynamic Equilibrium
MPI – Multi-photon Ionization
BS – Barrier Suppression
IBA – Inverse Bremsstrahlung Absorption
LSC – Laser-Supported Combustion Wave
LSD – Laser-Supported Detonation Wave
LSR – Laser-Supported Radiation Wave
LCAO – Linear Combination of Atomic Orbitals
TE – Thermodynamic Equilibrium
PLTE – Partial Local Thermal Equilibrium
MCE – Model of Coronal Equilibrium
CRM - Collisional Radiative Model
HDPE – High-Density Polyethylene
LDPE – Low-Density Polyethylene
PVC – Polyvinyl Chloride
PET – Polyethylene Terephthalate
PP – Polypropylene
DLVQ – Dynamic Learning Vector Quantization
RBF – Radial Base Function
ABD – Acrylonitrile Butadiene Styrene
PC – Poly-carbonate
SAN – Styrene Acrylonitrile
BFR – Brominated Flame Retardants
PCA – Principal Component Analysis
PLS-DA – Partial Least Squares – Discriminant Analysis
PETN – Pentaerythritol Tetranitrate
HMX – Cyclo-1,3,5,7-Tetramethylene-2,4,6,8-Tetranitramine
RDX – Cyclo-1,3,5-Trimethylene-2,4,6-Trinitramine
IMS - Ion Mobility Spectrometry
MS - Mass spectrometry
LC – Linear Correlation
Nd:YAG – Neodymium: Yttrium Aluminum Garnet
Nd:YLF – Neodymium: Yttrium Lithium Fluoride
Nd:YVO₄ – Neodymium: Yttrium Vanadate
KD*P – Potassium Dideuterium Phosphate
Ti:Al₂O₃ – Titanium Sapphire (Aluminum Oxide)
CV – Canonical Variates
PC – Principal Component
IE – Ionization Energy
WF- Work Function
IP – Ionization Potential
LDA – Linear Discriminant Analysis
QDA – Quadratic Discriminant Analysis
C-T - Czerny-Turner
ROC - Receiver Operator Characteristic
PMT – Photomultiplier Tube
APD – Avalanche Photodiode
PDA – Photodiode Array
CCD – Charge Coupled Device
iCCD – Intensified Charge Coupled Device
PFTE – Polytetrafluoroethylene
Nitros – Nitrogenated Samples
Oxys – Oxygenated Samples
Cyano – Cyanide Sample
PAHs – Polycyclic Aromatic Hydrocarbon Sample
Polys – Polymers
OCCN – Other Compounds Containing Nitrogen
FWHM – Full Width Half Maximum
RSD – Relative Standard Deviation
NIR – Near Infrared
UV – Ultraviolet
A.U. – Arbitrary Units
1 INTRODUCTION

1.1 Need for Sensing Technologies

In the sensing community there has been a continuing effort to research and develop robust and real-time sensors based on analytical techniques with a single sampling method. With the evolution of such technology, recalls such as the recent salmonella outbreak in peanut butter\(^1\) could be reduced or even prevented, as food monitoring protocols could be developed for real-time processing. In addition, a sensor capable of conducting remote stand-off sampling offers the prospect of analyzing samples that may not be locally accessible. Furthermore, a sensor that affords high sensitivity with minimal sample preparation can help reduce the life-threatening risks posed to first-responders\(^2\), with its ability to scan and detect hazardous objects and materials, before entering a possible compromised area. Upon development of such sensors, not only would areas such as public health (pharmaceutical products\(^3\) and trace elements in food\(^4, 5\)) profit, but other areas such as environmental studies (toxic metals in liquids\(^6, 7\) and soil analysis\(^8, 9\)), forensics (microanalysis applications\(^10\), glass analysis\(^11, 12\), hair and fiber identification\(^13, 14\), and gunpowder residue\(^15\)), space exploration (mineral phases and bio-signatures on Mars\(^16\)) and homeland security and defense (explosive\(^17\), biological\(^18\), nuclear\(^19, 20\), radiological\(^21\), and chemical detection\(^22\)) would benefit greatly.

In order to incorporate these necessary proficiencies, the proposed sensors not only need to collect particles from the sample of interest which form a chemical signature of the sample, but also differentiate this signature from that of the surrounding environment. If the need for a basic sampling technique is elementary, separation between the sample itself and its environment will not be as clear as if a more sophisticated protocol is utilized. In this case, it is up to the
detection and analysis algorithms to separate between the signature of the sample and that of the environment.

In theory there are many physical and chemical analytical schemes that should be applicable for detection of hazards, but the requirements of rapidity and robustness limit the type of useable instrumentation. The limitations are even stricter in the case of sensors developed for homeland security and defense purposes. In the civil and military defense community, there is a pressing need for the development of sensor technology capable of detecting hazardous and potential threats whether they are chemical, biological, radiological, nuclear, or explosive (CBRNE) in a real-time, stand-off configuration.

Since September 11, 2001, a focus has been placed on the detection of explosive devices as improvised explosive devices (IEDs) that could be deposited almost anywhere at any time. Not having access to military grade explosives, fabricators of IEDs often use their own explosive formulations, but even these explosives require the same common chemical building blocks, which consist of a fuel and an oxidizer. Some explosives have the fuel and oxidizer as part of the same molecule, such as trinitrotoluene (TNT), and some explosives are comprised of mixtures of separate fuels and oxidizers, such as ammonium nitrate combined with fuel oil (ANFO). While most explosives employ the oxidizer of the NO2 (nitro) group, IEDs tend to utilize a more diverse range of oxidizers, but the majority of fuels (considered organic compounds) available for use in IEDs are aromatic hydrocarbons such as toluene. Hence, a focus has been placed on using organic compound signatures as a method of possible explosive detection. A short overview of the existing techniques used for explosion detection will be described in the next sub-section.
1.2 Current Sensing Technologies for Explosives

Current sensing technologies utilized for explosive detection are broken into two categories, those developed for the detection of bulk explosive and those designed for residues. The first class seeks explosive materials by searching for the mass of explosive material within a device, either sealed away or in a bulk which does not readily release molecules. Typical techniques utilized for bulk sensing are X-ray techniques, neutron or $\gamma$-based sensors, and terahertz imaging. X-ray techniques use the fact that materials absorb and scatter X-rays differently depending upon the material density or chemical composition. When calibrated properly a film or detector can produce images as the X-rays pass through or are backscattered from the material from which explosive signatures can be inferred\(^25\). Similar to the concept of the X-ray technique, the neutron or $\gamma$-based techniques use the same transmission or backscattering to identify explosives. Although X-rays, the neutron\(^26\) and $\gamma$-based\(^27\) techniques use different excitation techniques, they all rely on computed tomography in order to synthesize an image of the irradiated object.

Terahertz (THz) detection\(^28\) offers a safer alternative to X-rays, neutron, and $\gamma$-based techniques, as the radiation poses either none or minimal health risks to either scanner or those being scanned\(^29\)-\(^31\). The terahertz radiation is readily transmitted through most non-metallic and non-polar mediums, allowing for the probing of dangerous materials through concealing barriers such as corrugated cardboard, clothing, shoes, book bags, etc. Although metals completely block or reflect THz waves, the reflectivity can be calibrated and measured, allowing for the detection of materials of interest\(^32\). Many materials of interest such as explosives, chemical agent, and
biological have characteristic THz signatures that make them easily identifiable from benign objects.

While bulk sensors have their place in the sensing of explosives, it is the trace explosive sensors upon which emphasis has been placed (where trace can be defined as milligrams of a substance\textsuperscript{33, 34}). Current techniques utilized for sensing and detection of trace explosive signatures include biosensors, amplifying fluorescence polymers, and spectroscopic techniques. Biosensors are either mammalian (such as dogs and rats), or insectisoid (such as bees\textsuperscript{35} and wasps\textsuperscript{36}) which have been routinely trained to sense and detect explosive aromas and vapors. While offering immediate results, there are several disadvantages to utilizing biosensors in a hazardous environment. For example, when using dogs to detect explosives, approaching a hidden explosive device puts both animal and handler in danger. In addition, dogs and rats can be thrown off a scent due to aromas such as food and sexual stimulations being present in the environment\textsuperscript{37}. Training due to scent is further complicated as explosives of all types vary dependent on their place of origin. For example, TNT manufactured in the United States of America (USA), is different from TNT manufactured in China or Canada, and it is difficult to obtain any information as most explosives are made under conditions of secrecy and no figure of output is published\textsuperscript{38}. Bees and wasps have shown promise in detection of explosives, being too small to actuate any explosive such as mines, but experience in domesticating insects is still forthcoming\textsuperscript{39}. As a chemical alternative to biosensors, Amplifying Fluorescence Polymers (AFP) have been developed.

AFPs are materials designed to fluoresce in the presence of ultraviolet light unless a nitroaromatic explosive compound is present. These polymers are designed to have a long chain with as many bonding sites as molecules forming the chain, and only one nitroaromatic molecule
is necessary to induce quenching of the entire chain hence appellation of “amplifying.”

Each of the polymer compounds, known as a chemophore, has an affinity for a particular class of analytes, and work is currently being done in order to combine the compounds in order to have a multiple sensor.

The last technique mentioned, spectroscopy, is utilized with the absorption, emission or scattering of electromagnetic radiation by atoms or molecules. Spectroscopic techniques are very diverse and offer a variety of excitation sources and means of detection. Unlike the methods of detection mentioned above, spectroscopic techniques can easily be used for detecting many substances. Each of the techniques has certain advantages and disadvantages but it is spectroscopic techniques that have the potential of developing a sensor capable of real-time sensing and analysis of multiple energetic compounds in a stand-off configuration.

1.3 Atomic Spectroscopy

Spectroscopic techniques have been employed to study the quantitative and qualitative elemental composition in many types of samples including but not limited to agricultural, chemical, environmental, geology, industrial, etc. Atomic spectroscopy can be separated into three closely related but separate components: atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), and atomic fluorescence spectrometry (AFS). Atomic absorption spectroscopy is based upon measuring the radiation absorbed by an atom. Atomic emission spectroscopy is based upon the observation of the emission from an atom excited by the absorption of energy as heat or as chemical energy; where emission spectroscopy can be defined as the measurement of the light emitted from flames or plasmas by chemical species. Atomic
fluorescence spectroscopy is based upon the re-emission of radiation from atoms which have absorbed light\textsuperscript{44}. The three spectroscopy techniques are illustrated below in Figure 1.

where the horizontal lines represent different energy levels in an atom. |E\textsubscript{o}\rangle denotes the lowest energy level in the atom (ground state of energy E\textsubscript{o}), and |E\textsubscript{i}\rangle, |E\textsubscript{j}\rangle, and |E\textsubscript{f}\rangle refer to other energy levels, where |E\textsubscript{j}\rangle and |E\textsubscript{f}\rangle are higher energies than |E\textsubscript{i}\rangle. A solid vertical represents either a transition involving the absorption or an emission of radiation as energy, whereas a wavy line represents a non-radiative transition.

The age of atomic spectroscopy is generally considered to have begun with Isaac Newton’s description of the visible spectrum in 1666\textsuperscript{45}. But it was not until 1802, however, that major steps into spectroscopy were taken with Wollaston’s report\textsuperscript{46} that the spectrum of the sun was composed of dark lines or bands. Fraunhofer\textsuperscript{47} was not only able to resolve the wavelengths of the dark lines and bands in 1823, but also determine their origin. Also in 1823, J. F. Herschel
published the first pictures of emission spectra. Both he and W.H.F Talbot\textsuperscript{48} were credited with using alcohol flames to detect the presence of certain substances.

In 1860, Bunsen and Kirchoff were credited with the discovery of atomic emission lines, by observing that colors imparted to a flame by metallic salts were very specific\textsuperscript{49}. However, it was their discovery and chemical isolation of the elements cesium and rubidium that many scientists credit Bunsen and Kirchoff as the founders of modern analytical spectroscopy. It was not until the beginning of the twentieth century, that atomic fluorescence was discovered by Wood\textsuperscript{50}.

Due to the discovery of the laser in the 1960’s, AES really became a forerunner in the spectroscopic field, as the intense laser output beam could be used to excite material into a state of optical emission\textsuperscript{51, 52} and to ionize material suitable for mass spectrometry\textsuperscript{53-55}. In the mid-1970s, the development of laser plasmas sources helped to further the progress of AES techniques. With the higher temperatures offered by these plasmas, AES was able to develop multi-element analytic capabilities.

\section*{1.4 Atomic Emission Spectroscopy Techniques}

Due to the minimal instrumentation necessary to conduct experiments, AES techniques are often preferred over other mass analysis techniques for elemental analysis that does not necessitate low limits of detection. There are a variety of excitation sources that can be used in AES, each with its own strengths and weaknesses, and thus certain excitation sources may be better suited for particular applications.
1.4.1 Flame Emission Spectroscopy

Flames were the original excitation source of AES, and can be dated back to the studies conducted by Herschel and Talbot. In addition, the work done by Kirchoff and Bunsen were fundamental in establishing this atomic excitation technique. However, in terms of modern usage it was Lundegardh’s work conducted in 1934 that gave principal impetus to flame excitation. In his work, Lundegardh used photographic recording of spectra and measured the optical densities of selected analytical lines to relative accuracies of about 5-7%. It was his extensive report that laid the foundation for rapid, accurate analyses of trace element constituents in biological samples. Following Lundegardh, who used a prism spectrograph to disperse the spectra excited by the flame, Barnes in 1945, was the first in the United States to produce a flame photometer, which used filters instead of a prism or grating. The flame photometer which coupled flame excitation methods with simple read-out devices provided high sensitivity and high reliability for the determination of the alkali metals in a simple liquid system. Examples of sensitivities for alkali metals are found below in Table 1.

Table 1: Detection limits in µg/ml in aqueous solution measured in nitrous oxide-acetylene or air acetylene premixed flames.  

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (Å)</th>
<th>N2O-C2H2</th>
<th>Air-C2H2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>6706.8</td>
<td>0.00003</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>5890</td>
<td></td>
<td>0.0005</td>
</tr>
<tr>
<td>K</td>
<td>7664.9</td>
<td></td>
<td>0.0005</td>
</tr>
<tr>
<td>Rb</td>
<td>7800.2</td>
<td></td>
<td>0.001</td>
</tr>
</tbody>
</table>
In flame spectroscopy, premixed gases are heated to ignition temperatures in the preheating zone, which is surrounded by the primary reaction zone. Although many the most energetic reactions take place in the primary zone, the zone is too thin to allow for the establishment of thermodynamic equilibrium, and the partially combusted gases and flame radicals (e.g. OH*, H*, C2*, CH*, and CN*) which propagate the flame pass into the interconal zone. It is in the interconal zone that equilibrium is established as the radicals combine, and it is usually considered the hottest part of the flame. Finally, in the secondary zone called the diffusion zone, the final flame products are produced when the hot, partly combusted gases come into contact with oxygen from the air. Typical flame temperatures can range between 2200-3200 °K48.

Flame emission spectroscopy was widely used until the 1920s when discharge techniques were developed. While still considered useful for specific applications such as for sodium and potassium measurements in blood59, it has been surpassed by plasmas45.
1.4.2 Arc and Spark Excitation

Arc and spark sources, have been popular as AES excitation sources since the 1920s, with many developments occurring in the late 1930s through the late 1940s\textsuperscript{45}. These sources were preferred due to their ability to identify most elements in the periodic table directly in solids, primarily on a semi-quantitative and qualitative basis. This made them preferable over flame emission, as the flames were not hot enough to cause emission from many elements\textsuperscript{60}. There were two forms of arcs that were commonly used as excitation sources for spectrochemical emission analysis, the direct current arc (DC) and the alternating current arc (AC).

Arcs can be defined as continuous electrical discharges of high energy between two electrodes. In the case of the DC arc, the sample is either packed into an anode electrode, or the sample, in the case of a metal, actually plays the role of the anode.

![Figure 3: Circuit diagram of a DC arc power supply (left) and AC arc power supply (right).](image)

Other than the electrodes, the rest of the equipment necessary for DC arcs is simple, requiring only a DC voltage source of 100-150 V at 5-30 A and a ballast resistor (Figure 3 (left)). The resistor was necessary to help stabilize and adjust the arc current which controlled the temperatures ranging between 4000-8000 °C of the DC arcs\textsuperscript{48}. Unfortunately, DC arcs are subject to considerable wandering of the electrode spots resulting in a poor reproducibility/precision, as
well as selective volatilization of the sample into the arc. However, even with these shortcomings, the DC arc is very sensitive and capable of detecting very low concentration levels due to the relatively large amounts of sample that is excited, and while the resulting spectrum primarily contained atomic lines, it was possible to observe some ion lines.

If an alternating current replaces the DC voltage source (Figure 3 right), the reproducibility/precision increases, but the sensitivity or detectability decreases as relatively smaller amounts of sample are vaporized and the signal-to-noise decreases. Also unlike the DC arcs, AC arcs are not subject to selective volatilization, but if the gap distance is not kept constant variations in line intensities occur. The discharge of an AC arc is considered to be more uniform or stable than the DC arc as its polarity reverses 120 times per second (for a 60 Hz source). However, higher potentials of 2000-3000 V at currents of 3-6 A are necessary in comparison with the DC arcs. While DC arcs are useful for sampling metals and organics, AC arcs are primarily utilized for liquid samples as the samples could be evaporated on the flat ends of the electrodes.

The electric spark excitation source can be considered as higher voltage AC arc source. In this case an electric spark is an electrical discharge across a gap between electrical conductors caused by a high potential difference typically between 10,000-50,000 V across the gap. The required voltage depends on the gap dimensions and the shapes of the electrodes (Figure 4).
For the spark to occur the capacitor has to be charged and discharged on each half-cycle to the voltage. With sufficiently high values of inductance and capacitance the spectra obtained from the spark appears more arc-like\textsuperscript{48}.

In general AC sparks have similar behaviour to the AC arcs in that they too have higher precision at the cost of sensitivity than DC arcs. This shortcoming, however, can be overcome using a method devised by Feussner\textsuperscript{61}, which yields a more stable and steady discharge from the spark, resulting in a highly reproducible consistent spectra with excellent analytical precision.

1.5  **Plasma Excitation Sources for Atomic Emission Spectroscopy**

The arc and spark excitation techniques were commonly used until development of plasma sources. The flame, arc, and spark excitation even when modified still suffered from poor stability, low reproducibility, and substantial matrix effects, in comparison with the plasma excitation sources\textsuperscript{62}. Plasma is defined as a partially ionized gas, which remains macroscopically neutral, and is a good conductor of electricity\textsuperscript{62}. When the sample is introduced into a plasma
source, it is evaporated and dissociated into free atoms similar to the arc and sparks, however, additional energy is supplied which results in exciting the free atoms and ions to higher energy states. In comparison with flames that reach temperatures up to 3200 °K, plasma sources temperatures are typically on the order of 8000 °K\textsuperscript{44}.

There are three dominant types of plasma sources utilized for atomic emission spectroscopy in use today: Inductively coupled plasmas (ICP), Direct current plasmas (DCP), and Microwave induced plasmas (MIP).

1.5.1 Inductively Coupled Plasmas

While different plasma sources have been developed, the most common plasma source, known as the inductively coupled plasma (ICP) was developed in the mid-1960s by two groups: Fassel and co-workers at Iowa State University, as well as Greenfield and co-workers at Albright and Wilson, Ltd. in England.\textsuperscript{45} Often utilized in a torch assembly (shown below in Figure 5) ICP excitation is usually preferred for applications due to the high temperature, long residence times, presence of little-to-no molecular species, optical thinness, and few ionization interferences.\textsuperscript{63, 64}
The excitation is generated from the coupling of a radiofrequency generator, which is normally supplied at a frequency of 27.12 MHz and delivers a power between 500-2,000 W, into a suitable gas via a magnetic field. The magnetic field can be induced through a two or three turn water-cooled copper coil. When seed electrons and ions are introduced into the gas, usually by a spark, the electrons are accelerated in the magnetic field and reach energies sufficient to ionize the gaseous atoms in the field. The plasma becomes self-sustaining as subsequent collisions with
other gaseous atoms in the field causing further ionization, and the sample as an aerosol is introduced at the center of the torch’s base through an inner tube. The hottest part of the ICP torch is between 8,000-10,000 °K, with the analytical part in the tail flame reaching temperatures ranging between 5,000-6,000 °K. A comparison of the detection limits of flame AES (which is particularly sensitive for alkali metals) and ICP-AES is shown below in Table 2.

Table 2: Instrumental detection limits (µg/l) attainable with flame AES and ICP-AES.

<table>
<thead>
<tr>
<th>Element</th>
<th>Flame AES</th>
<th>ICP-AES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Ba</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>In</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>K</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Na</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Sr</td>
<td>2</td>
<td>0.2</td>
</tr>
<tr>
<td>V</td>
<td>40</td>
<td>2</td>
</tr>
</tbody>
</table>

1.5.2 Direct Current Plasmas

A lesser known excitation source is that of direct current plasma (DCP). The stabilized DC arc plasmas form a heterogeneous group of plasma excitation sources, and greatly vary in their construction ranging from the conventional DC arc to the free burning flame-like plasmas. DCP has been shown to be particularly stable in the presence of samples, which contain high proportion of dissolved solids, but the analytical performance characteristics, in general, are considered to be slightly inferior to ICP, as fewer strong ion lines are observed. Currently, DC plasmas are divided into two groups which describe how the discharge is transferred away from
the arc column: current carrying DC plasmas, and current free DC plasmas also called plasma jets\textsuperscript{62}.

In current carrying DCPs, plasmas are capable of reaching temperatures above 5,000 °K. A modern plasma jet shown below in Figure 6 is divided into three electrode devices.

![Figure 6: Diagram of a three-electrode DC plasma jet.](image)

The plasma is sustained by the two DC arc-paths that discharge from the cathode constructed of tungsten to the two anodes constructed from graphite. This allows temperatures in the middle plasma jet to reach upwards of 10,000 °K, but in the viewing zone the temperature remains fairly constant in the range of 5,000-6,000 °K.

### 1.5.3 Microwave Induced Plasmas

As technology continues to improve, so do the excitation methods for AES and a more recent excitation source is that of microwave-induced plasma (MIP). Utilized the least in AES, MIP is an attractive source thanks to its low power requirements (a few hundreds of Watts or less) and simplicity in its system operated at atmospheric conditions in comparison with other
plasmas. MIP however, falls short in the fact that it will not tolerate solvents, is easily extinguished, and the detection limits are generally larger than ICP.\textsuperscript{45} A diagram of a microwave induced plasma source is shown below in Figure 7.

![Diagram of a microwave induced plasma source.](image)

Figure 7: Diagram of a microwave induced plasma source.

A major leap forward in the excitation sources of AES was made with the discovery of the laser. It was found that by focusing a powerful laser on a sample, elemental analysis could be done on the emission from the resulting plasma without assistance of an external field\textsuperscript{52}. This laser induced plasma excitation source was found to offer several unique advantages over the conventional methods of AES.
1.6 Laser Induced Plasma Optical Emission Spectroscopy

Since the 1960s, soon after the creation of the ruby laser\textsuperscript{66}, it was recognized that the intense laser pulse could not only be used to excite material into a state of optical emission\textsuperscript{67, 68}, but also to ionize a material for mass analysis\textsuperscript{51}. It was subsequently realized that during the laser ablation process, a laser plasma occurred\textsuperscript{51}. Further investigation into the laser ablation process revealed that if a single pulse of short enough duration and high enough focused power density was used, an optically induced plasma would form at the sample surface. It was found that the plasma light collected from the excited sample could be both spectrally and temporally resolved in order to yield both qualitative and quantitative information about the constituent elements allowed for and that this plasma, itself, could be used as an excitation source\textsuperscript{69}. Hence the laser induced plasma (LIP) was proposed as yet another source for atomic emission spectroscopy.

The LIP-AES was used a sampling method in conjunction with the electrode-generated spark due to its laser ablation properties which provided micro-sampling capabilities\textsuperscript{51}. Later renamed Laser Induced Breakdown Spectroscopy to more accurately reflect the process occurring and for the fact that LIPS was not useable in a database. Still considered to be an AES technique, LIBS was seen as an extension of the aforementioned excitation and vaporization schemes but to the optical frequencies\textsuperscript{70}. However, before LIBS could be fully explored as an analytical technique it was relegated to a mere scientific curiosity used to explore the fundamental characteristics of the laser plasma, due to the development of high-performance laboratory-based elemental analysis methods such as inductively-coupled plasmas (ICP)\textsuperscript{64}.

Recently, a renewed interest in LIBS as an analytical technique has occurred for several reasons. The first is the need for a new method of analyzing materials under conditions or in
areas that are currently not possible by contemporary analytical methods. As with other AES techniques, LIBS has the ability to simultaneously analyze multiple elements with good sensitivity. However, unlike the other sources, only optical access to the sample is necessary and thus LIBS offers the possibility of remote stand-off detection. Coupled with the ability to be combined with other methods of analysis such as mass analysis as well as use other power sources to enhance detection capabilities, LIBS is truly a versatile technique.

Progress made in the fields of lasers, spectrometers, and detectors is another reason for renewed interest in LIBS. Over the past ten years, there have been significant improvement to the instrumentation necessary to perform LIBS. With the advent of spectrometers with gated detectors it has become possible to temporally resolve the LIBS spectrum, reducing the complexity for the optimization of the detection. During early times in the plasma development, the LIBS spectrum is dominated by ionized atomic lines similar to other high temperature AES plasma excitation sources. The mid-life of LIBS emission is dominated by neutral atomic lines characteristic of lower temperature AES techniques, and during the latter times the spectrum is dominated by signatures from the formation of molecular radical.

In addition improvements have also been made to the ruggedness and compactness of LIBS systems. This has allowed LIBS to move outside of the laboratory and into real world applications. With this mobility in the real world, LIBS may be a solution to the sensing communities search for a technique that can be used for direct sampling with minimal sample preparation in a hostile environment. This is important to various services industries, for instance first responders who may have to enter hazardous areas. Being able to perform analysis of the hazardous environment from afar, would serve as a method of keeping the first responders safe.
1.7 Motivations and Strategies

If LIBS could be used to identify materials such as explosives and other hazardous materials in remote and real-time conditions it would be greatly beneficial to society in general. In order to compete with existing technologies such as ICP, the detection level of LIBS must be improved. LIBS is at an inherent disadvantage (as is any in situ system) as it does not ingest the molecules; hence there is no means of concentrating the sample for sensing, and thus greater sensitivities are necessary to produce comparable results\textsuperscript{25}. Thus if the resulting LIBS signature and/or the analysis from the spectrum can take into account potential interferents it may be possible to improve the limits of detection of the LIBS technique.

Since the laser induced plasma acts as both the sampling source and excitation source, the LIBS signature is dependent on the specific laser, the sample parameters, and the experimental atmosphere surrounding the sample. This makes it hard to distinguish whether the resulting plasma is representative of the sample, the surrounding atmosphere or both based on the amount of actual sample or analyte detected in the plasma. This issue is further complicated when using LIBS which is an atomic process to interrogate a sample that is comprised of the same elements as its surrounding environment. A possible solution to this problem is to surround the sample with a buffer gas that is heavier than air (i.e. argon) in order to suppress the recombination; hence any molecular bands that appear could be attributed to just the sample.

Most explosive fuels are organic in nature, and thus contain the same elements found in air. Due to the ambiguous nature of the emitters in an organic sample, the issue of whether or not the composition resulting from the emission of the plasma in LIBS is truly representative of the
analyzed sample must be addressed. This means that it is necessary to determine whether the interaction with the ambient background has distorted the data.

Utilizing just the atomic lines in the LIBS spectrum would make deciphering organic signatures from the signature of the surrounding atmosphere very problematic. However, if the molecular signature which has been shown to be evident in the LIBS spectrum\textsuperscript{52} can be used, it may be used to help discriminate organic compounds from not only the surrounding atmosphere but from each other further enhancing the detection of LIBS\textsuperscript{74}. While the molecular signature would be simple to analyze with a molecular spectroscopy technique such as Raman spectroscopy, which observes the scattering of light as it passes through a material medium and is particularly suited for molecules and crystals, but it would be useful to know if an optical emission technique such as LIBS can provide information on this molecular structure. Thus a better understanding of the relevant processes which are responsible for the LIBS signature and their relationships with different system parameters is needed to help with the improvement of LIBS as an analytical tool.

LIBS can be improved by systematically assembling a comprehensive understanding of all the physical and chemical processes that can occur in pulsed laser interactions with matter in an ambient gas environment. Through the aid of specific experiments a model can be developed that describes relevant processes needed to characterize the LIBS plasma. In fact a complete model will describe many facets of the laser-matter interaction, plasma formation and dynamics, radiative, atomic, and molecular processes, and spectroscopic emission over a broad range of laser irradiation and target scenarios. From both the experiments and the subsequent modeling, a better control of the current LIBS technique will be gained and the possibility of new and more powerful methods for spectro-chemical analysis may be introduced.
1.8 Overview of Thesis

This thesis investigates the potential of using LIBS as field-ready analytical technique for the sensing and detection of trace organic signatures. After a short overview of the fundamental physics behind the technique (Chapter 2), the current state of applications of LIBS to organic analysis, furthermore in a residual form, will serve as a base for this thesis (Chapter 3).

The experimental conditions and data analysis for the performance of LIBS during this thesis will be given in detail (Chapter 4) before entering in the core of the study. As such it was necessary to try and simulate the extreme testing conditions that would be similar to those found in the field. This was accomplished by utilizing residue signatures, or small localized random trace amounts of specific organic materials deposited on organic or non-metallic surfaces as samples. In addition, because of the limited amount of analyte it was necessary to perform these studies in a single shot regime, meaning any relevant identifying signal had to be captured in a single laser shot. Under such conditions, it was necessary to determine the parameters needed in order to optimize single shot signal collection, as well as identify any potential problems that may hinder the technique (Chapter 5).

In addition, to the sampling and detection, a limit was placed on the amount of time given to discrimination and identification of the organic residue. Real time analysis is essential for any field-portable technique, and thus methods of rapid discrimination and analysis were explored. In this study, data analysis techniques developed in analytical chemistry and image processing, known as chemometrics, were adapted and used for data reduction and interpretation. While not completed in this thesis, refined chemometric algorithms could be used in order to satisfy the
rapid analysis criterion. In addition another chemometric technique, ‘target factor analysis’, was explored as a classification technique for known organic material (Chapter 6).

Lastly, an exploration of organic aqueous solutions by LIBS was conducted. In this method, the laser interacts with a single mass-limited microscopic droplet of organic materials diluted into liquid solvent. This approach controlled many complicated substrate matrix effects, and allowed for the plasma interaction with a fixed mass sample that is completely evaporated/ionized by each laser pulse to be studied. Plasma parameters such as the temperature and density, as they characterize the plasma, were then compared with an one-dimensional model predictions generated by a 1-D model of plasma hydrodynamics (Chapter 7). In this manner a better understanding of the LIBS interaction regime could be gained.
2 PHYSICS OF LASER INDUCED BREAKDOWN SPECTROSCOPY

2.1 Introduction

The main principle of the LIBS technique is the creation of plasma, by a laser pulse containing the chemical compounds which characterize the solid target for emission spectroscopy measurements. As such, LIBS unites many different physical, chemical, and hydrodynamic processes. The processes include but are not limited to:

- Interaction of the laser energy flux with the target material, in which the laser energy is converted to thermal and kinetic energy of the species
- Ablation of the target material
- Plume formation of the ablated material
- Laser-plasma interaction (ex: inverse Bremsstrahlung and multi-photon ionization)
- Formation of shockwaves and plume expansion
- Reactions in the plume (ex: recombination, radiation processes, etc.)
- Plasma radiation and cooling

In this chapter discussion of different processes involved in the creation, propagation, and emission of the LIBS plume which determines the LIBS signal will be focused on from a physical perspective.

2.2 Parameters of Plasma for LIBS

Coined as the fourth state of matter, plasmas have unique physical properties distinct from solids, liquids, and gases. The name “plasma” was introduced into physics in the 1920s to describe a conducting gas, where the charged particles in the gas were the results of the
detachment of electrons from the constituent atoms or molecules\textsuperscript{75}. Thus the plasma can be characterized by the number densities of electrons ($n_e$) and atoms ($n_a$), the energy and velocity of the constituents characterized by their temperature ($T$). Common types of plasmas and plasma sources found in the laboratory are shown below in Figure 8.

As shown in Figure 8, LIBS plasmas are classified as weakly ionized and low temperature. LIBS plasmas are categorized as weakly ionized because they are typically less than 10\% ionized at the earliest observable time\textsuperscript{76}. The emission generated from the excited species in the LIBS plasma is attributed to the high temperature processes that occur in the plasma. From a chemistry standpoint, these processes are considered reactions of the gas-phase species emitted by the sample material and their interaction with the species of buffer gas or atmosphere\textsuperscript{77}. At
later times there is often the presence of atoms and radicals in the plasma due to the low temperature ($\leq 1$ eV). LIBS plasmas typically range in density from $10^{16} - 10^{20}$ cm$^{-3}$ and can reach temperatures upwards of a few electron-volts (eV) shortly after plasma initiation.

The temperature and density of the LIBS plasma are spread over a large range because of the numerous excitation sources that are available for use in LIBS applications. Due to the simplicity of just needing to focus down a laser to overcome a breakdown threshold, many commercially available laser systems have been used to create and study LIBS plasmas. These lasers vary in lasing media (KrF excimer lasers to solid-state lasers such as Nd:YAG and Nd:Glass), wavelength, pulse duration, and pulse energies $^{71}$. Theory and experiments have shown that at the earliest time of measurement (dependent on the signal to background ratio for the line emission to be distinct from the continuum) usually during the nanosecond laser ablation period, electron densities can be as large as $10^{20}$ cm$^{-3}$ with electron temperatures on the order of 3-4 eV (~34,800 - 46,400 K) $^{73, 78}$. However, LIBS plasmas are often measured a few microseconds after the plasma formation. This allows for the plasma to be considered in local thermodynamic equilibrium (LTE) conditions, the plasma being under recombination conditions. In this regime, densities can range between $10^{15} - 10^{18}$ cm$^{-3}$ and temperatures lie in the range 0.5 – 2.0 eV. $^{73}$

### 2.3 Laser Ablation and Vapor Gas

Laser ablation or the process of removing material from a target is a very complex process, but can generally be broken down into two successive stages. The first stage consists of the laser absorption of the target material which results in the excitation of the material characterized by a rise of temperature of its electrons and/or its atoms/molecules. The following
stage is the material removal and occurs typically when the temperature reaches the critical vaporization temperature causing ablation to occur and the ejected material to be vaporized, which initiates the formation of a plasma plume above the target surface. Before introducing the methods of laser interaction with the target material it is best to introduce the heat transfer equation.

The amount of energy that is transported into the target, assuming that: 1) the thermalization within the electron subsystem is negligible compared to the laser pulse duration and 2) the electron and the lattice subsystems can be characterized by their temperatures \( T_e \) and \( T_i \), can be described by the following one-dimensional, two-stream (or temperature) diffusion model\(^7^9\), \(^8^0\):

\[
C_e \left( \frac{\partial T_e}{\partial t} \right) = -\frac{\partial Q(z)}{\partial z} - \gamma (T_e - T_i) + S(z, t) \tag{2.3.1}
\]

\[
C_i \left( \frac{\partial T_i}{\partial t} \right) = \gamma (T_e - T_i) \tag{2.3.2}
\]

\[
Q(z) = -k_e \left( \frac{\partial T_e}{\partial z} \right) \tag{2.3.3}
\]

where \( C_e \) and \( C_i \) are the volumetric heat capacities of the electron and lattice subsystems, \( z \) the direction perpendicular to the target surface, \( Q(z) \) is the heat flux, \( S \) is the laser heating source term, \( \gamma \) is the parameter which characterizes the electron-lattice coupling, \( k_e \) is the electron thermal conductivity, respectively. It should be noted that for simplicity, the thermal conductivity in the lattice subsystem has been neglected in the above equations because the
lattice heat capacity is much greater than the electronic heat capacity, allowing the electrons to be heated to very high transient temperatures\textsuperscript{81}. The above equations have three characteristic time scales: $\tau_e$ is the electron cooling time, $\tau_i$ is the lattice heating time ($\tau_e \ll \tau_i$), and $\tau_l$ is the duration of the laser pulse\textsuperscript{81}.

$$\tau_e = \frac{C_e}{\gamma} \quad (2.3.4)$$

$$\tau_i = \frac{C_i}{\gamma} \quad (2.3.5)$$

These timescales define the different regimes of the laser material interaction, of which the focus is placed upon the nanosecond and femtosecond regimes.

### 2.3.1 Laser Heating

The laser heating source term $S$, can be further defined as\textsuperscript{82}:

$$S(z, t) = I_0(1 - R)q(t)\alpha \exp (-\alpha z) \quad (2.3.6)$$

where $I_0(1-R)$ is the (maximum) laser-light intensity that is not reflected from the surface located at $z=0$, and $R$ being temperature and wavelength-dependent. It should be noted that the reflectivity is also affected by the angle of incidence, the polarization of the laser beam, and the thickness of the sample of interest\textsuperscript{82}. The $q(t)$ represents temporal dependence or pulse width. The attenuation factor represented by $\alpha \exp(-\alpha z)$, denotes the absorption. If $\alpha$ is dependent on the temperature and the wavelength, then the laser-light irradiation of the sample causes the optical properties of the material to become inhomogeneous due to the temperature dependency.
2.3.2 Laser Light Coupling

When the laser radiation is incident on the surface of a material, some of the laser radiation is reflected, while the rest penetrates into the volume and is absorbed by the material. This leads to an excitation of the electrons which in some cases leads to melting and eventually evaporation, while in other cases it may lead straight to vaporization.

Primary interactions between light and matter are always considered to be non-thermal. In general, light couples with different states of matter by elementary excitations. In solids, this results in different types of electronic excitations i.e. inter and intraband excitations, excitons, etc., as well as the excitation of phonons, polaritons and magnons to name a few. In liquids and gases, light can induce electronic, vibrational, and rotational transitions within a single molecule. In all systems however, anharmonic or higher order multipolar interactions couple the elementary excitations together.

In a high laser irradiance regime (> 10^{8-9} \text{ W cm}^{-2}) often created by nanosecond lasers, high excitation densities are generated by thermal and non-thermal processes; where the time of thermalization is dependent on the laser parameters and the type of material. Typically, however, in metals the time between electron-electron collisions ($\tau_{e-e}$) is of the order of $10^{-14}$ to $10^{-13}$ s, whereas the electron-phonon ($\tau_{e-ph}$) relaxation times are generally two orders of magnitude less. For non-metals the interband electronic excitations times typically range from $10^{-12}$ to $10^{-6}$ s. In a single isolated molecule, the electronic excitation decays within $10^{-14}$ to $10^{-6}$ s, and a typical low excited vibrational level has a lifetime of $10^{-3}$ s.

The excitation and relaxation times mentioned above are significantly altered in the case of even higher laser intensity regimes, such as can be reached by femtosecond lasers. An
example of which is a highly excited vibrational level of a polyatomic molecule which may only have lifetimes ranging from $10^{-13}$ to $10^{-11}$ s\textsuperscript{82}. In addition, in the higher laser intensity regime non-linear optical phenomena such as multi-photon processes become non-negligible.

2.3.2.1 Femtosecond Laser-Coupling Processes

In the femtosecond regime laser irradiances can reach upwards of $10^{15}$ W/cm\textsuperscript{2}. These irradiances translate to a large electric field due to the fact that the laser irradiance, I (W/cm\textsuperscript{2}) is related to the root mean square (rms) value of the electric field strength, E (V/m) by:

$$I = 2.65 \times 10^{-3} < E^2 >$$ (2.3.7)

For example, an irradiance of I = $10^{15}$ W/cm\textsuperscript{2}, E is of the order of $\sim 10^9$ V/cm respectively. Due to the high electric fields generated by the laser it becomes possible for the laser pulse to interact strongly with the free electrons at the surface of a conductor (tunneling ionization), or generate initial electrons via multi-photon ionization (MPI) for insulators. Calculations completed by Zel’dovich and Raizer\textsuperscript{83} have shown that for direct removal of electrons from atoms during the duration of the laser pulse requires electric fields on the order of $10^8$ V/cm. As such, either multi-photon ionization or tunneling ionization is used as the primary means of femtosecond laser electron generation\textsuperscript{84}.

The dominant process that will occur in the femtosecond regime is determined using the Keldysh parameter\textsuperscript{85, 86}, which is a roughly estimated to be the product of the amount of time needed to tunnel through the resulting potential barrier and the period of oscillating electric field:

$$\gamma = \omega \tau = \frac{\omega}{|eE|} \sqrt{mE_g}$$ (2.3.8)
where $\tau$ is the time necessary for tunneling, $\omega$ is the frequency of the oscillating electric field, $E_g$ is the ionization potential of the material, and $m$ and $e$ are the effective mass and charge of the electron, respectively. In the limit at which $\gamma \ll 1$ tunneling ionization plays the dominant excitation mechanism, while in the other limit $\gamma \gg 1$ multi-photon absorption plays the major role\textsuperscript{85}.

Multi-photon ionization involves the simultaneous absorption of a number of photons by an atom or molecule that would cause the ejection of an electron from the valence band to the conduction band or even its ionization (Figure 9).

Multi-photon excitation\textsuperscript{87} is necessary to directly ionize species such as Ti\textsuperscript{+} (6.83 eV) and Al\textsuperscript{+} (5.99 eV) because the ionization energies are often much greater than the energies of the photons that are normally used. Despite the very small cross sections for multi-photon processes, irradiances as small as $10^{10}$ W/cm$^2$ are sufficient enough for weak multi-photon ionization to occur\textsuperscript{88}. 

![Multi-photon Ionization](image.png)
Tunneling ionization occurs when the applied electric field is becomes strong enough to distort the Coulomb field felt by the electron (Figure 10). The Coulomb potential shown below is modified by a stationary electric field such as:

\[ V(x) = -\frac{Ze^2}{x} - e\varepsilon x \]  

(2.3.9)

When \( x >> x_{\text{max}} \) is lower than the binding energy of the electron, then by quantum mechanics the electron may tunnel through the barrier with a finite probability as shown in Figure 10. If the barrier continues to decrease and fall below the \( E_{\text{ion}} \) threshold, then the electron will escape spontaneously. This process is known as barrier suppression (BS) ionization\(^89\).

![Diagram](image)

**Figure 10:** Tunnelling or barrier suppression ionization made possible by a strong external electric field.

The probability for the simple case of hydrogen-like atoms was derived by Keldysh\(^85\) in 1965 and is given by:

\[ \alpha_t = 4 \frac{me^4}{\hbar^3} \left( \frac{E_i}{E_h} \right)^{\frac{5}{2}} \frac{E_a}{E_{\text{L}(t)}} \exp \left[ -\frac{2}{3} \left( \frac{E_i}{E_h} \right)^{\frac{3}{2}} \frac{E_a}{E_{\text{L}(t)}} \right] \]  

(2.3.10)
where $E_i$ and $E_h$, are the ionization potentials of the atom and hydrogen, respectively and $E_a$ and $E_L$ are the atomic electric field and instantaneous laser field, respectively.

2.3.2.2 Nanosecond Laser-Coupling Processes

At longer wavelengths and longer pulse durations it becomes very hard for MPI to furnish initial electrons, hence other laser material interactions are necessary in the nanosecond regime. The first method of electron production is through the photoelectric effect; external for metals and internal for semiconductors and insulators. If the incident photons from the laser have a greater energy than the work function (the binding electron energy) of a material at its surface, the electron absorbing the photon subsequently has enough energy to escape the material. In most cases the photons must be in the visible to UV range in order to guarantee the escape of the electron. For example for electrons to escape from cesium, copper, or platinum a photon of wavelength 639 nm, 277 nm, and 231 nm respectively, is needed.

As mentioned above, the coupling of the light can generate high excitation densities both thermally and non-thermally. A thermal (photothermal) process occurs when the relaxation time of the excitation energy ($\tau_T$) is much smaller than that of the inverse excitation rate ($\tau_R$, approximately the pulse duration), which results in the laser being treated simply as a source of heat. When the overall thermalization of the excitation energy is slow, i.e., $\tau_T \geq \tau_R$, non-thermal (photochemical) processes occur. These photochemical processes can be defined as the chemical reactions of excited molecules that are induced by the laser radiation. The classification between these two phenomena and a third known as photophysical is complex but can be explained using a simple model displayed in Figure 11.
From Figure 11, it should be noted that $\tau_A$ and $\tau_{A^*}$ are the characteristic times for the reactions, while $\tau_T$ is the thermal relaxation time of the non-radiative transition from $A^* \rightarrow A$.

Thermal activation occurs when $\tau_T << \tau_A$, $\tau_{A^*}$ and $\tau_A << \tau_{A^*}$; photochemical activation occurs when $\tau_T > \tau_{A^*}$ and $\tau_{A^*} << \tau_A$; and finally the photophysical activation occurs when $\tau_T << \tau_A$, $\tau_{A^*}$ but $\tau_{A^*} << \tau_A$. From the timing scheme, it becomes evident that the limits of photophysical processes are the thermal and photochemical process. This is appropriate as both the thermal and non-thermal mechanisms directly contribute to photophysical processes.

2.3.3 Laser Ablation

After absorbing the laser light from either a nanosecond or femtosecond laser pulse the thermalization process of the electron subsystem occurs, followed by an energy transfer to the lattice, and heat transfer from the electrons into the target. The main difference between the regimes is that by the point of the electron relaxation the femtosecond pulse has ended before the electrons have relaxed back to the lattice, whereas in the nanosecond regime there is still interaction with the laser pulse. After the electron heating, laser ablation or material ejection
begins to occur when a sufficient electron concentration has been built up. The function of the laser ablation when conducting a chemical analysis, such as LIBS, is to convert a small quantity of mass from a solid sample into its vapor-phase constituents. These constituents, which should represent the exact composition of the solid, are then usually transported to an excitation source. The vapor itself consists of clusters, molecular radicals, atoms, ions, and electrons. However, a concern is raised around the non-stoichiometric generation of vapor, a process called fractionation\textsuperscript{91-93}.

There is significant evidence that fractionation is dependent on laser properties such as pulse duration, energy, and beam diameter, as these properties govern the processes of the underlying the release of the vapor from the solid sample. Russo \textit{et al.}\textsuperscript{94} have demonstrated that using femtosecond laser pulses at 800 nm it is possible that no relative fractionation may occur, but further studies are necessary for UV femtosecond ablation. In the nanosecond regime, the UV nanosecond laser ablation produces a reduced fractionation in comparison with the IR nanosecond regime.

Many studies have been completed comparing the laser ablation of solid targets by femtosecond pulses to nanosecond pulses\textsuperscript{95-97}. Margetic \textit{et al.}\textsuperscript{98}, indicated that in comparison, the ablation threshold is lower for femtosecond lasers pulses than with nanosecond laser pulses. Rudolph \textit{et al.}\textsuperscript{99} went further to show that on a piece of bariumalumoborosilicate glass in air an ablation threshold of 1.6 J/cm\textsuperscript{2} is necessary for a 130 fs pulse at 800 nm, whereas for a 10 ns pulse at 266 nm the ablation threshold was 2.4 J/cm\textsuperscript{2}. 

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2.3.3.1 Nanosecond Ablation Regime

During ablation with ns pulses the condition $\tau_L >> \tau_i$ is fulfilled, and nanosecond laser ablation occurs. In this case, the relaxation time of the materials (ex: $\sim 10^{-13}$ s for metals) is faster than the pulse duration and the absorbed laser energy can be regarded as being instantaneously turned into heat\textsuperscript{100}. The electron and lattice temperatures can be considered equal $T_e = T_l = T$ and Equations (2.3.1 - 2.3.3) reduce to\textsuperscript{81}:

$$C_l \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left( k_o \frac{\partial T}{\partial z} \right) + S(z, t) \quad (2.3.11)$$

where $k_o$ represents the heat diffusion in the lattice. The heating of metal targets by long laser pulses has been the subject of many theoretical and experimental studies\textsuperscript{101,102}. In this regime the absorbed laser energy first heats the metal to its melting point and subsequently to its vaporization temperature. This process occurs due to the fact there is enough time for the thermal wave to propagate into the target material. With enough heat, the breakdown threshold of the material is reached and once overcome results in the creation of a relatively large layer of melted material. With continual heating provided by the absorption of excess laser light the evaporation of the liquid metal begins to occur resulting in vaporization.

2.3.3.2 Femtosecond Ablation Regime

The ultrashort laser ablation regime\textsuperscript{103} occurs when the laser pulse duration is shorter than the electron cooling time $\tau_L << \tau_e$. For time scales much shorter than the electron temperature ($t << \tau_e$) which is equivalent to $C_e T_e / t >> \gamma T_e$, the electron-lattice coupling can be neglected\textsuperscript{81}. In this case Equation 2.3.1 can be solved, but the general solution is quite complex, but by neglecting the electron heat conduction term the equation can be reduced to:
\[ C_e \frac{\partial T_e}{\partial t} = 2 I_a \alpha \exp(-\alpha z) \]  

(2.3.12)

and gives

\[ T_e(z, t) = \left( T_o^2 + \frac{2 I_a \alpha}{c_e} t \exp(-\alpha z) \right)^{1/2} \]  

(2.3.13)

where \( I_a = I_o(1-R) \), and \( T_o = T_e(t=0) \) which is the initial temperature. At the end of the laser pulse the electron temperature is given by:

\[ T_e(\tau_L) \approx \left( \frac{2 F_a \alpha}{c_e} \right)^{1/2} \exp\left( \frac{-z}{\delta} \right) \]  

(2.3.14)

assuming \( T_e(\tau_L) >> T_o \), \( F_a = I_a \tau_L \) is the absorbed laser fluence, and \( \delta = 2/\alpha \) is the skin depth. Due to the energy transfer to the lattice and heat conduction into the bulk material the electrons are rapidly cooled after the laser pulse. The process of the hot electron relaxation dynamics after femtosecond excitation has been intensely studied\(^{104, 105}\). From these studies it has been shown that for fast electron cooling and a considerable energy transfer to the lattice the time scale is of the order of 1 picosecond. Unlike in the nanosecond laser ablation regime, in the femtosecond regime the ablation processes in most cases can then be considered as a direct solid to vapor transition.

### 2.4 Vapor Formation and Plasma Formation

Laser-induced breakdown can be defined as the generation, by the end of the pulse, of a practically totally ionized gas (plasma)\(^87\). Experimentally this is verified by the observation of a glow or flash in the focal region of the laser beam\(^{106, 107}\). Before the ionized gas can be created however, there is a need for initial electrons from which a cascade can be developed. In laser
induced breakdown the main mechanisms that lead to electron generation and growth, are dependent on the laser wavelength and the pulse duration.

2.4.1 Case of Femtosecond Pulses

In the femtosecond regime the ablation process in most cases can be considered as a direct solid to vapor transition. This is due to the large electric field that is introduced to the material by the incoming laser pulse. In the spot where the laser pulse interacts with the material the field is strong enough to ionize the material. The ionization causes the electrons to be expelled from the material leaving only positively charged ions in the material. After the completion of the laser pulse, there is a coulombic explosion, causing the removal of material. This explosion is due to the repulsion of the ions from one another in accordance with Coulomb’s law, as the like ions repel each other.

2.4.2 Absorption of Nanosecond Pulses by the Expanding Plasma

Once an initial electron has been generated the growth of the electron concentration (density) $n_e$, is governed by the following equation continuity equation:

$$\frac{d n_e}{d t} = v_i n_e + W_m I^m n - v_a n_e - v_R n_e + \nabla(\nabla n_e) + IBA$$  \hfill (2.4.1)

where $W_m$ is the multiphoton ionization rate coefficient and $m$ is the number of photons that have to be absorbed simultaneously in order to ionize the gas, $v_i$ is the impact ionization, and $v_a$, $v_R$ are the losses due to electron attachment, and recombination rates respectively, $D$ the diffusion coefficient for electrons, and $IBA$ is the inverse Bremsstrahlung absorption term. The total
impact ionization in the case of laser-induced breakdown is the sum of the ionization frequency due to single-impact collisions between electrons and atoms, and the photoionization frequency due to electron impact excitation to the first excited state followed by photoionization\textsuperscript{108}.

Nanosecond systems usually provide irradiances from $10^8$ to $10^{10}$ W/cm\textsuperscript{2}, and the electron generation is attributed to two different photon absorption processes: inverse Bremsstrahlung absorption, and photo-ionization. The inverse Bremsstrahlung absorption process is more prevalent when the excitation wavelength is in the infrared as opposed to the ultraviolet for photo-ionization. In the inverse Bremsstrahlung absorption process, the free electrons gain kinetic energy ($E_k$) from both the incoming laser beam, and from collisions with sample atoms, sample ions, gas atoms, and gas ions\textsuperscript{109}:

$$e^- e_k + i + \gamma \rightarrow i + e^- e_{k'} > E_k$$ (2.4.2)

where $e^-$ denotes a free electron, $i$ is an ion state, and $\gamma$ is the photon. At early times of the laser absorption process, IBA, is usually driven by collisions between electrons and neutral atoms; as the absorption process continues and ions become more prevalent collisions between electrons and ions becomes dominant. Electron-electron collisions do not produce radiation in the dipole approximation as the accelerations of the two electrons are equal and opposite\textsuperscript{110}.

The second nanosecond absorption process is the photo-ionization of the excited species. This occurs when the absorption of a photon is associated with the release of a bound electron\textsuperscript{109}:

$$\gamma + i_2 \rightarrow i_1 + e^-$$ (2.4.3)

where $e^-$ denotes a free electron, $i_1$ and $i_2$ are subsequent charge ion states of one element and $\gamma$ is the photon. MPI is usually more important for wavelengths $< 1$ μm, and the electron density
increases linearly with time for a constant irradiance. Both of these processes are followed by an
electron cascade growth.

The electron cascade growth\textsuperscript{11} otherwise known as avalanche ionization occurs when the
rate of electron excitation is much greater than the energy loss by phonon generation. The
electrons become so energetic that they are able to generate secondary electrons through impact
ionization of the atoms/ molecules. This process provides a great accumulation of electrons from
just an initial few.

2.4.3 Plasma Formation

Regardless of the laser ablation process, the material vaporized from the target interacts
with the surrounding atmosphere and exerts a high pressure on the surrounding material. The
generated plasma is dependent on parameters such as: the laser irradiance, the laser wavelength,
the target vapor composition, the size of the vapor plasma bubbles, and the ambient gas
composition and pressure\textsuperscript{72}. The subsequent interaction of the hot vapor with the cooler
surrounding atmosphere creates an intense shock and the wave is driven into the atmosphere via
the expansion of the high-pressure vapor, hence a shockwave as shown in Figure 12. The
shockwave then serves to transfer energy to the surrounding atmosphere by a combination of
thermal conduction, radiative transfer, and heating\textsuperscript{83}.

As the plasma transitions from a confined vapor state into a fully developed propagating
wave, there is the possibility that small clusters or nanoparticles may be included in the plasma.
These particles are capable of altering the basic electrical properties of the plasma, as they may
carry an electric charge. The clusters may also lead to an early decay of the plasma as they may
act as collectors for ions and electrons. Lastly, the emission from the nanoparticles may play a role in the optical properties of the plasma leading to erroneous assumptions and conclusions\textsuperscript{75}.

The forward direction along which the plasma starts to preferentially propagate is due to the strong temperature and pressure gradients in the axial direction as shown in Figure 12, relative to the corresponding lateral direction. Upon leaving the surface the species generate a recoil pressure into the substrate, and as the laser pulse is still present in the nanosecond case, the ablated material will create a shockwave. The resulting vapor plume continues to absorb and scatter the incident laser light thus shielding the substrate.

Figure 12: General shockwave formation along with a plasma and laser radiation profile and a temperature and pressure profile.
2.4.3.1 Shockwaves

The propagating wave and hence the type of plasma can be classified into three groups: 1) laser-supported combustion (LSC) wave, 2) laser-supported detonation (LSD) waves, and 3) laser-supported radiation waves (LSR). The three waves are distinguished by their characteristic velocity, pressure, and effect that the radial expansion has on the evolution of the plasma. The configuration of a general shockwave is shown above in Figure 12 with regions of interest labeled. It should be noted that the radial expansion may or may not affect the propagating absorption based upon the propagation mechanism.

At low laser irradiances typically just above the intensity at which plasma formation begins, laser-supported combustion waves are produced. An example of the LSC wave is shown below in Figure 13.

Figure 13: Laser-support combustion wave formation.
In the LSC wave, there are three separate zones with the shocked gas being separated from the plasma and absorption zone. The incident laser radiation travels through the transparent shocked gas and is absorbed within a large value of the plasma plume, and thus the substrate is shielded from the incident light. As the plasma expands outwards into the shocked gas there is a sharp decrease in the temperature of the plasma. The actual LSC wave is considered to be the front edge of the plasma seen here as the absorption zone, which propagates into the shocked gas region.

Raizer\textsuperscript{112} was the first to study these waves and it was initially assumed that the primary propagation method was that of thermal conduction. However, further studies conducted by both Boni and Su\textsuperscript{113} and Jackson and Nietsen\textsuperscript{114} suggested that radiative transfer could also contribute a role in the propagation\textsuperscript{45}. The main mechanism of propagation however can be attributed to the transfer from the hot plasma to the cool high-pressure gas which is created in the shockwave. The velocity of the wave is relative to the gas in which it propagates but is usually considered to be subsonic, and is often defined by the characteristic velocities of the shock speed, the LSC wave speed, and the velocity of the shocked air\textsuperscript{87}. For spot sizes typically of laser pulsed interactions, the plasma is often optically thick in the extreme ultraviolet spectral range in the radial direction\textsuperscript{87}.

Laser-supported detonation waves are produced with intermediate laser irradiances (I > 10^8 W/cm\textsuperscript{2})\textsuperscript{82}, and are controlled by the absorption of the laser energy. An example of the LSD wave is shown below in the Figure 14.
The ignition and propagation of these waves were originally studied both theoretically and experimentally by several groups Maher et al.\textsuperscript{115}, Sterverding\textsuperscript{116}, Berget’son et al.\textsuperscript{117}, and Weyl et al.\textsuperscript{118}. Due to the precursor shock being sufficiently strong additional heating by energy transport from the plasma is unnecessary as the shocked gas is hot enough to begin absorbing the laser radiation\textsuperscript{45}. The laser absorption zone immediately follows the shockwave and travels at the same velocity, which is analog to a chemical detonation wave which has been modeled by both Ramsden and Savic\textsuperscript{119} and Raizer\textsuperscript{120}. From the pressure profile the highest pressure occurs at the shock, before being significantly absorbed. The temperature profile shows a sharp increase at the shock front, and continues to increase in response to the laser radiation. After the laser
absorption zone there is a decrease in the temperature, unlike in the LSC due to the difference in expansion speed.

In comparison with a LSC wave, the LSD wave moves at approximately twice the speed at the same irradiance, heats up to approximately four thousand times as much mass, and is approximately four times the predicted wave pressure. However, due to the laser heating much more mass, the LSD wave has a lower temperature in comparison with the LSC wave. Lastly, in comparison with the LSC wave the LSD wave is neither an efficient radiator, nor an effective method of transferring the plasma radiation to the surface.

The final laser supported propagation wave is the laser-supported radiation wave which is generated from sufficiently high laser irradiance ($I > 10^9 \text{ W/cm}^2$), and is shown in the Figure 15 below.
Figure 15: Diagram of a laser-supported radiation wave.

The plasma radiation is so hot that ambient gas is heated to temperatures where laser absorption begins prior to the arrival of the shockwave arrival. Ideally, the laser absorption should be initiated without any change to the density, and thus the pressure profile results would solely be from the strong local heating of the gas rather than the propagating shockwave. This was shown by Raizer\textsuperscript{120} to be an example of an overdriven absorption wave. Bergert’son \textit{et al.}\textsuperscript{117}, went further to successfully model these supersonic waves, and numerically confirm that a quasi-steady approximation is suitable for the transient plasma initiation and formation process.

In comparison with LSC and LSD waves, the LSR wave increases more rapidly with laser irradiance, conversely the temperature and pressure increase is quite slow. Although LSR is
named for the plasma radiative transport, the reradiated power is a fraction of the incident laser power and is much less in the LSR wave than the LSC wave. Hence, LSR waves are not energy-efficient sources of radiation.

2.4.3.2 Critical Density

Under the Drude Model of a plasma, the electrons behave as a system with a characteristic frequency, \( \omega_p \), is defined as:

\[
\omega_p = \sqrt{\frac{4\pi n_e e^2}{m_e}}
\]  

(2.4.1)

where \( n_e \) is the electron density, and \( m_e \) and \( e \) are the mass and charge of the electron, respectively. When the laser (at frequency \( \omega_L \)) interacts with the plasma, it is absorbed if its frequency is lower than the plasma frequency but will be reflected if its frequency is higher. At the point where \( \omega_L = \omega_p \) the bulk of the plasma is shielded from further direct interaction from the laser radiation, as the incident electromagnetic wave is completely reflected when \( n_e \) reaches the critical density, \( n_{cr} \), given to be:

\[
n_{cr} = \frac{m_e \omega_p^2}{4\pi e^2} \approx \frac{1.1 \times 10^{21}}{\lambda_{\mu m}} \text{ cm}^{-3}
\]

(2.4.2)

where \( \lambda_{\mu m} \) is the laser wavelength in microns. A table of critical densities for common laser wavelengths is displayed below.
Table 3: Critical densities for common laser wavelengths.

<table>
<thead>
<tr>
<th>Laser</th>
<th>(\lambda) ((\mu)m)</th>
<th>(n_{cr}) (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>10.6</td>
<td>(10^{19})</td>
</tr>
<tr>
<td>Nd: YAG fundamental</td>
<td>1.06</td>
<td>(1 \times 10^{21})</td>
</tr>
<tr>
<td>Ti: Sapphire</td>
<td>0.8</td>
<td>(1.72 \times 10^{21})</td>
</tr>
<tr>
<td>Nd: YAG second harmonic</td>
<td>0.532</td>
<td>(4 \times 10^{21})</td>
</tr>
<tr>
<td>Nd: YAG third harmonic and excimer</td>
<td>0.355</td>
<td>(9 \times 10^{21})</td>
</tr>
<tr>
<td>Nd: YAG fourth harmonic</td>
<td>0.266</td>
<td>(1.55 \times 10^{22})</td>
</tr>
<tr>
<td>KrF</td>
<td>0.248</td>
<td>(1.76 \times 10^{22})</td>
</tr>
</tbody>
</table>

2.5 Plasma Expansion and Processes

The plasma expansion process for both the femtosecond and nanosecond regimes is often described using hydrodynamic theory, which treats the plasma behavior as a continuum fluid. The assumption is justified due to the fact that during the initial stages of expansion the densities are high, but as the plasma expands the density continuously decreases\(^9\). Plasma expansion is described with the Euler equations of hydrodynamics for the conservation of mass density, momentum, and energy are used\(^1\):

\[
\frac{\partial \rho}{\partial t} = -\frac{\partial (\rho v)}{\partial x} \tag{2.5.1}
\]

\[
\frac{\partial (\rho v)}{\partial t} = -\frac{\partial}{\partial x} \left[ p + \rho v^2 \right] \tag{2.5.2}
\]

\[
\frac{\partial}{\partial t} \left[ \rho \left( E_d + \frac{v^2}{2} \right) \right] = -\frac{\partial}{\partial x} \left[ \rho v \left( E_d + \frac{p}{\rho} + \frac{v^2}{2} \right) \right] + \alpha_{IB} I - \varepsilon_{rad} \tag{2.5.3}
\]

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where $\rho$ is the mass density, $v$ is the velocity, $E_d$ is the internal energy density, the product of $I$ and $\alpha_{IB}$ gives the local laser energy absorption by the plasma, $\varepsilon_{rad}$ is the amount of energy in the Bremsstrahlung process, and $p$ is the local pressure based on the ideal gas law.

To solve the complex system of equations [Eqs (2.5.1)-(2.5.3)], it is necessary to consider two additional equations defining, the pressure and the internal energy. Assuming that the evaporated material follows the ideal gas law, the pressure ($p$) and internal energy density ($\rho E$) can be expressed as:

$$p = (1 + x_e) \frac{\rho kT}{m} \quad (2.5.4)$$

and

$$\rho E = \frac{\rho}{m} \left[ \frac{3}{2} (1 + x_e) kT + IP_1 x_{i1} + (IP_1 + IP_2) x_{i2} \right] \quad (2.5.5)$$

where $x_e$ represents the fraction of electrons, $x_{i1}$ and $x_{i2}$ represent the singly charged and doubly charged ions in the vapor, respectively, and $IP_1$ and $IP_2$ represent the first and second ionization potentials of the target material, respectively. As is the case of most models, the underlying assumption that the plasma is a continuum fluid is subject to question at distances far away from the target.

2.5.1 Plasma Processes

Plasmas have helped contribute to the establishment of quantum mechanics through their service as sources of radiation for spectrochemical analysis and atomic structure determination. Laser induced plasmas have various kinetic processes, equilibrium conditions, atomic processes, and molecular processes that affect the emission of radiation from the plasmas.
2.5.1.1 Processes in Population Kinetics

The radiation emitted from plasma is determined by a combination of a large number of physical processes. Many researchers including McWhirter and Hearn\textsuperscript{121}, Salzmann\textsuperscript{122}, and Cowan\textsuperscript{123} to name just a few, have formulated and completed both extensive descriptions and calculations on the various processes that are involved in the dynamics of laboratory plasmas. As such, several general types of processes are considered in the kinetics of plume plasma.

The general processes of importance are: dissociation, recombination, charge transfer, ionization, reactions between neutral species and ions, electron-ion recombination/dissociation reactions, electron attachment-detachament reactions, electron-impact dissociation, radiative decay of electronically excited atoms, electron-impact excitation of species, chemical reactions of excited species, electronic quenching, and thermal activation of excited species both photoabsorption and photoionization\textsuperscript{88}.

Some of the most important processes in laser plasmas are listed below:

Electron-ion recombination in three-body collisions:
\[ 2e + A^+ \rightarrow e + A \] (2.5.6)

Ionization of atoms or molecules by electron impact (collisional ionization):
\[ e + A \rightarrow 2e + A^+ \] (2.5.7)

Photorecombination of an electron and an ion:
\[ e + A^+ \rightarrow A + \hbar \omega \] (2.5.8)

Atomic photoionization:
\[ \hbar \omega + A \rightarrow A^+ + e \] (2.5.9)

Elastic collision of electrons with atoms and molecules:
\[ e + A \rightarrow e + A \] (2.5.10)
Excitation as a result of photon absorption:

\[ \hbar \omega + A \rightarrow A^* \]  \hspace{1cm} (2.5.11)

Spontaneous radiation of an excited atom:

\[ A^* \rightarrow \hbar \omega + A \]  \hspace{1cm} (2.5.12)

Smirnov\textsuperscript{75} gives a more extensive summary of the elementary plume processes that occur in an ionized gas.

2.5.1.2 Plasma Equilibrium

As the plasma expands, there would ideally be a time at which the distribution of energy among the different states of the assembly of particles would be in equilibrium. A temperature, \( T \), can be defined for each particular form of energy, as well as used to define the relation between the neutral and charged particles of different chemical species densities, the light emission, and the absorbance spectra\textsuperscript{76}. Complete thermodynamic equilibrium (TE) for plasma exists when all forms of energy distribution are described by the same temperature. The continuous spectrum generated from this plasma coincides with that of black-body radiation. This results in the TE plasma being optically dense at all radiation wavelengths, resulting in photons that are emitted by one particle are reabsorbed by another, and thus a loss in information about the nature of the elementary emitter.

There is no plasma existing in nature, or in a laboratory that fully satisfies the definition of TE, and thus approximations are adopted to describe the plasma state. LIBS plasmas when characterized by the rate determining mechanism of electron collisions can often be described by a state known as local thermodynamic equilibrium (LTE). For LTE thermodynamics to be valid...
the plasma must be both optically thin and the electronic density requirement $^{124}$ must be high enough to make the electron collisions the primary relaxation process.

$$n_e \geq 9 \times 10^{17} \left( \frac{\Delta E}{E_H} \right)^2 \left( \frac{T_e}{E_H} \right)^{1/2} \text{ cm}^{-3}$$  \hspace{1cm} (2.5.13)

where $\Delta E$ (eV) is the largest interval between adjacent energy levels of the ions, and $T_e$ the temperature is in eV. The most popular condition usually reported in literature to determine if a LIBS plasma is in LTE is the McWhirter criterion $^{125}$:

$$n_e (cm^{-3}) > 1.6 \cdot 10^{12} T^{1/2} (\Delta E_{mn})^3$$  \hspace{1cm} (2.5.14)

where $T$ and $\Delta E_{mn}$ are expressed in K and eV, respectively. However as pointed out by Cristoferetti et al. $^{126}$, that while the McWhirter criterion is necessary for LTE it is not a sufficient condition to insure LTE. McWhirter $^{125}$ originally derived his condition to describe homogenous and stationary plasmas, a requisite which is not met by laser induced plasmas.

Cristoferetti et al. proposed two additional criteria necessary to ensure LTE conditions for time-dependent and inhomogeneous plasmas. The first condition accounts for the transient behavior of the plasma by restricting the temporal variation of the thermodynamics to be small over the times characterizing the establishment of the excitation and ionization equilibrium. The second condition requires the spatial gradient of the temperature and electron density to be larger than the distance travelled by a particle by diffusion during the time of relaxation to equilibrium. If all three of the conditions are met then it can be safely assumed that the plasma is in local thermodynamic equilibrium.
Under LTE conditions, the collision processes are more important than the radiative ones so the non-equilibrium of radiative energy can be neglected, while for every point it is still possible to find a temperature parameter that satisfies the Maxwell distribution $f(v)$, the Boltzmann distribution $(N_k/N_l)$ and the Saha relation $(K(T))$.

$$f(v) = 4\pi \left(\frac{M}{2\pi k_B T}\right)^{3/2} v^2 \exp\left\{-\frac{Mv^2}{2k_B T}\right\}$$  \hspace{1cm} (2.5.15)

where $M$ is the particle mass and $v$ is the velocity.

$$\frac{N_k}{N_l} = \frac{g_k}{g_l} \exp\left\{-\frac{\Delta E_{kl}}{k_B T}\right\}$$  \hspace{1cm} (2.5.16)

where $\Delta E_{kl}$ is the energy difference between the levels $k$ and $l$.

$$K(T) = 2 \left(\frac{2\pi mkT}{\hbar^2}\right)^{3/2} \left(\frac{Z^i}{Z^0}\right) e^{-E_i/kT}$$  \hspace{1cm} (2.5.17)

where $Z^i$ and $Z^0$ are the partition functions of the neutrals and ions, respectively. Thus unlike its TE counterpart, the LTE plasma provides information not only about the temperature, and the densities of the particles.

Measurement studies conducted on LIBS plasmas often assume that the plasma is optically thin and the opacity is not important. These assumptions, which help to satisfy the requirements necessary for LTE, lead to an isotropic expansion of the radiation which is not substantially reabsorbed by the plasma. However, it is possible that the plasma may be optically thick, and the opacity must be taken into account for a better analysis of the plasma, as it is sensitive to the composition, temperature, and spectral composition of the radiation.
Behringer et al.\textsuperscript{128} have shown the influence of the opacity on the emitted radiance of spectral lines, the line intensity ratios, the effective collisional-radiative ionization and recombination rate coefficients, and the changes of the population of the excited states.

2.6 Plasma Radiation and Emission

As the plasma radiates outward from the sample and cools it begins to emit light characteristic of the sample. In atomic systems (atoms, molecules, ions, electron-ion plasmas) photons are absorbed or emitted during electronic transitions from one energy state to another. Excitation occurs when a photon is absorbed by an atom, molecule, etc. and in order to emit a photon an excited atom loses its excitation energy by transferring it to the emitted photon. Figure 16 shows an energy level diagram of the most elementary atomic system consisting of a proton and electron, which in the bound states constitutes the hydrogen.

![Figure 16: Plasma radiation processes.](image)

The zero energy level separates the free and bound states of the electron with the energy in the bound states represented by a negative value and consisting of certain discrete values. In the free
state with positive energy (hydrogen ion) the electron energy can assume any value and the energy spectrum is continuous. All electronic transitions can be divided into three groups using the continuity criterion and they are: i) free-free transitions (bremsstrahlung radiation), ii) free-bound transitions (recombination radiation), and iii) bound-bound transitions (resonance or line radiation). Free-free and bound-free transitions result in continuous emission spectra, while the bound-bound transitions in atoms result in line spectra whereas in molecules they result in the formation of band spectra.

2.6.1 Free-Free Transitions

The free-free transition occurs when a free electron collides with another particle, as shown in Figure 17, but remains free.

![Figure 17: Free electron collides with a positive ion but remains free. The impact factor is represented by b.](image)

In the scattering interaction the electron loses a portion of its kinetic energy and slows down. The decrease in acceleration causes the emission of a photon with energy equal to the lost portion of the kinetic energy. This slowing down or “braking” action is known as Bremsstrahlung radiation.

\[
e^− + E_i + Z \rightarrow e^− + E_f + Z + h\nu_{ff}, \quad h\nu_{ff} = E_i - E_f \quad (2.6.1)
\]
From Figure 16, there appears to be no upper limit to the free electron range. However, from classical scattering theory the change in energy can be measured by the change in velocity:

\[ \Delta v = \frac{Ze^2}{mb^2} \left( \frac{2b}{v} \right) \]  

(2.6.2)

where \( v, m, \) and \( e \) are the electron velocity, mass and charge, respectively, and \( Ze \) is the ion charge. The maximum impact factor is approximately the electron Debye length\(^{129}\), whereas the minimum is the larger of either the DeBroglie wavelength of the electron or the classical distance of closest approach \( (b_{\text{min}} \approx \frac{Ze^2}{mv^2}) \). Hence the limits of the electron energy range can be determined using the kinetic energy.

The emission coefficient for the Bremsstrahlung process is\(^{124}\):

\[ \varepsilon_{ff}(\omega) = \frac{16(\alpha a_0)^3 E_H}{3(3\pi)^{1/2}} \left( \frac{E_H}{kT} \right)^{1/2} \exp \left( -\frac{\hbar \omega}{kT} \right) n_e \sum Z^2 n_z \]  

(2.6.3)

where \( \alpha \) is the fine structure constant \( (\alpha = 1/137) \), \( a_0 \) is the first Bohr radius, \( E_H \) is the ionization potential of a hydrogen atom, \( n_e \) is the electron density, and \( n_z \) is the density of ions stripped of \( Z \) electrons. In LIBS, the emission from the free-free transitions constitutes a broad continuum spectrum.

2.6.2 Free-Bound Transitions

The free-bound transition occurs when a free electron is captured by an ionized atom.
Figure 18: Free electron being captured by an ion.

The electron then transitions from a free state to bound state of lower energy. Again as a consequence of this transition a photon is emitted with the surplus of energy.

\[e^- + E_i + Z \rightarrow (Z - 1) + h\nu_{fb}, \quad h\nu_{fb} \leq E_i + E_\infty^{Z-1}\]  \hspace{1cm} (2.6.4)

The emission coefficient for this process is\textsuperscript{124}:

\[\epsilon_{bf}(\omega) \approx \frac{32(a\alpha_0)^3E_H}{3(3\pi)^{1/2}} \left(\frac{E_H}{kT}\right)^{3/2} \exp\left(-\frac{\hbar\omega}{kT}\right) n_e \sum_z n_z \frac{z^4}{n^3} \exp\left(\frac{z^2E_H}{n^2kT}\right) n_z\]  \hspace{1cm} (2.6.5)

where \(n\) is the quantum number of the bound state. In the LIBS regime, this emission corresponds to emission in the extreme ultra-violet (UV) as an upper bound and near UV-visible (Vis) as a lower bound. A typical LIBS detection system is capable of detecting emission between 200 nm and 1.1 \(\mu\)m; due to the spectral response of the silicon detector.

### 2.6.3 Bound-Bound Transitions

Most of the line emission gathered from a LIBS spectrum is attributed to the bound-bound transitions of the atoms or ions from a higher bound state to a lower bound state.
The change of energy as the electron transitions from an upper level to a lower level for a hydrogen-like atom can be calculated from the Rydberg formula\textsuperscript{130}:

\[
\Delta E = R \cdot Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)
\]  
(2.6.6)

where \( R \) is the Rydberg constant (1.097373*10\(^7\) m\(^{-1}\)), \( Z \) is the atomic number of the element of consideration, and \( n_f \) and \( n_i \) are the final and initial electron shell energy level respectively. There are a variety of plasma spectroscopy books that review these conditions and processes in great detail; however a cursory explanation is given below. The atomic selection rules follow the notation from Foot\textsuperscript{131}.

2.6.3.1 Atomic Structure

In general hydrogen atom wave functions are described by four quantum numbers which are the principal quantum number \( n \), the angular momentum quantum number \( l \), the \( z \)-component of the angular momentum quantum number \( m_l \), and the \( z \)-component of the spin angular momentum number \( m_s \). It should be noted that the spin angular momentum quantum number \( s \) has the value of \( 1/2 \) for all electrons. With the absorption or emission of photons there is a state
change in the Hydrogen atom, which constitutes a change in one or more quantum numbers resulting in a different wavefunction. In a single electron atom, the allowed transition rules are found in the table below:

Table 4: Selection rules for allowable atomic transitions for a single electron system.

<table>
<thead>
<tr>
<th>Quantum Number</th>
<th>Range</th>
<th>Selection Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta n$</td>
<td>$0 - \infty$</td>
<td>0, 1, 2,... can be any integer</td>
</tr>
<tr>
<td>$\Delta l$</td>
<td>$0 - (n-1)$</td>
<td>$\pm 1$</td>
</tr>
<tr>
<td>$\Delta m_l$</td>
<td>$-l - +l$</td>
<td>0, $\pm 1$</td>
</tr>
<tr>
<td>$\Delta m_s$</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

Selection rules for a multi-electron system are very similar to the single-electron hydrogen atom system. For atoms with $Z < 20$ both the orbital angular momentum $l$, and the spin angular momentum $s$, are modified to account for the electrons coupling and thus generating an overall orbital angular momentum $L$ and spin angular momentum $S$. In addition, it is possible to couple the orbital angular momentum with the total spin angular momentum to yield a total angular momentum $J$, which also has a z-component $M_J$. This modified coupling scheme is known as the LS coupling scheme, and the electronic energy levels of items are known as terms and are labeled by the term symbol, $^{2S+1}L_J$. The $2S+1$ term is known as the multiplicity, and the $L$ term has the following notation where $L = 0 \rightarrow S$, $L = 1 \rightarrow P$, $L = 2 \rightarrow D$ … etc. It should be noted that it is forbidden to transition from a $L = 0$ to a $L = 0$, and from a $J = 0$ to a $J = 0$.

For atoms that have a $Z > 20$, the LS coupling scheme is still useful, however the jj-coupling scheme yields a better approximation of the electronic behavior. In the jj-coupling scheme, the assumption is made that the orbital angular momentum and the spin angular
momentum of the individual electrons will couple to make a total electronic angular momentum \( j \).

Table 5: Selection rules for the LS coupling scheme.

<table>
<thead>
<tr>
<th>Quantum Number</th>
<th>Selection Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta n )</td>
<td>0, 1, 2,… can be any integer</td>
</tr>
<tr>
<td>( \Delta L )</td>
<td>0, ( \pm 1 )</td>
</tr>
<tr>
<td>( \Delta l )</td>
<td>( \pm 1 )</td>
</tr>
<tr>
<td>( \Delta J )</td>
<td>0, ( \pm 1 )</td>
</tr>
<tr>
<td>( \Delta S )</td>
<td>0</td>
</tr>
<tr>
<td>( J = )</td>
<td>L+S</td>
</tr>
</tbody>
</table>

2.6.3.2 Molecular Structure

Molecules are defined as the bonding of two or more atoms in such a way that the resultant total energy is lower than the sum of the energies of the constituents\(^\text{132}\). In comparison with the atoms, molecules are significantly more complicated due to the fact that they have more centers, one for each atom in the molecule. This leads to not only energy levels corresponding to different electronic arrangements, but also additional states which correspond to the vibrational and rotational motions. For simple linear diatomic molecules the Linear Combination of Atomic Orbitals (LCAO) is often used to describe either the molecular wave-functions or the molecular orbitals. This system utilizes the directional dependence of the spherical-harmonic functions for the atomic orbitals as a method of solution.

Since the electrons in a molecule do not move in a central field the total angular momentum of the electrons is not a constant. Hence, while there is coupling of the angular
momentum for the electrons it will be different from the atomic case. In considering a diatomic molecule which has a cylindrical symmetry, the only constant of motion is along the symmetry axis and is the $z$ component of the electron orbital angular momentum $L_z$. As shown in the figure below the total angular momentum will precess about the axis of symmetry.

![Figure 20: Total angular momentum $L$ precessing about axis of symmetry.](image)

The projection of $L$ onto the axis is characterized by the quantum number $M_L$ which ranges from $L$ to $-L$ in steps of $L-1$. Since the internuclear field is very strong there is a substantial energy separation between states with different $M_L$ values. The absolute value of $M_L$ is designated as $\Lambda$ where $\Lambda$ similar to the atomic case is represented by different symbols based on the state ($\Lambda = 0 \rightarrow \Sigma$, $\Lambda = 1 \rightarrow \Pi$, $\Lambda = 2 \rightarrow \Delta$, $\Lambda = 3 \rightarrow \Phi$, etc).

Also similar to the atomic case the resulting spin quantum $S$ of the electrons is also needed to characterize the molecular states. The multiplicity $2S+1$ is placed similarly to the atomic case in the upper left index of the $\Lambda$ symbol, e.g. $^3\Pi$. Lastly, $\Omega$, the total electronic
angular momentum along the internuclear, ranges from $\Lambda^+\Sigma$ to $|\Lambda-\Sigma|$ in steps of $\Lambda^+\Sigma-1$, is placed on the lower right hand index of $\Lambda$. More detailed information on molecular structures can be found in Pearse’s book, *Identification of Molecular Spectra*. It should be noted that the LIBS technique is limited to the detection of electronic transitions, as it cannot currently resolve the vibrational and rotational transitions.

2.6.3.3 Line Emission

The energy of the emitted photon is well defined, and the emission coefficient for the line emission as defined by Griem (the radiated power per unit volume, per unit solid angle, and per angular frequency) is:

$$
\varepsilon(\omega) = L(\omega) \frac{h\omega^3 r_0}{2\pi c} \frac{g_n^Z}{g_m^Z} f_Z^{mn} n_m^Z
$$

(2.6.7)

where $L(\omega)$ is the normalized line shape or profile, $Z$ denotes the species of the $z^{th}$ ionization stage, the $g$’s are the statistical weights of the lower (n) and upper (m) states of the line radiation, $f$ is the oscillator strength, and the n term represents the number of ions in the $m^{th}$ excitation level. The lines that are emitted from the bound-bound transitions range from the near UV as an upward bound down to the near infrared in the lower bound. A typical LIBS spectrum is shown below in Figure 21.
The emissivity of a spectral line (i.e. number of photons emitted per unit time and per unit volume) is equal to the product of its radiative transition probability multiplied by the emitting excited level density. The line profile is also important because it contains information not only of the emitter but also of the surrounding plasma environment. However, the line profile must be considered carefully due to various line broadening effects that occur. A natural Lorentzian profile emerges due to the finite lifetime of the excited states, but the Doppler and Stark broadening effects, as well as the spectrometer contribution will also have to be accounted for.

Another concern in determining the line emission is that of self-absorption. This is capable of occurring in plasmas that have high-density conditions, and involves the plasma absorbing its own emission. Self-absorption causes a distortion in the spectral line profile, which leads to an apparent broadened line. In order to prevent the self-absorption from interfering with the measurements it is necessary to verify that the lines that are selected for measurements do not occur in optically thick plasmas. The “optically thin” limit can be verified by a procedure described by Cremer and Radeziemski.
2.7 Plasma Modeling

The investigation of the behavior of complex physical systems has traditionally been carried out through both experiments and theory. With the advent of the laser, both approaches have been used to study, analyze and predict the results of laser-induced plasmas. Laser fusion plasmas have been extensively studied. However, LIBS plasmas, (which have lower densities and lower temperatures in comparison with fusion plasmas) have not been studied as significantly, due to the numerous physical and chemical processes that cannot be neglected.

The idea of using computer simulations to study and analyze plasmas is over fifty years old. As a result it has become a very large and extensive subject, employing a wide range of techniques and attacking a vast array of physical problems\textsuperscript{135}. In fact, every experimental technique that is currently accepted by the analytical community has a modeling effort behind it. Computer simulations of plasmas can be divided into many categories with the equilibrium models being the most prevalent in this case. Equilibrium models consist of thermodynamic equilibrium (TE), local thermodynamic equilibrium (LTE), partial local thermal equilibrium (PLTE), model of coronal equilibrium (MCE), and collisional-radiative model (CRM)\textsuperscript{76}. While these codes are often used to describe the LIBS plasma, they often have to be modified in order to be accurate. The LIBS plasma does not begin in equilibrium; in fact due to the small momentum transfer in collisions between bodies of very different masses, time scales for equilibrium between electrons and atoms can be very long\textsuperscript{88}.

Modeling a LIBS plasma is a very difficult task in which complex problems such as determining the equilibrium rate may arise. Many models focus on the physics of the propagation and expansion of the plasma, frequently opting to concentrate on a particular aspect.
For instance, there are three models that are often used to model the expansion and propagation of the plasma: the laser-supported combustion (LSC), the laser-supported detonation (LSD), and the laser-supported radiation (LSR). They differ in their predictions of the opacity and energy transfer properties of the plasma to the ambient atmosphere. At the low irradiances used in LIBS experiments, the models that most closely match experiment are LSC and LSD. This is due to the relatively low temperature and density of the plasma.\textsuperscript{71}

More recently, models for laser-induced plasmas have become more sophisticated and have started to incorporate both chemistry and physics. One code, NEQAIR96, has been used to compute the emission and absorption spectra for atomic and diatomic molecules, as well as the transport of radiation through a non-uniform gas mixture to a surface.\textsuperscript{136} In another code (which has been developed as a computational model by Dors and Parigger\textsuperscript{137}) plasma equilibrium kinetics are implemented in ionized regions, and non-equilibrium, multi-step, finite-rate reactions are implemented in non-ionized regions. The computational fluid dynamics model predicts species concentrations, free electron number density decay, blast wave formation and dynamics, and flow field interactions of the laser spark decay as a function of time.\textsuperscript{71}

While codes have started to implement chemistry and physics, the incorporation of both is just rudimentary, meaning that neither of the two is allowed to fully evolve. The LIBS plasma is unique in that both chemistry and physics play an active role, and the augmentation of either role can lead to a misinterpretation of experimental results.

2.7.1 MEDUSA Code

Med103\textsuperscript{138} or MEDUSA is a one dimensional Lagrangian hydrodynamic code that contains models of most laser-plasma coupling physics, electron, and radiation transport. It was
initially developed for the application of inertial confinement fusion, however it can be adapted for lower temperature plasmas. In the code, the electrons and ions are treated as interpenetrating fluids, and Maxwell’s Equations along with fluid mechanics is used to describe the plasma state.

Propagation of the plasma is conducted using a Lagrangian hydrodynamics code in order to allow for longer simulation times however, the longer simulation time does not come without a cost. The gain of modeling a much larger system for a significant length of time forces the reduction of the information content for the simulation. Only, the crudest velocity space information is kept such as the root mean square particle velocity (the temperature), the mean particle mass drift velocity (the fluid velocity), and the electron drift velocity relative to the ions (the electric current)\(^{135}\). The electron and ion densities and temperatures, average ion state, and plasma parameters such as the viscosity, velocity, and pressure are determined in each individual cell.

MEDUSA solves the group of equations in a moving frame numerically for the simple case in one dimension. The equations are solved using the Crank-Nicholson scheme and the Gauss elimination method and several iterations are performed at each time-step. As a result the MEDUSA code yields four dependent variables: the electron and ion, the density, and the velocity at each position as a function of time. From these four variables, other plasma properties such as the plasma expansion, plasma radiation, etc. can be determined. Examples of MEDUSA results can be found below.
Figure 22 (a-d): MED103 calculations of $T_i$, $T_e$, $v$, $n_e$, respectively, at various times of a 5 ns laser pulse for a graphite wafer target.

The code uses cells as means to calculate energy balance transport in a self-consistent manner over a number of time steps. The ion and electron temperatures are solved using the Navier-Stokes equation and are supplemented by separate heat conduction equations with a variety of additional effects included.
3 LIBS FOR ANALYSIS OF ORGANICS

3.1 Introduction

LIBS has been shown to be an emerging diagnostic method for many applications, due to its ability to perform rapid analysis of various materials. Many researchers have been working with LIBS in order to show that the technique can be used for molecular identification of various species. This chapter will review this application of LIBS for analysis of organics, and its use on residues.

3.2 LIBS for Organics

The atomic composition of organic materials—carbon, hydrogen, oxygen, and nitrogen—gives the expectation of line emission from the four elements, either neutral or ionized. Unfortunately, these signatures are not only ubiquitous in nature, but they are weak emitters in comparison with many metal atoms, thereby complicating the analyses of the organic species. In order to address these complex issues, researchers have established theoretical models to describe the composition and chemistry of the plasmas produced from organics. Other researchers have attempted to increase the understanding of the signatures from organic plasmas through targeted experiments.

3.2.1 Plasma Composition, Chemistry, and Emission

Due to the complex nature of the LIBS plasma, it is difficult for a single model to completely describe the plasma as pointed out in the previous chapter. Hence several models have been proposed which address the various issues affecting the plasma composition. In order to address the influence that non-equilibrium states play in the plasma composition.
has utilized two temperature models proposed by Potapov\textsuperscript{146} and Chen\textsuperscript{147} which both take into account the thermodynamic disequilibrium present in the plasma. He uses the physical models to study the effects that occur on the composition of C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}N\textsubscript{t} plasmas out of thermodynamic equilibrium based on the selection of internal temperatures. As they are physical models, it was necessary to establish a general computation system which would accurately model the composition of the C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}N\textsubscript{t} plasmas. Therefore assumptions were made that the compounds were gaseous in nature, and 32 chemical units were considered including: electrons (e\textsuperscript{-}); 11 monatomic species (C, C\textsuperscript{+}, C\textsuperscript{++}, H, H\textsuperscript{+}, O O\textsuperscript{+}, O\textsuperscript{++}, N, N\textsuperscript{+}, N\textsuperscript{++}); and 20 diatomic species (C\textsubscript{2}, C\textsubscript{2}\textsuperscript{+}, H\textsubscript{2}, H\textsubscript{2}\textsuperscript{+}, O\textsubscript{2}, O\textsubscript{2}\textsuperscript{+}, N\textsubscript{2}, N\textsubscript{2}\textsuperscript{+}, CH, CH\textsuperscript{+}, CO, CO\textsuperscript{+}, CN, CN\textsuperscript{+}, OH, OH\textsuperscript{+}, HN, HN\textsuperscript{+}, NO, NO\textsuperscript{+}. Furthermore due to the temperature range considered 5,000-30,000 K polyatomic species were considered negligible\textsuperscript{148}, and 32 equations which were obtained through thermodynamics laws and relative proportion laws between the carbon, nitrogen, hydrogen, and oxygen atoms and radicals were written.

Koalaga \textit{et al.}\textsuperscript{149} designed experiments that specifically target potential experimental diagnostics of the plasma parameters necessary in order to test and validate both models, and found that the model proposed by Chen \textit{et al.}\textsuperscript{147} is best suited for plasmas with energetic constraints, while Potapov’s model\textsuperscript{146} is best suited for plasmas with entropic constraints. While Koalaga attempts to explain the influence of plasma parameters based on selection of internal temperatures using physical models, he points out that an alternative method of kinetic modeling may be utilized. He mentions that he did not use this method due to fact that some of the necessary kinetic coefficients in complex plasmas such as C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}N\textsubscript{t} are unknown. This kinetic method however was the basis of studies conducted by Babushok \textit{et al.}\textsuperscript{77,150} who used a kinetic
model to study the plasma plume from cyclotrimethylenenetrinitramine commonly known as the explosive RDX.

Babushok et al. have developed a kinetic model in order to analyze the processes responsible for the LIBS signature and incorporated processes involving ion chemistry, excitation, ionization, and other processes affecting neutral and ion species. In addition, the model includes processes of formation and quenching of excited H, N, and O atoms, as well as a submodel for the formation of the C_2 molecule. Similar to the physical models used by Koalaga, many different reactions were incorporated into the kinetic model and included reactions of charged species such as: e^-, H^+, O^+, O_2^+, N^+, NO^+, N_2^+, H_2^+, OH^+, H_2O^+, O_2^-, O^-, C^+, CO^+, CO_2^+, CH_3^+, CH_4^+, CH^+, CH_2^+, C_2H_3^+, C_2H_2^+, N_4^+, N_2O_2^+, N_3O^+, N_2O^+, N_2^+, NO_2^+, NO_3^+, NO^-, N_2O^-, NO_3^-, and NO_3^- in order to describe the plume of the plasma. Overall the kinetic model contained 137 species with 577 reactions, without incorporating excited C atom states. In the case as pointed out by Koalaga, where kinetic data was absent, the data was estimated based on analogy (for example some temperature dependencies of rate constants were approximated with dependencies valid at flame temperatures) or with the use of empirical rules. As with Koalaga, the kinetic model was validated through experimental runs with similar or matching parameters. Regardless of the model selected there are numerous species and reactions necessary to accurately model the plasma composition of even the simplest organic molecule.

The complexity of the plasma composition has also been directly studied by various researchers in an attempt to increase the understanding of the dominant processes in the plasma, and address complications that may not be evident in a model. Locke et al. studied the emissions generated from various simple carbon-containing vapors, and found that strong atomic lines (C, H(\alpha), H(\beta), O, Cl, and F) as well as molecular bands (C_2, CH, and CCl) were highly
observable. Abdelli-Messaci et al.\textsuperscript{152, 153} studied the emission of graphite under a nitrogen atmosphere at laser energies ranging from 3-60 J/cm\textsuperscript{2}. From the plasma emission, the spatio-temporal evolution of the C, C+, and N+, as well as the C\textsubscript{2}, CN, and N\textsubscript{2}\textsuperscript{+} were observed. Portnov et al.\textsuperscript{154} studied the emission of organic compounds specifically aromatic nitrocompounds (NCs) and polycyclic aromatic hydrocarbons (PAHs) and found that besides the common atomic and ionic lines of C, H, N and O products and C\textsubscript{2} and CN molecular bands, minor impurities of Ca and Na were observable in the plasma emission. Lastly, St-Onge et al.\textsuperscript{155} studied the carbon emissions following the laser ablation of graphite and organic samples in ambient air using a 1.064 μm laser.

3.2.2 LIBS for Organics: Applications

While fundamental issues pertaining to the use of LIBS on organics continue to be studied and addressed, LIBS has been successfully implemented in the sensing and detection of organics. In the field of recycling, LIBS is often used to identify polymers in real time in order to increase material recycling efficiency. LIBS has also been used in the defense industry for the detection of energetic materials, mainly explosives. As the fundamental understanding of LIBS on organics continues to grow, further applications to organics using LIBS will be found.

3.2.2.1 Polymer Identification

Sattmann et al.\textsuperscript{156} has successfully utilized LIBS for the identification of polymers such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polypropylene (PP) in order to develop an efficient method for material recycling and thus reduce the increasing waste streams. In addition Sattmann et al. employed the use of a dual pulse configuration in order to yield a higher signal-to-noise
ratio than that of a single pulse and thus gained more analytical spectral features. The polymers were identified using the Cl I 725.66 nm line, and the C/H ratio, consisting of the C I at 247.86 nm and the H\textsubscript{β} at 486.13 nm emission lines. The selected intensities were the input values of several artificial neural networks such as feedforward, dynamic learning vector quantization (DLVQ), or radial base function (RBF) networks\textsuperscript{157} for classification of the spectra. The neural networks were able to classify clean samples of PE and PP with accuracies in the range of 93-96%, and > 99% for PET and PVC.

Anzano \textit{et al.}\textsuperscript{158} conducted a similar study to that of Sattmann and coworkers, and found that in addition to the C I, C\textsubscript{2}, CN, H, N, and O emitters, the H/C I ratio and the C\textsubscript{2}/C I ratio was necessary in order to identify the polymer of interest. They developed a program for the polymer identification using the following signal ratios (in order of importance): H/C I, O/N, C\textsubscript{2}/C I, CN/C I, and H/C\textsubscript{2}. Polymer materials were correctly classified into their groups of PET, PVC, polyolefins (PE and PP), and PS. Only the polyolefins failed to be separated into PE and PP and thus were left as the polyolefin group.

In addition to recycling plastic bottles and other polymers, LIBS has been used to recycle the end-of-life waste electric and electronic equipment (EOL-WEEE), which consist of telephones, computer keyboards, or household appliances. In order to improve their mechanical, electrical, and chemical properties, various polymers such as acrylonitrile-butadiene-styrene (ABD), poly-carbonate (PC), and styrene acrylonitrile (SAN), are often doped with additives such as flame retardants, antioxidants, fillers, dyes and pigments in varying concentrations\textsuperscript{159}. The downgrade of the highly valuable technical polymers must be avoided by separating out the recyclable based on the purity of the material. Due to the environmental hazard of some of the materials, mainly pieces containing brominated flame retardants (BFR) and heavy metals,
immediate separation from the waste stream which is to be recycled is necessary. As with Sattmann and Anzano, identification of both the polymer and the critical additives are done with LIBS on a prototype automatic identification and sorting line\textsuperscript{160}.

### 3.2.2.2 Explosives Detection

With the promising results of the identification of polymers consisting mainly of carbon, hydrogen, nitrogen, and oxygen, a focus has been placed on utilizing LIBS to identify energetic compounds. Most plasmas from energetic compounds are organic in nature and contain the same elemental (C, N, H, O) and molecular emitters (CN, C\textsubscript{2}) that can be found in polymers. Real time direct detection of energetic materials and explosives is crucial for military and civil protection. There have been many studies that utilize LIBS for the detection of energetic materials, improvised explosive devices (IED)\textsuperscript{161, 162}, substrate-related effects of explosives\textsuperscript{163, 164}, and chemical and biological threat detection\textsuperscript{18, 22}. With the various advantages that LIBS has over other detection techniques, new regimes such as remote detection\textsuperscript{165} and femtosecond detection\textsuperscript{166} have been introduced into the sensing and detection of explosives.

Building on the studies that were conducted for polymer detection, Wang \textit{et al.}\textsuperscript{167} explored seven types of plastics (ABD, HDPE, PET, PMMA, PP, PS, PVC) and compared them with the trinitrotoluene (TNT) in the nanosecond regime using both 1064-nm and 266-nm wavelengths. They compared the signal-to-“peak to peak noise” ratios of the collected LIBS spectrum and tried to discriminate the TNT from the common polymers which are comprised of similar constituents. They found that since the light absorbed in the plasma scales with the square of wavelength, the 1064-nm wavelength heats the plasma more efficiently and as a result the emission intensity increases more strongly in comparison with the 266-nm. The near-infrared
wavelength was also found to be advantageous over the ultra-violet in that the signal obtained was not only more intense but had less overall variations. However, the 266-nm did have its advantages in that the plasma generation is less dependent on the material, which was noted by the similar absorption of the UV light and the varying absorption of the NIR light. Based on their findings Wang et al., postulated that a combination of simultaneous pulses of NIR and UV, may be advantageous for the detection of explosives.

Rai et al.\textsuperscript{161}, used LIBS to characterize two similar organic nitro-compounds by measuring the intensity of the atomic lines. Based on the work by Yinon\textsuperscript{34}, Rai et al., choose the nitro-compounds 4-nitroaniline (C\textsubscript{6}H\textsubscript{6}N\textsubscript{2}O\textsubscript{2}) and 4-nitrotoluene (C\textsubscript{7}H\textsubscript{7}NO\textsubscript{2}) in order to validate that the O/N intensity ratio could be used as a unique parameter to discriminate each nitro-compound from an explosive. They found that in order to improve the reliability of their discrimination technique, statistical techniques of linear correlation and principal component analysis (PCA) for the identification of the compounds utilized were necessary. The statistical techniques utilized, known as chemometrics, and have been adapted from algorithms often found in analytical chemistry.

Chemometrics is necessary for the discrimination between different types of explosives. De Lucia Jr. et al.\textsuperscript{162} studied a number of energetic compounds including black powder, neat explosives (TNT, PETN, HMX, and RDX), propellants (M43 and JA2), and military explosives (C4 and LX-14). They found that they were able to differentiate the explosive compounds based on the O/N peak ratios which were greater in comparison with the surrounding air atmosphere. In another study, done by De Lucia Jr. et al.\textsuperscript{168}, comparison between non-explosive and explosive material and chemometrics were used in order to minimize the confusion between the elemental emissions from the surrounding environment with those related to an explosive material. The
model used in this study was based on a partial least squares discriminant analysis (PLS-DA), and was based on the cross-validation classification error technique which compared the model against test sets, and was confirmed using independent test sets. Hence they determined that LIBS coupled with chemometrics may be a promising avenue for explosive detection and discrimination.

Lastly as femtosecond lasers become more affordable and common place in laboratories, they are being utilized as excitation for various techniques such as LIBS. McEnnis et al. have used femtosecond LIBS to study TNT. They found that unlike in the nanosecond regime, only molecular species (C₂ and CN) were present in the spectrum meaning that there were no elemental contributions from the explosive. De Lucia Jr. et al. further expanded on this study by adding in more explosives. In agreement with McEnnis, they found no elemental constituents in the TNT spectra however they were able to observe the constituent atomic elements present in several explosive samples. In conclusion, they determined with some reservations that femtosecond LIBS was advantageous over nanosecond LIBS in allowing the generation of plasmas at lower laser fluences, which resulted in less continuum background, less air entrainment, and less substrate interrogation. However, these advantages over the nanosecond regime could only be recognized at low femtosecond fluences.

3.3 LIBS for Organic Residues

Using LIBS to detect explosives is still relatively new, but a variety of cursory studies have been conducted as discussed in the previous sections. In most cases, the organics are in the form of a bulk sample, and thus the so-called substrate effects can be ignored, however this becomes more problematic if the bulk samples are reduced down to trace amounts of materials or
residual signatures. Much debate has been given to the definition of residues found in the field in the LIBS community. Most LIBS studies have used commercial solutions with typical concentrations of 1.0 mg/mL (1000 parts per million) or 0.1 mg/mL (100 parts per million) as typical residues, while others have prepared their own solutions of varying concentration. However the golden standard or goal for sensing technologies limits of detection is on par with that of canines.

Arguments of actual sensitivity levels that a dog’s noise can achieve are still ongoing, however trained canines can sense and detect aromas or residual signatures on the order of parts per quadrillion (ppq), which is approximately femtograms ($10^{-15}$ g), of material. A picogram ($10^{-12}$ g) is currently the detection limit under controlled settings for classic chemistry methods such as ion mobility spectrometry or mass spectrometry. So currently a dog is able to detect on the order of 1000 times below classical chemistry techniques$^{25}$. It should be noted that dogs are trained to sniff aromas or trace signatures of the material of interest and not the container which encloses the material, and hence the explosives are successively wrapped in a different packages. Although the amount of material necessary for canine sensing is quite low, interferents such as pheromones, sickness, or possible placement of acrid materials to hide the scent of the energetic materials may raise the limit of detection.

While the limits of detection for residues using LIBS have not been set, addressing this issue will not be easy for a number of reasons, chief among these is accurately defining what a residue is. All possible definitions of a residue deal with the amount of material on a substrate, however, how the material is spread across the surface of the substrate then comes into play. It is possible that one may consider a residue to be a thin-film, such that a small amount of material is distributed evenly across the surface, or alternatively a large concentration may be placed at one
location. Still yet another possible definition maybe a certain amount of material is placed within a certain analysis area. Lastly, a residue may be defined as small deposits of material placed randomly on the surface area. Until the LIBS community is able to collectively agree to the definition of a residue as other methods used for explosives detection (ion mobility spectrometry (IMS) and mass spectrometry (MS)) have done, it will be very hard to determine any limits of detection, and thus accurately compare studies conducted by various research groups.

3.3.1 Current Studies on Organic Residues

While studies have been conducted using LIBS to detect organic residues on a substrate, these substrates have mainly been metallic\textsuperscript{172, 173}. Currently a study completed by Gottfried \textit{et al}.\textsuperscript{174} has been the leading resource against which others have compared their work. In this study numerous topics were addressed including improving sensing and selectivity of LIBS for residue explosives detection, applying LIBS for a standoff detection of explosives, techniques for reducing air entrainment into the plasma, and the use of various chemometric algorithms to improve identification of explosive residues utilizing LIBS. A synopsis of the conclusions from this work, which pertains to this thesis, will be given.

Gottfried \textit{et al}. recognized that the contribution from the oxygen and nitrogen signals in the surrounding atmosphere could drastically impede the identification of the explosive material. As such they determined that by either using double-pulse LIBS or surrounding the sample with a buffer gas (such as argon) the air entrainment into the plasma could be effectively reduced. However, they also determined that in a ‘real world’ setting the ability of LIBS to detect residues may hinge upon a single laser shot, as this shot could ablate most or all of the residue. In order to
address the single shot limitation, Gottfried et al. explored various chemometric algorithms that would allow for the detection residues containing energetic material.

3.3.1.1 Importance of Chemometrics

Many of the chemometric approaches involve the cross-validation technique as mentioned previously, making it necessary to collect a library of reference samples and determining what information will be collected and compared. The first chemometric algorithm utilized by Gottfried et al.\textsuperscript{174}, was a simple Linear Correlation (LC), which measured the strength of the relationship between two variables, and they choose to use the full LIBS spectra, which contained approximately 9000 data points, as variables. For their selection of samples included in library, they selected RDX, TNT, aluminum, dust, and oil. An unknown energetic material Comp-B was compared against the library although it was not included. The linear correlation technique resulted in a large number (98\%) of false positives (incorrectly assigned samples) when a comparison of fingerprint residues was compared against the library, and a large number (96\%) of false negatives (completely failed to classify sample) when a mixture of crushed RDX and dust was compared against the library.

In order to reduce the amount of data necessary for comparison purposes, they constructed a second library consisting of 9 summed peak intensities, and 20 intensity ratios, which contained emission lines from the substrate in addition to those from the sample residue. Using the abbreviated data set the number of false positives obtained was reduced down to 90\%, however the false negative rate for the crushed RDX and dust mixture increased to 100\%. They determined that using linear correlation which is solely dependent upon intensity information
from the substrate/background, would be ineffective for residue identification on different substrates.

The second chemometric algorithm that was explored was Principal Component Analysis (PCA) which enables data compression and information extraction from a combination of variables that describe major trends in the data. Using the same sample set as in the linear correlation, they first elected to use six intensity ratios as their comparison variables. They found that their algorithm was only able to classify a sample as ‘explosive’ or ‘not-explosive’, and using their library they were able to accurately group all the explosives as explosives. This grouping was even more pronounced when they changed their comparison variables from the six ratios, back to the second library utilized in the linear correlation algorithm (consisting of 9 summed peak intensities, and 20 intensity ratios). They concluded that the PCA algorithm was a useful tool for identifying whether samples are the same or different, potentially what variables are responsible for the difference.

The last chemometric algorithm that was examined was Partial Least Squares – Discriminant Analysis (PLS-DA) which is a multivariate technique which generates predictor variables from an inverse square discrimination method while attempting to capture variance and achieve correlation. They found that models built on the 9 summed peak intensities and 20 intensity ratios premise resulted in the best discrimination and concluded that the PLS-DA technique was the best for discriminating different types of explosives using LIBS despite their similarity in molecular structure. However, the PLS-DA does introduce a certain subjective threshold for discrimination, and Bayesian statistics are necessary in order to minimize the number of false positives and negatives. Thus PLS-DA is really dependent on where one chooses
to place threshold in determining the number of false positive and false negatives that the user is willing to accept.

Following the study done by Gottfried et al., others have focused on particular aspects of the broad study and further expounded upon a particular section. One such study conducted by Lazic et al., expanded on Gottfried’s study by incorporating more explosive and explosive-like samples. They also explored other fundamentals that could lead to improvements into energetic residue detection. They made mention of the fact that due to the uneven distribution of the residues on their support there were large shot-to-shot fluctuations of the line intensity ratios. They also pointed out that both the atomic and molecular emission intensities, along with their ratios were strongly affected by the amount of support material which also happens to be ablated. As a consequence, the aluminum support which was the same used in Gottfried’s experiments, resulted in higher plasma temperatures for increased support ablation, resulting in more efficient line excitation, higher fragmentation, and higher atomization rates of residue materials.

Lazic et al., also focused on using PCA with the initial six intensity ratios proposed by Gottfried for discrimination of their residues. They concluded that the chemometric tools which rely on trends within the data set can compromise sample classification due to an abrupt change in the line intensities and their ratios. This is highly probable when passing from the analysis of a thick residue to that of a thin residue supported by the substrate. Thus in order to improve the classification, they determined that it would be necessary to introduce other parameters related to both the plasma temperature and chemical reactions, as well as improve the linearity in the line intensities and/or their ratios. From their expanded set of samples, Lazic et al. were only able to correctly classify three types of explosives 100% correctly from nine explosives and six other organic residues. They concluded that from their study in many cases when applying algorithms
such as PCA on single shot spectra, it would not be possible to discriminate explosives from interfering materials.

### 3.3.2 Proposed Studies for Organics

The two in-depth studies conducted by Gottfried et al. and V. Lazic et. al. have utilized LIBS in the single shot regime on an aluminum substrate for detection of organic residues. While the experiments were similar, conflicting results regarding LIBS’s ability to accurately discriminate organic residues were presented. Both, however, agreed that in order to increase sensitivity and detection limitations it is necessary to increase the signal-to-noise ratio in the single shot regime. Even if the substrate on which the residue is placed is well characterized, developing a stable library becomes difficult due to the variable amount of sample from one spot to another. In addition, Lazic determined that the substrate matrix effects must be accounted for as the use of an aluminum support resulted in higher plasma temperatures for increased support ablation, resulting in more efficient line excitation, higher fragmentation, and higher atomization rates of residue materials.

The question arises as to the role that the substrate plays in detecting energetic residues. More specifically, if the energetic residue were to be placed on either a non-metallic or organic substrate would it still be possible to discriminate explosive residues. The issues regarding the laser characteristics and the acquisition parameters, the surrounding atmosphere (including the gas composition and the pressure), the interaction geometry, and the collection optics (including the geometrical setup) would still need to be addressed as they strongly affect the analytical capabilities of LIBS especially in a single-shot regime\textsuperscript{175}. In addition the role that chemometrics plays in helping LIBS to detect and classify energetic materials must be addressed. It remains to
be answered if there is a possible algorithm that can use LIBS data to reliably detect energetic residues and what are the limits of this detection.

If the effect of the substrate is totally removed from the problem, how does this affect the LIBS signature? The contributions to the resulting signature should only come from the sample and the atmosphere. If the atmosphere could be removed, the signature strictly from the organic could be isolated. The LIBS processes for organic materials could be intensively studied, and characterized. However, as most organics have limited emitters are in the visible range standard techniques for characterization of the plasma cannot be used. Alternative methods to measure the plasma temperature and density must be investigated. The new methods could also be utilized to study the evolution of the plasma as the sample is surrounded by different ambient atmospheres. This knowledge could then be incorporated into theoretical models improving their accuracy, and better model the LIBS interaction.
4 EXPERIMENTAL REGIME AND ANALYSIS

The basic components of any LIBS experimental system consist of the following:

- a pulsed laser
- a focusing system used to focus the laser pulse onto the target sample
- a light collection system that collects the emitted light and transports it to the detection system
- the detection system which consists of a spectrometer or another method of spectrally filtering and dispersing the light and a detector to record the light
- a computer and other electronics that allows for the gating of the detector, the firing of the laser, and the storing and interpretation of the spectrum

Particular components will be focused on in this chapter. In addition, this chapter will focus on deducing the primary plasma parameters from a spectrum in order to characterize the LIBS plasma, as well as the post-processing of the data. The post-processing section will introduce modern chemometric algorithms that allow for rapid data reduction and interpretation, and methods of evaluating the results of the analysis.

4.1 Laser Fundamentals

The laser plays an important role in LIBS as the sampling source by laser and the main excitation source of the extracted matter. There were two laser systems utilized in the experiments that were conducted. Sigman provides a rigorous treatment of laser fundamentals in his book entitled “Lasers’’\textsuperscript{176}. Technical aspects of the lasers used in the experiments will be given here.
4.1.1 Nanosecond Laser

The Neodymium: Yttrium Aluminum Garnet (Nd:YAG) laser is one of the most common excitation sources utilized in many LIBS studies due to its reliability, compactness, and its high focused power density. The laser is a typical 4-level system configuration, with a relatively long upper level lifetime of 230 µs. This allows for the population to be accumulated over the duration of the pumping cycle when the laser is used in the Q-switching mode\(^{177}\). As displayed in Figure 23, the fundamental wavelength of the Nd:YAG laser is 1.064 µm, as it is the strongest emission of a neodymium ion in a YAG matrix.

![Energy level structure of the Nd:YAG laser.](image)

The two common host materials or solid-state crystals for this ion are the yttrium aluminum garnet (YAG) and glass. When doped in YAG (Y\(_3\)Al\(_5\)O\(_{12}\)) the Nd:YAG crystal produces emission at 0.94 µm and 1.32 µm in addition to the 1.064 µm as they all have the same upper energy level.
For the experiments conducted in the nanosecond regime a Brilliant Nd:YAG laser manufactured by Quantel was utilized. The Brilliant Nd:YAG crystal was optically pumped by a single flash-lamp, and was Q-switched in order to achieve short but high energy pulses. At its standard repetition rate of 10 Hz, the Brilliant system was capable of achieving laser pulses with a duration of ~ 6 ns and an energy of 360 mJ at its fundamental wavelength of 1064 nm. Lastly the laser had a beam divergence of approximately 0.5 mrad which was measured at 1/e² of the peak (85% of the total energy).

4.1.2 Femtosecond Laser

The most widely used tunable solid state lasers on the market today are the titanium sapphire (Ti:Al₂O₃) lasers.¹⁷⁸ These lasers gain their name from the doping of a sapphire (aluminum oxide) crystal with titanium ions at a concentration of approximately 0.1% by weight.¹⁷⁹ Their emission wavelength ranges from 660 nm – 1180 nm, and these lasers have the broadest gain width of any laser. In addition to their tunability, these lasers are capable of producing terawatts of peak power, with pulse durations shorter than 100 femtoseconds when mode-locked and amplified. This makes this laser ideal for generating high-density and high temperature radiating plasmas when the pulses are focused onto solid targets.

Titanium sapphire lasers similar to the Nd:YAG lasers, are of a 4-level system configuration. Both the ground state (²T₂) and the first excited state (²E) extend upwards with a series of overlapping vibrational levels as shown in Figure 24.
These different but closely separated vibrational states are the cause the laser tunability. While excitation of the electrons from the ground state can be done by flash-lamp pumping, this method is often inefficient, as typical flash-lamps pulse durations are much greater than the upper laser level lifetime of the laser crystal (3.8 µs at room temperature). A more efficient method is to pump the Ti:Al₂O₃ with a frequency-doubled Nd:YAG (532 nm) or Nd:YLF (523.5 and 526.5 nm) as the Ti:Al₂O₃ has fairly efficient absorption at these wavelengths as displayed in Figure 25.
The titanium sapphire laser system used for the femtosecond studies consisted of a Spectra Physics Tsunami mode-locked titanium sapphire (Ti:Al₂O₃) oscillator which was diode-pumped by a Spectra-Physics Millennia Pro. The Millennia Pro is continuous-wave neodymium-doped yttrium vanadate (Nd:YVO₄) crystal laser which provides approximately 4.35 Watts of pump energy. From the pumping by the Millennia Pro, the Tsunami is capable of producing < 35 femtosecond pulses at a 75 MHz repetition rate. This produces a spectrum centred at 800 nm with a FWHM of 65 nm and a continuous power ranging between 400-450 mW. Following the oscillator the laser beam enters a Z -cavity configured Spitfire regenerative amplifier.

The Spitfire amplifier is pumped by a Positive Light Evolution laser, which is a Q-switched diode pumped Nd:YVO₄ laser operating at a 1 kHz repetition rate producing pulses of
approximately 200 ns, and a power of 20 W. The laser light makes approximately 12 -14 passes in the regenerative amplifier which has the option of running at either a 1 kHz or a 10 Hz repetition rate. At the 1 kHz repetition rate the amplifier produces pulses of approximately 3 mJ of energy. Following the regenerative amplifier the laser light enters a double pass amplifier.

The double pass amplifier is pumped by a Spectra Physics Quanta Ray Pro laser. The Quanta Ray is a flashlamp pumped outer-cavity frequency doubled Nd:YAG laser which provides approximately 350 mJ of pump power for the double pass amplifier. Limited by the repetition rate of the Quanta Ray, the double pass amplifier operates at 10 Hz and amplifies the pulses from the regenerative amplifier up to 40 mJ. The final stage of the laser chain is the recompression of the laser pulse which is done by a folded Treacy\textsuperscript{181} compressor. After recompression the laser system produces pulses of 25-30 mJ with a pulse duration of approximately 40-50 fs running at 10 Hz. Although the laser was run at repetition rate of 10 Hz, a mechanical shutter was used in order to allow for a single shot operation. The mechanical shutter is controlled by the spectrometer camera which itself is synched with the laser’s main clock.

4.1.3 Laser Light Valve

The studies conducted in the nanosecond regime were conducted at low energy levels often < 15 mJ. In order to attenuate the energy of the laser without changing the separation between the flashlamp and Q-switch or supply voltage (which could drastically affect the performance), a light valve was constructed. The light valve consisted of a zero order $\lambda/2$-wave plate (Tower Optical Corporation AO25DZ $\frac{\lambda}{2}$ 1064) followed by a high energy Nd:YAG polarizing cube beamsplitter (Newport 05BC25PH.9). The linearly polarized beam from the laser
was first passed through the $\lambda/2$-wave plate which was placed into a circular rotating mount. Following the $\lambda/2$-wave plate which rotated the plane of polarization the light entered the polarizing beam splitter cube as shown below in Figure 26:

![Figure 26: Light valve configuration used in nanosecond studies.](image)

The rotation of the $\lambda/2$-wave plate controlled the amount of polarization which subsequently determined the amount of light that travelled in either the S or P direction. This allowed for the amount of energy to be reduced without having to change the laser parameters.

4.1.4 Frequency Conversion

The high peak power characteristic of the Nd:YAG laser permits wavelength conversion from the near-infrared (1064 nm) all the way to the ultraviolet (266 nm). This process of wavelength conversion is accomplished through the nonlinear processes of frequency doubling and frequency mixing. Essentially the laser light is passed through a birefringent crystal, such as potassium dideuterium phosphate (KD*P), whose index of refraction is dependent on the polarization of the propagating waves. In the crystal if the ordinary index supporting the propagation of the incoming wave matches the extraordinary index of another wave the two
waves propagate in both the same phase and speed. This phase matching phenomenon allows for frequency conversion to occur, but relies heavily on the temperature of the crystal and the angle between axes of the crystal and the direction of the polarization.

Two types of conversion were used in order to obtain the 2\textsuperscript{nd} harmonic (532 nm) and the 4\textsuperscript{th} harmonic (266 nm) of the Nd:YAG fundamental wavelength. The type I crystal has an input along the ordinary axis, while the output is polarized along the ordinary axis leaving the remaining input wavelength linearly polarized. The type II takes an input that is at an angle between the ordinary and extraordinary axes, and while the output remains polarized along the extraordinary axis, the remaining input wavelength is elliptically polarized\textsuperscript{182}.

Either type of crystals can be used to double the frequency from 1064 nm to 532 nm. However, the type II crystal was utilized as it had a 20% higher conversion efficiency than the type I crystal. The 4\textsuperscript{th} harmonic generation was done by first creating the 2\textsuperscript{nd} harmonic, and then mixing 532 nm wavelength light with itself in a second KD*P crystal. In the case of the 4\textsuperscript{th} harmonic the KD*P II crystal was found to be more efficient by approximately 10\%\textsuperscript{180}. It is important to note that the frequency conversion was done outer-cavity and after the laser had passed through the light valve.

4.2 Spectrometers

Spectrally filtering and dispersing the light collected from the plasma emission is a vital step for LIBS. In fact, the basis of the LIBS measurement is the collection and analysis of the spectrum of the emission\textsuperscript{71}. As such, properties that are important in selecting a spectrometer are:
the bandwidth and the resolution. The parameters of the spectrometer that determine these properties are the grating and the focal length of the optics.

A grating is little more than a piece of an optically smooth glass substrate on which grooves have been ruled, and has been coated with a highly reflecting layer (either metal or dielectric film). The grooves, when illuminated coherently, can be considered as small radiation sources which when considered as a coherent superposition reflect light. If the partial waves from different grooves are all in phase then constructive interference occurs resulting in a large total intensity. Alternatively, if the light is in different directions the contributions made from the small radiators cancel each other out resulting in destructive interference.

If a parallel light beam is incident onto two adjacent grooves as shown in Figure 27, the grating equation can be derived\textsuperscript{182}.

\[ \Delta s = l (\sin \alpha - \sin \beta) \]

Figure 27: Parallel light beam incident on a grating.
where \( \alpha \) is the angle of incidence to the grating normal, and \( \beta \) is the angle of the reflected light.

As mentioned above, constructive interference is obtained when the path difference \( \Delta s = \Delta s_1 - \Delta s_2 \) for those directions \( \beta \) of the reflected light is an integer multiple \( m \) (being the order of diffraction) of the wavelength (\( \lambda \)). Replacing \( \Delta s_1 \) with \( l \sin \alpha \) and \( \Delta s_2 \) with \( l \sin \beta \) the grating equation is obtained.

\[
l(\sin \alpha \pm \sin \beta) = m\lambda \quad (4.2.1)
\]

where the negative sign is taken if \( \beta \) and \( \alpha \) are on opposite sides of the grating normal as shown in Figure 27; otherwise the minus sign is used.

The angular dispersion or the angular separation of two wavelengths whose difference is \( d\lambda \) is defined as \( d\beta/d\lambda \) can be obtained by differentiating the fundamental grating equation resulting in:

\[
\frac{d\beta}{d\lambda} = m \frac{d\cos \beta}{d\cos \beta} \quad (4.2.2)
\]

where \( \beta \) is the angle between the normal to the grating and the diffracted beam, and \( m \) is the order of the spectrum. The resolving power is shown in Equation 4.2.3:

\[
R = \frac{\lambda}{\Delta \lambda} = mN \quad (4.2.3)
\]

where \( N \) is the number of lines on the grating illuminated by the light to be dispersed. It should be noted that the resolving power is not directly dependent on the number of grooves since, for planar gratings of a given size:

\[
R = mN = \frac{W(\sin \alpha \pm \sin \beta)}{\lambda} \quad (4.2.4)
\]
where \( W = N \cdot d \) is the illuminated width\(^{183}\).

In LIBS, there are two types of spectrometers that are commonly utilized in detection systems, the Czerny-Turner and the Echelle, each being suitable for particular applications. The Czerny-Turner spectrometer design as shown in Figure 28 can be found in most LIBS detection systems.

![Figure 28: Design of a Czerny-Turner spectrograph.](image)

The Czerny-Turner design consists of an entrance slit followed by a mirror which collimates the light sent through the slit into a parallel beam. This beam is then directed onto a grating where it is diffracted off the grating at different angles following the grating equation (4.2.1). The grating can be either reflective or transmissive, and while reflective gratings are common in most spectrometers, transmissive gratings are often preferred since they are more efficient over a broad spectrum without aberration due to the reflective grating. But the materials used for these
gratings are often not transmissive in the ultraviolet region, restricting their use to visible spectroscopy\textsuperscript{183}. The dispersed light is then directed onto a second concave mirror where the mirror focuses the light into spectrum lines and directs the signal to the image plane.

The Czerny-Turner’s ability to gather light is restricted by the $f/#$ (Equation (4.2.4)) of the spectrometer, where the lower the $f#$ the more light the instrument is capable of collecting.

$$f/\# = \frac{f}{D}$$  \hspace{1cm} (4.2.4)

where $D$ is the diameter of the mirrors and $f$ is the focal length (distance from the entrance slit to the first mirror). In addition to maximizing the amount of light collected, the Czerny-Turner also has the option of selecting the spectrograph resolution. Resolution can be gained by increasing the grating groove density but does so at the expense of the spectral range, and the signal strength. The resolution can also be increased by decreasing the input of the entrance slit, but again this is done at the cost of the signal strength.

The spectral resolution needed for the analysis depends mainly on the analyzed sample. Factors that must be considered include: (1) the complexity of the sample, (2) the number of elements to be monitored, (3) whether the elements that are monitored are done simultaneously or sequentially, and (4) the location of the emission lines in the spectrum\textsuperscript{184}. The Czerny-Turner is able to satisfy most of the factors, but depending on the resolution needed and the size of the spectral window, monitoring many elements simultaneously may yield problems. In order to address the shortcomings of the Czerny-Turner, another spectrometer has been introduced for use in LIBS applications.

The Echelle design is shown below in Figure 29 shows that a prism is placed in front of the grating which adds a pre-dispersion stage before the grating dispersion.
The main difference between the two spectrometers lies in the diffraction grating. The Echelle grating is designed for use in high orders and at angles of illumination greater than 45 degrees to obtain high dispersion and resolving power by the use of high orders of interference. The grating is used at such a large angle that the Echelle produces spectra of very high dispersion, but it only does so over a short wavelength range in each grating order as shown by the free spectral range equation shown below:

\[ \delta \lambda = \frac{\lambda}{m} \]  

(4.2.5)
where $m$ for an echelle grating can range from 10 – 100$^{183}$. A prism placed such that its
dispersion is at right angles to the grating, stacks the orders vertically over one another so as to
create a two-dimensional display of wavelength versus order$^{182}$.

While the grating used for an Echelle often has fewer lines per millimeter than a
conventional spectrometer grating, the dispersion is such that a large wavelength range may be
monitored with reasonable spectral resolution. Hence, the Echelle provides a wide-ranging
wavelength coverage, generally providing a span from 190 nm to 800 nm which is the most
useful range for LIBS detection as the strongest emission lines of most elements lie in this
region$^{71}$. The resolving power normally depends on the specific Echelle, but it normally lies in
the range from 2500 - 10,000$^{182}$.

Both types of spectrometers were utilized in the following studies. The CT spectrometer
was a PI Acton 2500i was a 0.5 m focal length spectrometer equipped with 3 gratings: a 150,
600, and 1800 lines/mm The Echelle spectrometer was a SpectraPro® HRE Echelle
manufactured by Princeton Instruments/Acton. This spectrometer had a focal length of 250 mm
and an aperture ratio of f/10. Although originally equipped with a 25 µm input aperture, this was
replaced with a 50 µm aperture in order to increase light throughput.

4.2.1 Spectral Ghosts

Inaccuracies in the ruling of a gradient made during the manufacturing process can result
in constructive interference from parts of the grating from wrong wavelengths. These unwanted
maxima are known as grating ghosts, and occur for a given angle of incidence $\alpha$ into the wrong
direction $\beta$ $^{182}$. Grating ghosts are usually negligible however with an intense incident radiation at
a certain wavelengths the ghosts may become comparable to other weak lines in the spectrum. An example of grating ghost lines is shown below in Figure 30.

![Figure 30: Spectrum displaying ghost lines (g) due to the intense hydrogen alpha line.](image)

4.3 Detectors

As mentioned in section 4.2, the final stage of a spectrometer focuses the light onto a light detection device. There are many different detectors that have been developed, but for LIBS detection systems, devices such as photomultiplier tubes (PMTs), avalanche photodiodes (APDs), photodiode arrays (PDAs), charge coupled devices (CCDs), and intensified charge coupled devices (iCCD) are common. Again the required analysis determines the detector best suited for the LIBS measurement, and among the listed detectors there is a significant difference between the PMT/APD and the PDA/CCD/iCCD.
The PMT and APD belong to a class of high-speed detection devices that are capable of providing a temporal history of the light incident on the detector down to a sub-nanosecond resolution. The PMT has a spectral response tailored to a spectral region, and when placed on a spectrometer can be used to monitor a single wavelength. This makes it useful for mapping out the decay response of the plasma light. The APD provides the same function and can be considered as the semiconductor analog to the PMT as it exploits the photoelectric effect and secondary emission to convert the incident light into electricity. In comparison with the PMT, the APD has both a high signal-to-noise ratio and a high quantum efficiency. In addition the APD can be used as a single photon detector when run in Geiger mode. Both detectors are very useful when detecting a single peak emission, but if numerous peaks must be monitored simultaneously, the second set of detectors would be better suited for the task.

The PDA and CCDs, belong to a class of detectors that are known as light integrating devices. Like the other class, these devices collect the incident light for a period of time, usually in the range of microseconds, and then the collected light which has been stored as charge is read out. The difference between the classes however, lies in the way the data is read out. This second class of detection devices are constructed as array devices, which means that although multiple lines may be monitored simultaneously, the array has a limited readout speed. The readout speed is restricted due to the fact that signal stored on each pixel has to be read out sequentially and one pixel at a time, and the array must be emptied before it can be reset for the next measurement. The PDA may have a faster readout rate than a CCD due to the fact that it is a one-dimensional arrangement of diodes. The CCD on the other hand is a two-dimensional array of photodiodes that can provide intensity information along two axes.
An additional element known as a microchannel plate (MCP)\textsuperscript{185} can be added to both the PDA and CCD in order to gate out the incoming light. By placing the MCP in front of the array detectors, it acts as an optical shutter, preventing light from reaching the detector when not activated, and when activated it acts as a signal amplifier as shown in Figure 31.

![Figure 31: Design of an intensified charge coupled device.](image)

The amplification of the light which can be on the order of a 1000 times is done by converting the light to electrons, amplifying the electrons, and then reconverting the electrons back to photons to be detected by the detector. By gating the MCP at appropriate times, nanosecond time resolution of the plasma light can be accomplished. Detection arrays outfitted with an MCP have been designated as intensified detectors, hence the difference between the PDA/CCDs and iPDA/iCCDs.

The selected detector used in the studies was a PIMax Gen II iCCD camera manufactured by Princeton Instruments/Acton. The camera was equipped with a UV sensitive 512 x 512 iCCD, where the pixel size was 12.8 µm x 12.8 µm.
4.3.1 Spectrometer Calibration

It was necessary to calibrate the spectrometer for both wavelength and spectral responsivity. The wavelength calibration was done by placing a mercury lamp (PenRay, UVP) in front of the fiber of the spectrometer which was coupled to the input aperture. Using the algorithm provided in the WinSpec 32 software, the offset, adjustment, and dispersion were measured and calculated for both the Czerny-Turner and Echelle spectrometers.

For measuring the spectral responsivity of the spectrometers it was necessary to use calibrated sources of known spectral irradiance (units of mW m\(^{-2}\) nm). Two sources were necessary due to the neither lamps covering the entire wavelength range. For the near UV range (200 nm- 400 nm) a deuterium lamp (Newport Corp, Oriel Part# 63945, Lamp Serial Number: 577443) was utilized. Alternatively, for the visible to infrared range (250 nm – 2400 nm) a tungsten lamp (Newport Corp, Oriel Part# 63355, Lamp Serial Number: 7~1621) was utilized. As there was overlapping regions between the lamps, the deuterium lamp was used until the 260 nm and the tungsten was utilized from 260 until 900 nm. The spectral responsivity was compared against the polynomial provided by NIST and using Equation (4.3.1) the adjusted or spectrally adjusted spectrum was obtained.

\[
\text{Spectrum}_{\text{real}} = \text{Spectrum}_{\text{acquired}} \times \frac{\text{Calibration Curve}}{\text{Spectrum}_{\text{lamp}}} \tag{4.3.1}
\]
Figure 32: Corrected spectrum for water taken under vacuum.
Deducing Primary Plasma Parameters from a Spectrum

As explained in Chapter 2, the plasma emission is highly dependent on its temperature and the diversity of its constituents. This is why the emission spectrum of a plasma is a diagnostic for the calculation of temperature and its densities.

4.4.1 Plasma Temperature

With the assumption that the population of the ionic energy levels follows the Boltzmann distribution:

$$\frac{N_i}{N} = \frac{g_k \exp\left(-\frac{E_k}{k_B T}\right)}{Z(T)}$$

(4.4.1)

where $g_k$ is the degeneracy or number of states with having energy $E_k$, $k_B$ is the Boltzmann constant, $T$ is the temperature, $N$ is the total number of particles and $Z(T)$ is the partition function.

The plasma temperature can then be determined from the line intensity of spectral emission lines from different upper levels. The spectral line radiant intensity is given by:

$$I = \frac{h v g A N}{4 \pi} = \left(\frac{h c N g A}{4 \pi \lambda Z}\right) \exp\left(-\frac{E}{kT}\right)$$

(4.4.2)

where $h$ is Planck’s constant, $c$ is the speed of light, $A$ is the transition probability, and $v$ is the line frequency. If the plasma conditions of LTE and optical thinness have been met, then using a pair of spectral lines with different upper energy levels of the same element and ionization stage, the plasma temperature can be calculated from the intensity ratio of the lines. An example of atomic copper lines with their oscillator strengths and energy levels is displayed below in Table 6.
Table 6: Copper spectral lines with the same ionization and different upper energy levels.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$g_i$</th>
<th>$g_k$</th>
<th>$A \ (s^{-1})$</th>
<th>$E_{low}$ (eV)</th>
<th>$E_{high}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>324.75</td>
<td>2</td>
<td>4</td>
<td>1.39E+08</td>
<td>0</td>
<td>3.817</td>
</tr>
<tr>
<td>406.264</td>
<td>4</td>
<td>6</td>
<td>2.10E+07</td>
<td>3.817</td>
<td>6.867</td>
</tr>
<tr>
<td>465.112</td>
<td>10</td>
<td>8</td>
<td>3.80E+07</td>
<td>5.072</td>
<td>7.737</td>
</tr>
<tr>
<td>521.82</td>
<td>4</td>
<td>6</td>
<td>7.50E+07</td>
<td>3.817</td>
<td>6.192</td>
</tr>
</tbody>
</table>

By considering two lines, $\lambda_{ij}$ and $\lambda_{mn}$, of the same species but with different upper energy level values, and upon linearization of Equation (4.4.2), the Boltzmann plot equation is obtained:

$$\ln \left( \frac{I_\lambda}{gA} \right) = -\ln \left( \frac{4\pi Z}{hcN} \right) - \frac{E}{kT}$$

(4.4.3)

Upon plotting the left-hand side of Equation (4.4.3) against $E$ results in a slope of $-1/kT$, and the plasma temperature can be obtained through linear regression without the knowledge of the first term on the right-hand side.

![Boltzmann plot example](image)

Figure 33: Example of a Boltzmann plot to determine the temperature of a plasma. The resulting excitation temperature is 0.79 eV ± 0.40%.
4.4.2 Electron Density

The H$_\alpha$ line has historically been used by astronomers to diagnose solar flares\textsuperscript{186} and the activity of the sun\textsuperscript{187}. The same line can be used to calculate the electron density of a plasma emission spectrum by measuring the Stark broadening of the line. In this case, the Balmer series transition H$_\alpha$ line, at 656 nm was monitored.

A typical H$_\alpha$ line recorded from a copper-sulfate pentahydrate doped water droplet is shown in Figure 34.

![Figure 34: H$_\alpha$ line for a copper-sulfate pentahydrate doped water droplet in air taken 140 ns after the formation of the plasma.](figure)

The FWHM of this particular H$_\alpha$ peak is 3.37 nm, and the corresponding temperature to this point (calculated using the method described in the previous section with Cu emission lines) was
found to be 0.79 eV with an error of 0.041 eV. The electron density can then be found using the following equation\textsuperscript{188}:

\[ N_e(H_\alpha) = 8.02 \times 10^{12} \left( \frac{\Delta \lambda_{1/2}}{\alpha_{1/2}} \right)^{3/2} \text{cm}^{-3} \]  

(4.4.3)

where \( \Delta \lambda_{1/2} \) represents the FWHM of the line in Å, \( \alpha_{1/2} \) is the half width of the reduced Stark profiles in Å, where precise values of \( (\alpha_{1/2}) \) for the Balmer series can be found in H.R. Griem’s \textit{Spectral Line Broadening by Plasmas}, Table AIII.a\textsuperscript{188}. The electron density from this \( H_\alpha \) was then calculated to be approximately \( 5.0 \times 10^{18} \text{ cm}^{-3} \).

### 4.5 Chemometric Plasma Models

Modern spectroscopy techniques such as LIBS routinely produce large amounts of data with high dimensionality. In the case of LIBS, the dimension of the data is a spectrum consisting of spectral intensities (photon counts) at several hundred wavelengths. In order to calculate mean values and their standard deviations for different variables of interest multivariate statistics are utilized; in addition the covariance or correlation which measure the strength of the relationships between variables may also be calculated\textsuperscript{189}. Using multivariate data can be confusing or misleading when one examines a single variable at time, as real differences may or may not show up in a single variable, but may require recognition of a multivariate trend. Therefore it is necessary to utilize chemometric techniques in order to: 1) eliminate noise and redundancy from the data, 2) extract as much information as possible from the data, and 3) sift through data quickly and efficiently to reveal relationships that will help to make accurate predictions about unknown samples\textsuperscript{190}.
In this study, a variety of chemometric techniques have been applied to the data generated by the LIBS technique. In order to eliminate redundancy and noise from the data an unsupervised dimensionality reduction technique known as Principal Component Analysis (PCA) was utilized. After which the data was arranged into user defined classifications based on analytical models constructed using techniques such as Target Factor Analysis (TFA), Linear Discriminant Analysis (LDA), and Quadratic Discriminant Analysis (QDA). The models were then employed to predict classifications of unknown samples, and were cross-validated using metrics such as the jack-knife technique, the Euclidean Distance, and the Mahalanobis Distance which compared the equivalency between the model and the test data. Lastly, the chemometric techniques were evaluated using Receiver Operator Characteristic (ROC) curves, and confusion matrix tables.

4.5.1 Pre-Processing

Before using the data in any way, it is pre-processed. Preprocessing is defined as any mathematical manipulation of the data prior to initial analysis in order to remove or reduce irrelevant sources of variation (either random or systematic). This procedure must be performed prior to any data handling in order to account for non-representative variations. Selecting an optimal preprocessing algorithm may require some iteration between the preprocessing and initial analysis step in order to ensure random and systematic variations are removed. It is necessary to review the data afterwards as multivariate statistical analyses is sensitive to preprocessing, and the entire analysis may be compromised from inappropriate preprocessing.
In general there are two methods to preprocess the data either by a single variable or by an entire sample. In variable preprocessing, one operates on one variable at a time over all the samples. Whereas in sample preprocessing, one operates on a single spectrum over which all the variables of interest are processed. It should be noted that if a sample is removed from the data set the preprocessing of variables would need to be repeated however, the sample preprocessing would not. In this study, preprocessing was conducted on both the variables and the spectra.

Preprocessing can be divided into four methods: normalization, weighting, smoothing, and baseline correction. Normalization is performed on data in order to remove the sample-to-sample variability, by adjusting all the samples to be on the same scale. In weighting, more influence is placed on either a variable or sample thus giving it more emphasis in the analysis. The last two methods smoothing and baseline correction, reduce the random variation and the systematic variation, respectively\textsuperscript{191}. In this study, three methods of preprocessing were utilized: normalization, baseline correction, and auto-scaling.

4.5.1.1 Baseline Correction

In this study, the intensity of a line was considered as the intensity value at the center wavelength of the emission. In order to determine this height, it is necessary to evaluate the background intensity level in order to remove any offset. To obtain this value of the intensity the raw signal was corrected for the background baseline as a linear function.
In order to remove the linear baseline, the spectrum must be put in the form of:\(^\text{191}\):

\[
S(\lambda) = S_o(\lambda) + (\alpha + \beta \lambda) + N(\lambda)
\]  \hspace{1cm} (4.5.1)

where \(S(\lambda)\) is the measured spectra, \(S_o(\lambda)\) is the pure signal (without noise and offset) and \(\alpha\) and \(\beta\) are the coefficients of the linear slope and \(N(\lambda)\) the noise of the spectrum. The coefficients \(\alpha\) and \(\beta\) are calculated by using two or more points that contain baseline information. This was done by selecting points above and below the peak, and fitting a linear line through them. The estimated line is then subtracted from sample vector, leaving the signal without the offset. The
points selected for estimating the linearly sloping baseline must be selected so as not to remove a portion of the sample vector.

![Figure 36: Baseline corrected spectrum.](image)

4.5.1.2 Normalization

Normalization is necessary to remove the sample-to-sample variability which is often largely due to the shot-to-shot stability of the laser, but may be attributed to a variety of other factors. In order to normalize a vector (a set of variables, or sample spectrum) there are usually three techniques to do so including normalization to a unit area, unit length, or normalizing in a range [0,1].

By dividing each element of the vector by the 1-norm \( \sum_{j=1}^{nvars} |x_j| \) the vector is normalized to a unit area of 1\(^{191}\). If one divides each element in the vector by the 2-norm, \( \sqrt{\sum_{j=1}^{nvars} x_j^2} \), the
vector is normalized to a unit length (length of 1). Lastly, it is possible to normalize the vector from values ranging from 0 to 1. This is accomplished by transforming the data such as:

\[ y_j = \frac{x_j - \min(x_j)}{\max(x_j) - \min(x_j)} \] (4.5.2)

Whichever technique is used for normalization, it is necessary to re-examine the data after the normalization process to ensure that important information has not been removed.

4.5.1.3 Auto-Scaling

Auto-scaling, which is accomplished by mean centering and variance scaling (in either order), is often used in the preprocessing of variables.\textsuperscript{191} This preprocessing step places the variables on a more equal scale, and removes any inadvertent bias. Mean centering is accomplished by first calculating the mean of the variable over the samples. The mean value is then subtracted from all the elements in the vector. Mean centering is followed by variance scaling, which is achieved by dividing each element in the variable vector by the standard deviation of the variable. Variance scaling is performed to remove artificial weighting that may be imposed by the scale of the variable.

4.5.2 Constructing Analytical Models

4.5.2.1 Principal Component Analysis

Principal Component Analysis (PCA)\textsuperscript{192-194} is a multivariate technique that is used to reduce the dimensionality of the data by optimizing the number of informative variables. PCA relies on the fact that the original variables are not necessarily independent of one another, but have a
correlation due to underlying information. In general PCA can be summarized as a projection of the multivariate data into a lower dimensional subspace by transforming the originally selected informative variables into a new set of orthogonal and uncorrelated variables. The new variables are called Principal Components (PCs) and are a linear combination of the original correlated variables. The amount of information conveyed by each principal component is optimized to represent the maximum variance. In addition, the optimization of the PCs has the additional advantage of removing redundancy and noise from the data set.

4.5.2.2 Constructing an Analytical Model for Dimensional Reduction

In order to apply PCA to a data set, the data \( (d_{i,k}) \) must first be separable into the following\(^{193}\):

\[
d_{i,k} = \left[ \sum_{j=1}^{n} r_{i,j} c_{j,k} \right] + \text{error} \tag{4.5.1}
\]

where \( d_{i,k} \) is the spectral data that is made up of the contributing spectra (where \( k \) is the variable of the \( i^{th} \) sample). The spectral data can be further decomposed into a product of two matrices and written in matrix notation as:

\[
[D] = [R]_{abstract} [C]_{abstract} \tag{4.5.2}
\]

where the two matrices are abstract. In this case, the full data matrix consisted of the samples and the variables of interest: atomic carbon C I at 248 nm, hydrogen alpha line H\( \alpha \) at 656 nm, atomic nitrogen N I at 746 nm, and atomic oxygen O I at 777 nm peaks as well as the diatomic species CN violet bands (\( \text{B}^2\Sigma - \text{X}^2\Sigma \)) at 388 nm and the C\(_2\) Swan bands (\( \text{d}^3\Pi_g - \text{a}^3\Pi_u \)) at 516 nm were selected. Using five spectra for each sample from a test scenario, the intensity from the selected
spectral line emission is averaged for each variable per respective sample. In order to determine if the variable peak is statistically significant, the peak intensity was required to be 3 times larger than the surrounding noise; else a null value is placed in the variable’s place holder. This data was then used to construct the data matrix, which is shown in Figure 37.

![Data Matrix](image)

**Figure 37: Construction of the Data Matrix**

In order to construct the PCs, the covariance matrix of the data is first created. The covariance matrix is necessary in order to determine the highest variance and the lowest covariance among the variables. The data matrix is pre-multiplied by its transpose, the product of which is the covariance matrix (Figure 38).

\[
Z = D^T D \quad \text{or} \quad Z = [D][D]^T
\]  \hspace{1cm} (4.5.3)

where \(Z\) is the covariance matrix, and depending on how \([Z]\) is formed determines the size of the matrix that the computer must sift through. For instance if \([D]\) is a 6 x 36 matrix, the covariance matrix can either be a 6 x 6 (which examines the covariance of the variables), or 36 x 36 (which examines the covariance of the samples) matrix dependent on the formulation utilized. However, the data analysis process is consistent either way and the results are equivalent.
Performing an eigenanalysis (diagonalization) on the covariance matrix yields the variance of the PCs (eigenvalues) and the PCs themselves (eigenvectors [C]) which form a new basis of orthonormal vectors. The eigenvectors coefficients (Loadings) are the coefficients of the linear combination of the original variables.

Figure 39: Diagonalization of the Covariance Matrix.
A user-defined tolerance level is then selected based on the variance to determine the number $n$ of PCs that are necessary to create the analytical model. As an example, the PCs with the variance contributing to 99% of the total variance were generally selected, in order to optimize the data and reduce the noise and redundancy in the data set. In the case illustrated in Figure 40, the first PCs constitute over 99% of the variance for the data set. Therefore the last three PCs would only add noise and redundancy back to the data.

![Figure 40: Results of the eigenanalysis performed on the covariance matrix.](image)

Once the user-defined limit has been selected, data is transformed into the new coordinate system by:

$$[R^+] = [D][G^+]^T$$

(4.5.4)

By projecting the original data matrix onto the subspace of the first three PCs yields the *Model Scores* (Figure 41), or the coordinates of the data matrix transformed into the new basis.
The model scores then constitute the reference or the library against which tests of the same scenario are compared.

4.5.3 Cross-Validation of Analytical Model

In order to test the predictions of the analytical model for unknown samples, forty spectra of known material per sample were collected. The analytical model was constructed utilizing the first twenty shots, and the second twenty shots were used as test cases. Once the eigenvectors and eigenvalues were known for the first twenty spectra, and the appropriate tolerance of variance was selected, a second set of scores known as test score were constructed. The same procedure of generating the library data matrix is followed in order to produce the second data matrix. The second data matrix was multiplied by the same PCs generated in the model construction, the product of which yielded the Test Scores or predicted scores (Figure 42).
The test scores are then compared to the model scores, by calculating the Euclidean Distance between them.

4.5.3.1 Euclidean Distance Metric

PCA is not a true classification technique, however the projection of the data into a lower dimensional space may provide a useful graphical display of the relationships among samples and of the clustering of samples into groups\textsuperscript{189}. When trying to place an unknown sample as a member of a particular cluster there is a need for a quantitative assessment. In this case, the quantitative assessment is for the pattern similarity or grouping that is found by PCA. If each pattern is treated as a point in a p-dimensional space, then simplest measure of distance between patterns is based on the Pythagorean Theorem, and is known as the Euclidean Distance\textsuperscript{191, 194}. Assume in Figure 43 that the reference group is the middle point and the rest of the points are unknown samples.
Using the Euclidean Distance, the closer the points the smaller distance, then the more likely the similarity of the points whereas the further apart the points the more dissimilar the groups. In Figure 43, T1 above the central point is the closest point, and T4 is the furthest point.

The Euclidean Distance was used to measure the distance between the test model scores and the library scores. For validation purposes the unknown samples were just the second set of spectra of the known samples. A Euclidean Matrix was built comparing the model score along the vertical and the test scores along the horizontal as displayed in Figure 44.
Along the diagonal of the Euclidean Matrix the distance in the ideal case would be zero, since the sample is compared to itself. However, due to uncontrollable factors i.e., the shot-to-shot stability of the laser or the amount of residue in the shot, the distance may not be null. Distances in the off-diagonal however, should result in distances greater than those in the diagonal due to the fact that different samples are being compared.

4.5.4 Receiver Operator Characteristic Curves

Receiver Operator Characteristic (ROC) curves are used to evaluate the analytical models that are constructed from PCA. Traditionally, the ROC curve is comprised of a plot of the sensitivity (the proportion of the correctly identified samples) versus the 1-specificity (the proportion of incorrectly identified samples). The values constituting the sensitivity are known as the “true positives”, while the values constituting the 1-specificity are known as the “false positives”
Figure 45 shows examples of ROC curves. Curve A represents an ideal ROC curve (in this case perfect discrimination) in which the area under the curve is 1.0. This means that all of the true positive values are assigned before any false positive value based on a given figure of merit (the Euclidean distance in the case discussed here). The values on the diagonal of the matrix in Figure 43 are all smaller than the values off-diagonal. Curve D on the other hand, represents the opposite extreme case, that of random discrimination. This means that there is equal probability of assigning either a true positive or a false positive. As such, the area under Curve D is 0.50. Curves B and C represent examples of real solutions, and since the Curve B has a greater area than that of Curve C, Curve B would be considered a better analytical technique than the technique used by Curve C. The higher the area under the curve results in the higher the specificity and sensitivity of the analytical technique.
4.6 Constructing Supervised Analytical Models

As previously stated, PCA is not a classification technique but a data reduction technique that groups samples by the largest variance. While identifying differences between patterns may lead to an understanding of the chemical basis, variance is not discrimination. The goal of classification is to establish rules that can be reliably used for predicting group memberships of new data on the basis of data with known group memberships\textsuperscript{197}. In addition, it is necessary to validate and evaluate the performance of these rules. Lastly, unlike PCA in which the group information was not required thus defining it as an unsupervised procedure, classification techniques are categorized as supervised methods. This means that in a classification technique, the groups to which objects belong are already known, and the multivariate data structure of the group objects are described by the characteristics of the group.

4.6.1 Target Factor Analysis

Target Factor Analysis (TFA)\textsuperscript{193} serves a mathematical bridge which converts abstract solutions generated by principal component analysis (PCA) into physically significant parameters or factors that are representative of the original experimental data. Target Factor Analysis (TFA) also allows for the verification of the presence or absence of suspected components. This is done using the truncated score matrix obtained from the PCA model:

\[
[R^\dagger] = [D][C^\dagger]^T
\]  \hspace{1cm} (4.6.1)

The \(l\)\textsuperscript{th} column of the transformed row matrix is obtained after multiplying by a transformation vector:

\[
\bar{R}_l = [R^\dagger]T_l
\]  \hspace{1cm} (4.6.2)
where $\vec{R}_l$ is the predicted vector and $T_l$ is the transformation vector. The transformation vector is obtained by:

$$T_l = \left[\lambda^\pm\right]^{-1} \left[R^\pm\right]^T \vec{R}_l$$

(4.6.3)

where $\left[\lambda^\pm\right]$ and $\vec{R}_l$ are the diagonal eigenvalue matrix composed of only the $n$ principle eigenvalues and a test vector, respectively. Thus using a test vector $\vec{R}_l$, a predicted vector $\vec{R}_l$ can be calculated:

$$\vec{R}_l = \left[R^\pm\right]\left[\lambda^\pm\right]^{-1} \left[R^\pm\right]^T \vec{R}_l$$

(4.6.4)

Average correlations between the test vector and the resulting predicted vector are measured and evaluated.

$$r = Corr[\vec{R}_l, \vec{R}_l]$$

(4.6.5)

The strength of the TFA process relies on the fact that the created library contains only the samples of interest. This means that the library has to be made using a stable and repeatable technique, as well as pure samples. After the library has been created, the unknown samples can be compared against it by using the components of the library as $\vec{R}_l$, one at a time. If the unknown sample contains elements present in the library then it is identified as such, regardless of background and other interferents.
4.6.2 Linear Discriminant Analysis

Linear discriminant analysis (LDA) was first derived by R.A. Fisher\textsuperscript{198} in 1936 as a method for discriminating between varieties of iris flowers based on physical measurements. Also known as canonical variates analysis, LDA seeks to minimize the distance between samples of the same group, while maximizing the distance between the groups this criterion is known as the Fisher ratio. Similar to PCA, LDA constructs a new set of axes that best separates the data into groups. The criterion is that the groups are separated as much as possible and not an unsupervised variance\textsuperscript{199-201}. A linear combination of the original x-variables form the discriminant axes known as canonical variates or CVs.

Canonical variates are determined by finding the eigenvectors of the Fisher ratio, represented in matrix form as:

$$W^{-1}B$$

(4.6.6)

where $W^{-1}$ represents the inverse of the pooled within-groups sum of squares and cross product-matrix, and B represents the between-groups sum of squares and cross-products matrix. The sorted eigenvalues of the Fisher ratio represents the between–to-within groups variance accounted for by each CV. Similar to PCs in PCA, the number of CVs in LDA can never exceed either the number of groups minus one, or the number of variables\textsuperscript{189}. It should also be noted that while the Fisher method does lead to linear classification functions, the method does not explicitly require the covariances to be equal for the multivariate normal distributions of the groups\textsuperscript{197}. However, failure to fulfill these assumptions leads to suboptimal minimizing of misclassifications.
4.6.3 Quadratic Discriminant Analysis

If the covariances between canonical variates are found not to be equal as shown in Figure 45, the linear rule will not be optimal in terms of a minimum probability of misclassification. In this case the data may be better described by a quadratic relationship. Quadratic discriminant analysis (QDA)\textsuperscript{197, 202} does not require homogeneity of covariances\textsuperscript{203}. This is advantageous over the LDA, because in addition to discriminating differences among variables and variances, QDA can also discriminate among means, and barring any differences between the means accurate classifications can still be derived,

There is a data restriction that must be adhered in order to accurately utilize QDA. Friedman\textsuperscript{204} has pointed out that analysis using the quadratic relationship is ill-posed if the class sample size (N\textsubscript{k}) is smaller than or equal to the dimension of the measurement space (p), and very poorly posed whenever N\textsubscript{k} is not considerably larger than p. For example, if the problem has five variables then the discriminant function for LDA and QDA is, respectively\textsuperscript{205}:

$$f = a + bx_1 + cx_2 + dx_3 + ex_4 + fx_5 \quad (4.6.7)$$

$$f = a + bx_1 + cx_2 + dx_3 + ex_4 + fx_5 + gx_1x_2 + \ldots + px_4x_5 + qx_1^2 + \ldots + ux_5^2 \quad (4.6.8)$$

Accounting for mixed terms the quadratic model needs to estimate 21 parameters for each group, in contrast to the six parameters needed for the linear model. Not all of the parameters are independent however, and thus the data population does not require a strict number of (3 x 21) cases for a fit to the quadratic model. Tests must be run however to guarantee that there is not an over-fitting of the data.
4.6.4 Classification Cross-Validation and Metrics

Similar to the PCA, the analytical models constructed from the classification techniques utilized first set of spectra, while the second set of spectra were used as test cases for cross-validation purposes. However, instead of using the Euclidean Distance as metric the Mahalanobis distance\textsuperscript{189,206} was selected. The Mahalanobis distance, \( D^2 \), is a covariance adjusted distance measure, which is calculated from the centroid of a specified group of samples, and takes into account both the variances of the individual variables and their correlations with one another\textsuperscript{189,204}, and is represented by\textsuperscript{197}:

\[
D^2 = d'Z^{-1}d
\]  \hspace{1cm} (4.6.8)

where \( d \) represents the vector of differences at each variable between a point and a group mean, and \( Z^{-1} \) is the inverse of the covariance matrix for the group to which the distance is calculated\textsuperscript{206,207}. In addition, the Mahalanobis distance can be employed to plot ellipses (or ellipsoids) of chosen levels of confidence around each group. In Figure 46 ellipses of equal confidence levels are drawn around group means represented as points. It should be noted that if the ellipses tilt in different directions than the covariance matrices are not equivalent.
In Figure 46 the smallest Mahalanobis distance from the center sample to the closest of the group centroids is represented by T2. Points T3 and T4 represent group centroids of equal distance from the reference sample, while T1 represents the largest Mahalanobis distance from the central sample. In regards to the ellipses, the ellipse for the group at the top is not tilted representing a very low possibility that the sample from this group to be found at the position of the center sample, whereas the orientation of the T2 ellipse makes it highly likely that sample may have originated from this cluster.

4.6.5 Jack-knife Technique

The Jackknife method\cite{208,209} of removing a single case at time and using it as test case serves as a form of cross-validation and removes bias. For a total of N samples, the discriminant function is computed using N-1 samples. A single sample is left out and then classified on the basis of the function rule derived for the N cases. This process is repeated until every sample in the data set
has been left out once and classified. The jack-knife technique provides both a method of using the same sample for both rule derivation and classification, as well as an unbiased estimate of the accuracy that could be expected in a completely new sample. If the percentage for correct classification in the classification matrix is significantly lower in the respective Jackknife prediction than it may be indicative of too many predictors in the model\textsuperscript{205}.

4.6.6 Confusion Matrices

The confusion matrix is another method similar to the ROC curve examines the performance of classifiers. However, the confusion matrix yields more information beyond the specificity and the sensitivity\textsuperscript{210} as shown in Table 7.

Table 7: Example of a confusion matrix.

<table>
<thead>
<tr>
<th>Actual</th>
<th>Predicted</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Negative</td>
<td>Positive</td>
</tr>
<tr>
<td>Negative</td>
<td>TN</td>
<td>FP</td>
</tr>
<tr>
<td>Positive</td>
<td>FN</td>
<td>TP</td>
</tr>
</tbody>
</table>

where $TN$ (True Negatives) is the number of predicted cases that were correctly identified as negative, $FP$ (False positives) is the number of negative cases that were incorrectly identified as positive, $FN$ (False negatives) is the number of cases positive cases incorrectly identified as negative, and $TP$ (True Positives) is the number of correctly identified positive cases. From the confusion matrix, the sensitivity can be deduced:

$$Sensitivity = \frac{TP}{TP+FN} \quad (4.6.9)$$

as well as the specificity:

$$Specificity = \frac{TN}{TN+FP} \quad (4.6.10)$$
In addition to these metrics, the precision ($P$) which is the proportion of the predicted positive cases that were correct can be found by:

$$P = \frac{TP}{TP+FP} \quad (4.6.11)$$

as well as the accuracy ($AC$), defined as the proportion of the total number predictions that were correct, which is found by:

$$AC = \frac{TN+TP}{TP+TN+FP+FN} \quad (4.6.12)$$

These additional calculated values give a clearer picture as to the overall performance of the classifying technique.
5 PARAMETRIC STUDY OF SINGLE SHOT LIBS OF ORGANIC RESIDUES

5.1 Motivation

The strength of LIBS, besides its simplicity in instrumentation, is its ability to adapt the excitation source to the analyte. As mentioned earlier, however, in order to improve the sensitivity and selectivity of LIBS for detection purposes, an optimal LIBS system configuration must be determined. This chapter will explore the parameters necessary for an optimized collection of a LIBS spectrum of a heterogeneous residue placed on a non-metallic substrate, all in a single shot. Protocols for both making and placing a residue on a silicon wafer will be described. A study of parameters that affect detection such as the laser wavelength, pulse duration, and atmosphere will be conducted.

In addition to the sensing and detection parameters, an analytical model built using principal component analysis (PCA) will be explored, in order to ascertain whether variance is enough for natural groupings to occur. The principal components (PCs) that are calculated from the PCA model will be examined, as well as the respective score plots that are generated from the PCs. Lastly the analytical technique is evaluated through receiver operator characteristic (ROC) curves. From this systematic study, parameters for an optimized setup will be selected.

5.2 Experimental Setup

The laboratory setup that was used for these parameter studies is shown below in Figure 47. Important pieces of the setup that enabled control of parameters are described below in detail.
5.2.1 Atmosphere

The ambient atmosphere, which has been pointed out previously, plays a vital role in the LIBS process. Two ambient atmospheres were selected for this set of experiments, air and argon. Argon was selected for three reasons: 1) it is a noble gas and thus should be inert under most conditions, 2) it has a higher vapour pressure than air and should displace air, and 3) it is less expensive than other noble gas. The atmosphere was controlled by placing the sample into sample holders as shown in Figure 47. The first sample holder was used in the nanosecond experiments, and made from quartz glass with a polytetrafluoroethylene (PFTE) cover. A small hole was placed in the cover to allow for an argon jet of 20 psi to flow into the sample chamber. The quartz, while fairly transparent to most wavelengths, did have some absorption of the laser energy. While using the femtosecond laser white light was generated in the quartz preventing the formation of a plasma. In order to address this issue, the second sample holder was used. In this
case, the opening to the sample holder was unobstructed allowing the laser to form a plasma on the sample. The hole in the top allowed for a jet of argon to flow over the sample. This jet was found to suppress the air recombination similar to a full ambient argon atmosphere.

5.2.2 Lasers

Exploration and control of the pulse duration was done using both a femtosecond and a nanosecond laser system. The femtosecond laser system produced a pulse-energy of 1.4 mJ, and had a beam diameter of approximately 6 mm FWHM which was focused using a 100 cm convex lens, resulting in an irradiance of $1.47 \times 10^{14}$ W/cm$^2$. The pulse width was approximately 40 fs and was centered at wavelength of 800 nm. Although the laser was run at repetition rate of 10 Hz, a mechanical shutter was used in order to allow for a single shot analysis.

The nanosecond segments of the experiments were performed using a Quantel Brilliant Laser. The beam diameter was approximately 6 mm and was focused using a 7.5 cm convex lens. A light valve was used to reduce the pulse energy to 3.5 mJ, which resulted in an irradiance of $6.20 \times 10^8$ W/cm$^2$. The same Quantel laser was used to perform the experiments at 266-nm as well. The pulse energy at 266-nm was set to match the tests run at 1064-nm. In order to ensure that only a single shot was fired, the laser’s single shot button was used.

5.2.3 Spectrometers

In this study, the spectrometers would need to cover a wavelength range from 240 – 800 nm, as the peak for the variables are in this range. The variables that were selected were the C I (247 nm), the CN Violet bands (388 nm), the C$_2$ Swan bands (516 nm), the H$_\alpha$ (656 nm), the N I (746 nm), and the O I (777 nm) Due to limitations of the spectral range of the Czerny-Turner (C-
T) spectrometer equipped with a 600 lm/mm grating, it was necessary to concentrate on each variable of interest separately. Unlike the Echelle spectrometer, where the whole spectrum could be collected in a single shot, the C-T spectrometer would have to combine at least five spectra in order to generate a single spectrum ranging from 240 – 900-nm, as shown in Figure 48.
Figure 48: Czerny-Turner spectrometer (top 6 graphs) compared with an Echelle Spectrometer.
This brought up issues of reproducibility due to the laser’s shot-to-shot stability, as well as the amount of residue collected in each shot, since each shot had to be taken on a fresh sample spot. An example of this problem is illustrated below in Figure 49.

Assuming that A, B, and C, are spots that have been sampled by the laser, then the trouble in assembling an accurate library with the C-T becomes apparent due to the fact that only one variable could be recorded at time. Thus, if A, B, and C were to represent the variables carbon, CN, and C₂, each variable would contain different amounts of residue which could lead to an unfair weighting being placed upon certain variables and thus skew the results leading to possible misclassification of the organic samples. In addition, it should be noted that the shot-to-shot stability of the laser source could provide different coupling effects as well as plasma temperature effects leading to further misclassifications. With an Echelle spectrometer, all the variables of interest are caught in a single laser shot, such that C, CN, and C₂ are recorded simultaneously for A, B, and C respectively. As such, in order to treat the C-T data in the same
fashion as the Echelle, it would be necessary normalize each window to account for the shot-to-shot fluctuation, as well as ensure that each shot had the same amount of residue collected as the others. In this regard, it was easier to treat the Echelle data more along the lines of the C-T. Equivalent regions of interest or windows containing the variables selected for the C-T data were used in the Echelle data.

The Echelle also made it possible to study the spectrum as whole, such that if necessary, entire spectra could be used as variables instead of using certain emitters as representatives for the sample. However, in electing to use the whole spectrum instead of selected peaks care must be taken to ensure that the spectrum does not contain any spectral interferents.

5.2.4 Samples

5.2.4.1 Substrate

The selection of the substrate on which the sample is placed, was found to play a major role in LIBS. Many LIBS studies that have investigated organic residues have often placed their samples of interest on metallic substrates\textsuperscript{174, 175}. The main reason for this choice was the ease of separating the signature of the residues and the substrate. But it does not necessarily identify all of the matrix effects that can occur between the laser pulse, the atmosphere, the sample, and the substrate. However, metallic substrates are often selected due to the information that can be extracted from using their rich spectrum in the UV and visible wavelength range, such as the plasma temperature and plasma density mentioned in sections 4.4.1 and 4.4.2, respectively.

Caution must be taken when selecting a metal as a substrate. Studies have shown that the metals can increase the ablation rate, and thus increase the temperature of the plasma, leading not only to a more efficient line excitation, but also to higher fragmentation and atomization rates of
residue material. While the increase in temperature may lead to desirable effects in helping to detect organic signatures, in real world scenarios it is very unlikely that the organic signatures will be on such simple substrates. Substrates of interest could include polymer coatings such as car paint.

The ultimate goal of residue detection lies in the ability to detect a residue on an organic substrate. Below in Figure 50 is a LIBS spectrum of white car paint. The spectrum is very complex and has a number of emitters; hence, detecting a residue on such a substrate would yield quite a challenge.
Figure 50: Spectrum of white car paint. (Divided into three spectra in order to show variables of interest.)
From Figure 50, it should be noted the spectral lines that would be used for detection of the residue are already present in the substrate. While not included in this investigation, the detection of organic residue on an organic substrate was studied at a later time. From Figure 51, which is a spectrum of graphite, the spectrum is not as complex, due to the limited number emitters in the visible and the UV, and the emitters from the substrate overlap those that are being sought for characterization of the residue.

![Figure 51: Spectrum of graphite (experimental conditions).](image)

In an effort to move towards a real world scenario substrate such as the car paint or plastics where there may be few or many emitters in the spectral range of interest, this study was conducted using silicon wafers as a substrate for two main reasons. First, the silicon as shown in Figure 52 was found not to interfere or mask any lines of interest that would be used to identify the organic residue.
Secondly, like the metal substrate, the silicon may increase the temperature slightly, but the ionization energy needed for the silicon is closer to that of non-metals. As previously mentioned in Chapter 2, the ionization energy (IE) is the minimum energy necessary to remove the most weakly bound electron from the atom, and the work-function (WF) is the minimum amount of energy needed for an electron to escape from the surface of a material. The work-function for aluminum and silicon are 4.02 eV and 4.52 eV respectively, whereas for solid polymers the wave-function can range from 4.3 -6 eV. The ionization potential for aluminum and silicon are 5.99 eV and 8.15 eV, respectively, whereas for solid polymers the IP ranges from 10 – 13 eV. Both the IP and WF for silicon are more in line with the polymer or organic substrates, and this
should have decreased the amount of collisional heating contributed from the silicon, in comparison with a metal such as aluminum.

5.2.4.2 Residues

A variety of organic samples was used throughout the experiment, and can be found in the Appendix. These samples were predetermined based on their chemical structures. They were either energetic compounds (explosives), compounds with similar structure but not explosives (explosive-like), non-explosive organic compounds, and lastly polymers. Of the sixteen samples fourteen were prepared in a similar fashion. The organic sample was measured and mixed with the respective amount of solvent in order to achieve a 1000 ppm solution. Table 8 lists the organic samples and their respective solvents.
Table 8: Organic material and the respective solvents.

<table>
<thead>
<tr>
<th>Organic Sample</th>
<th>Abbreviation</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Dinitrobenzene</td>
<td>1,4-DNB</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>2,4-Dinitrotoluene</td>
<td>2,4-DNT</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Tris (hydroxymethyl) aminomethane</td>
<td>THAM</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Theophylline</td>
<td>TP</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Cyclo-1,3,5- trimethylene-2,4,6- trinitramine</td>
<td>RDX</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>2,4,6- Trinitrotoluene</td>
<td>TNT</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Pentaerythritol tetranitrate</td>
<td>PETN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>1-Cyanonaphthalene</td>
<td>1-CN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Pthalic Acid</td>
<td>PA</td>
<td>ethanol alcohol</td>
</tr>
<tr>
<td>1,2,4,5- Benzenetetracarboxylic Acid</td>
<td>1,2,4,5 BTCA</td>
<td>ethanol alcohol</td>
</tr>
<tr>
<td>Benzophene</td>
<td>BP</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>BA</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Anthracene</td>
<td>Anth</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>Fluor</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>PS</td>
<td>hexane</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>PIB</td>
<td>hexane</td>
</tr>
</tbody>
</table>

Using an Eppendorf pipette, 70 µL of solution was deposited onto a 1 cm x 1 cm square silicon substrate. Two minutes for the acetonitrile, and four minutes for the hexane and ethanol alcohol.
was allowed to elapse in order to let the solvent evaporate thus leaving only an organic residue. The only two samples that were prepared in a different manner were the polystyrene and polyisobutylene. Due to the nature of these samples it was necessary to spin coat the organic substances onto the silicon, and follow with a post bake of approximately one minute. An estimate for the deposition of the organic onto the silicon substrate was calculated to leave a residue of approximately 50 µg/cm². This calculation made the assumption that the 70 µL of the 1000 ppm solution was distributed evenly on the 1x1 cm substrate. On average, for the spin-coated materials a scratch-test done on the residue approximated a thickness of 500 nm.

![Residue Examples](image)

Figure 53: Example of an explosive-like (2, 4 dnt), non-explosive organic (fluoranthene), and thin-film polymer (pib) residue on a silicon wafer.

Each residue dried on the silicon wafer in a different crystallization, making it hard to determine what a typical residue would be.

As a result of the evaporation technique the organic residues varied in their homogeneity across the substrate. Some residues appeared to have analyte everywhere, while in other samples, there appeared to be large areas where analyte was absent, as displayed in Figure 7. This is important to note, due to each laser shot occurring on a fresh spot on the sample. As a consequence of this random sampling, the area interrogated may or may not have contained any of the organic solute.
The inhomogeneity of the residue also raised the issue of the development of a stable library. In order to build the library of spectra in which to compare against, it is important that the library spectra contain analyte. While in the lab, this problem can be resolved by accurately mapping the residue on the substrate and tracking where the laser has hit; this is not the case for field analysis. With LIBS’s ability to remotely sample, it may not be possible to map the sample due to various reasons (toxic environment, hazardous objects impeding physical sampling, etc.), thus an alternative methodology has to be developed in order to determine if the spot of interest contains analyte. A simple solution is to search for carbon signatures including atomic carbon, or CN and C₂ molecular emission.

5.3 Results and Discussion

5.3.1 Normalization of Analytical Model

Before the analytical model could be constructed the data needed to be normalized in order to minimize inherent variance that may have been introduced into the experiment such as the variation of laser power from shot-to-shot. As shown in Table 9, there was a high variability in the UV regime which could be attributed to the outer-cavity frequency conversion crystals. In addition, it was necessary to normalize the data in order to account for the hydrogen which was highly variable. If left un-normalized, the hydrogen peak could easily dominate the spectrum, thus biasing the data.
Table 9: Laser statistics at various wavelengths.

<table>
<thead>
<tr>
<th>Laser Statistics</th>
<th>1064 nm</th>
<th>266 nm</th>
<th>800 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>1064 nm</td>
<td>266 nm</td>
<td>800 nm</td>
</tr>
<tr>
<td>Average Value</td>
<td>3.36 mJ</td>
<td>3.04 mJ</td>
<td>1.35 mJ</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>47 µJ</td>
<td>0.454 mJ</td>
<td>66 µJ</td>
</tr>
</tbody>
</table>

A normalization algorithm was written in-house and had to be slightly modified for the different spectrometers. After collecting the peaks for each variable for the ten spectra, the mean of each variable was then determined. As previously mentioned in section 4.6.1, a data matrix was constructed with the samples as the rows and the mean values of the variables C, CN, C₂, H, N, and O as the columns. In order to normalize the data matrix, each sample's mean variable intensity was divided by the 2-norm. This normalization method as pointed out in section 4.5.1.2 resulted in vectors of unit lengths.

5.3.2 Principal Component Analysis

As discussed in section 4.6, while PCA is not a classification technique it can be used to give insight into inherent structures in the data. In this study, PCA was used as a mathematical tool to transform the variables of interest into uncorrelated orthogonal variables. By keeping track of the samples throughout the mathematical process, it was possible to label the scores in the new coordinate system. This allowed for a comparison of the data based on variance and pre-determined groups.
The selected samples were separated into defined classes based on their molecular structure. These classes were known as the nitrogenated samples (nitros), the oxygenated samples (oxys), the polycyclic aromatic hydrocarbons (PAHs), cyanides (cyanos), and polymers and are shown Table 10.

Table 10: Organic samples based on user defined groupings.

<table>
<thead>
<tr>
<th>Group</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitros</td>
<td>1,4-DNB</td>
</tr>
<tr>
<td></td>
<td>2,4-DNT</td>
</tr>
<tr>
<td></td>
<td>THAM</td>
</tr>
<tr>
<td></td>
<td>TP</td>
</tr>
<tr>
<td></td>
<td>RDX</td>
</tr>
<tr>
<td></td>
<td>TNT</td>
</tr>
<tr>
<td></td>
<td>PETN</td>
</tr>
<tr>
<td>Cyanos</td>
<td>1-CN</td>
</tr>
<tr>
<td>Oxys</td>
<td>PA</td>
</tr>
<tr>
<td></td>
<td>1,2,4,5 BTCA</td>
</tr>
<tr>
<td></td>
<td>BP</td>
</tr>
<tr>
<td></td>
<td>BA</td>
</tr>
<tr>
<td>PAHs</td>
<td>Anth</td>
</tr>
<tr>
<td></td>
<td>Fluor</td>
</tr>
<tr>
<td>Polymers</td>
<td>PS</td>
</tr>
<tr>
<td></td>
<td>PIB</td>
</tr>
</tbody>
</table>
This study was considered a pseudo-blind test as no physical verification was made as to whether a shot hit an area containing residue, as would be the case out in the field. However, enough shots were taken to ensure that at least twenty spectra contained signal. Signal from the laser shot was verified by using a signal-to-noise ratio for the variables. From the twenty shots, the first ten shots comprised the data for the model, and the test case was composed of the second ten shots. For all the tests studied three PCs were necessary for the analysis as they constituted a cumulative variance greater than 95% of the data.

5.3.3 Results Involving Atmosphere

The first parameter studied using a PCA analytical model was the background atmosphere above and surrounding the sample. The argon atmosphere serves to confine the plasma expansion as the density of the argon gas is higher than either the vacuum or air atmosphere. This dense atmosphere around the plasma prevents excited atoms from forming stable compounds such as oxides\textsuperscript{212}. In addition, the smaller thermal conductivity and heat content of the argon (0.0387 cal/cm s deg and 0.0763 cal/g deg) in comparison with N\textsubscript{2} and O\textsubscript{2} (0.0566 and 0.0573 cal/cm s deg, respectively, for the thermal conductivity and 0.178 and 0.156 cal/g deg, respectively), serves to increase the intensity of the spectral emission brought about by the high plasma temperature and prevent plasma cooling thus elongating the period of emission\textsuperscript{213}.
The argon atmosphere did help to quench the air recombination effects as shown in Figure 54. As a result the C I emission was stronger in the argon environment, as opposed to the CN band which had a stronger signal in the air atmosphere. This difference should be made evident in the eigenvectors or loadings from the PCA, as they should not be equivalent in both atmospheres. The variance in the CN should have been high for the samples in argon, as only the cyano group had a natural CN bond. The variance in the C and N variables would probably not have had as dynamic a variation as they were inherent in most of the samples. This hypothesis was studied with the examination of the eigenvectors yielded from PCA.

The amount of variance represented by PC1 is shown below in Table 11, for both atmospheres.
If 90% accuracy for reconstituting the data is selected, then Table 11 indicates that only PC1 is necessary, and if only the first PC is selected as a means of separation the resulting grouping would have been equivalent. The differences in the separation of the groups between the two atmospheres lie mainly in the composition of PC2 and PC3, which described similar amounts of variance in both regimes. For this study the rule of one was selected, which meant that if an eigenvalue percent was greater than 1% then it was kept. A caveat to this rule allowed PC3 in the air data to be kept due to the relatively large difference between PC3 and PC4.

Figure 55: Principal component composition for 1064 nm in air and argon atmospheres.
Contrary to the first hypothesis posed above, Figure 55 indicates that PC1 had a similar composition in both atmospheres. In air the PC1 was constructed of C (0.032 a.u.), CN (0.135 a.u.), C2 (0.038 a.u.), H (0.405 a.u.), N (0.29 a.u.), and O (0.839 a.u.), whereas in argon PC1 was constructed C (0.1 a.u.), CN (0.16 a.u.), C2 (0.032 a.u.), H (0.386 a.u.), N (0.286 a.u.), and O (0.638 a.u.). The values are fairly similar but the argon relies more on the C by 0.068, and the air relies more on the oxygen by 0.201 a.u..

PC2 in argon was found to lack a dependency on carbon (0.004 a.u.), but was strongly dependent on hydrogen (0.779 a.u.), followed by a nearly equivalent dependency on CN (0.545 a.u.), and O (-0.685 a.u.). The equivalent dependence indicates that the data has no preferential alignment with either of these two original variables. A significantly smaller but equivalent dependence was placed on the C2 (0.059 a.u.) and N (-0.082 a.u.) emitters. Similar to the PC2 in argon, PC2 in air had a strong dependency on CN (0.659 a.u.), H (0.605 a.u.), and O (-0.439 a.u.), but CN and H had approximately the same dependency followed by O. While the composition of PC2 had strong dependencies on the same variables, the configuration was varied. A stark contrast was found in the construction of PC3. Under argon, PC3 relied heavily on CN (0.789 a.u.) followed by the H (-0.474 a.u.) and N (0.361 a.u.) emitters; the rest of the dependency was split between the C2 (0.118 a.u.), C (0.068 a.u.), and O (-0.067 a.u.) emitters again indicating that there was no preference in alignment for these variables. Whereas, the PC3 in air, depended heavily on the CN (-0.703 a.u.) and H (0.684 a.u.) variables, and the rest of the reliance was split approximately equally over the C (-0.05 a.u.), C2 (-0.058 a.u.), N (-0.141 a.u.), and O (-0.11 a.u.).

It should be noted that there are different projections for the air and argon regime. The oxygen is the only variable that remains constant in phase for both the atmospheres. Therefore a
different model would need to be constructed for each regime if three PCs are utilized. However, if PC3 is not used over 98% of the data could still be represented. The score plots shown below in Figure 56 and Figure 57 indicate that the slight differences in the PCs do lead to a change in the grouping.

Figure 56: Score plot of the organic samples in an air sampled and excited by 1064 nm.

Figure 57: Score plot of the organic samples in an argon atmosphere sampled and excited by 1064 nm.
In the ambient air conditions, there is a distinct separation between the polymers, and the other categories of organics as shown by the large distance from the centroid of the polymer group to any other centroid. This separation is mainly due to the PC1 and is further separation occurs due to PC2 and PC3. There appeared to be an outlier in the nitros that was separated from the others mainly due to PC3. In the argon, again PC1 appears to separate the polymers from the other groups. The cyano in this case is separated from the nitros, oxys, and PAHs, by PC3. In both regimes, PC1, PC2, and PC3, do not appear to separate the nitros, oxys, and PAHs to a great extent.

In order to gain a better understanding of the 3-D plots, estimated centroids for the different groups were calculated. The distance from the centroid to the furthest member of the group defined the radius of an ellipse, which would include all the members of that respective group. In addition, the distance from one group’s centroid to another group’s centroid was calculated. The results of the calculations are shown in Table 12 and Table 13 for the two atmospheres. The group measurement is inclusive of all of the organic groups. It should be noted that these distances are based on the score’s coordinates and have an arbitrary meaning outside of helping to better visualize the data.
Table 12: Radii of centroids for the different organic groups and distances between the groups in an air atmosphere sampled and excited by 1064 nm.

<table>
<thead>
<tr>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of cluster (a.u.)</td>
<td>0.403</td>
<td>0.156</td>
<td>0.101</td>
<td>0.028</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance between centroids of clusters (a.u.)</td>
<td>0.000</td>
<td>0.065</td>
<td>0.076</td>
<td>0.008</td>
<td>0.084</td>
</tr>
<tr>
<td>Group</td>
<td>Nitros</td>
<td>Oxys</td>
<td>PAHs</td>
<td>Cyanos</td>
<td>Polymers</td>
</tr>
<tr>
<td>Nitros</td>
<td>0.065</td>
<td>0.000</td>
<td>0.047</td>
<td>0.059</td>
<td>0.149</td>
</tr>
<tr>
<td>Oxys</td>
<td>0.076</td>
<td>0.047</td>
<td>0.000</td>
<td>0.069</td>
<td>0.150</td>
</tr>
<tr>
<td>PAHs</td>
<td>0.008</td>
<td>0.059</td>
<td>0.069</td>
<td>0.000</td>
<td>0.090</td>
</tr>
<tr>
<td>Cyanos</td>
<td>0.084</td>
<td>0.149</td>
<td>0.150</td>
<td>0.090</td>
<td>0.000</td>
</tr>
<tr>
<td>Polymers</td>
<td>0.327</td>
<td>0.390</td>
<td>0.399</td>
<td>0.334</td>
<td>0.251</td>
</tr>
</tbody>
</table>

Table 13: Radii of centroids for the different organic groups and distances between the groups in an argon atmosphere sampled and excited by 1064 nm.

<table>
<thead>
<tr>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of cluster (a.u.)</td>
<td>0.399</td>
<td>0.111</td>
<td>0.092</td>
<td>0.008</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance between centroids of clusters (a.u.)</td>
<td>0.000</td>
<td>0.054</td>
<td>0.063</td>
<td>0.069</td>
<td>0.075</td>
</tr>
<tr>
<td>Group</td>
<td>Nitros</td>
<td>Oxys</td>
<td>PAHs</td>
<td>Cyanos</td>
<td>Polymers</td>
</tr>
<tr>
<td>Nitros</td>
<td>0.054</td>
<td>0.000</td>
<td>0.031</td>
<td>0.032</td>
<td>0.105</td>
</tr>
<tr>
<td>Oxys</td>
<td>0.063</td>
<td>0.031</td>
<td>0.000</td>
<td>0.008</td>
<td>0.087</td>
</tr>
<tr>
<td>PAHs</td>
<td>0.069</td>
<td>0.032</td>
<td>0.008</td>
<td>0.000</td>
<td>0.093</td>
</tr>
<tr>
<td>Cyanos</td>
<td>0.075</td>
<td>0.105</td>
<td>0.087</td>
<td>0.093</td>
<td>0.000</td>
</tr>
<tr>
<td>Polymers</td>
<td>0.373</td>
<td>0.424</td>
<td>0.435</td>
<td>0.442</td>
<td>0.384</td>
</tr>
</tbody>
</table>

In the ambient air conditions, there is a distinct separation between the polymers and the other categories of organics as shown by the large distance from the centroid of the polymer group to any other centroid, in agreement with the visual interpretation. This was a positive sign
that there was enough difference in the LIBS signature of the polymers to allow for differentiation from the other groups.

There appeared to be a single nitro sample that was separated from the others. In the case of PCA, this separation could be the result of that particular spectrum having a significant difference in the amount of the analyte in comparison with the other spectra. The higher or lower signal would cause the sample to appear different from its respective group. If the decision to include that particular nitro in the nitros group, then the cyano would have to be included as well as the radius of the nitro group 0.156 a.u. is larger than the distance between the two groups’ centroids (0.149 a.u.). For the nitros, oxys, and PAHs there appears to be no clear separation based upon the variance and the distance between the nitro and oxys (0.047 a.u.) and the nitros and PAHs (0.059 a.u.) only differ in distance by 0.012 a.u.. Of all the groups, the PAHs have the closest clustering with a distance of 0.028 a.u.. If the nitro outlier were not included in the nitro group, then the polymers would have the largest group separation (0.134 a.u.) and a case could almost be made that they are not in the same group. In order to make this case more polymer samples are necessary.

While a similar scenario appears in the argon environment, there is less of a separation between the cyano and nitro and oxy groups. The cyano distance between the nitro group, the oxy group, and the PAH group in air was 0.149 a.u., and 0.150 a.u. respectively, in comparison with argon’s 0.105 a.u. and 0.087 a.u.. The cyano is approximately the same distance for the PAHs group, differing only by a distance of 0.003 a.u.. Alternatively the polymers had a further separation from the other groups in argon (on average a distance of 0.421 a.u.) in comparison with the air (on average a distance of 0.343 a.u.).
The argon quenching of radical recombination, may be the cause of a closer grouping of the PAHs (0.008), relative to the air regime (0.028 a.u.). However, similar to the air regime the variance was not enough to clearly separate the nitros, oxys, and PAHs from each other as shown in tables above. The argon regime did seem to offer a slight advantage over the air regime in the case of moving the outlying nitro closer to the nitro group reducing the clustering distance by 0.045. The overall clustering distance in the argon (0.399 a.u.) was approximately the same as in the air (0.403 a.u.).

The difference between the air and argon scattering may be attributed to the influence of the inverse Bremsstrahlung heating of the plasma and surrounding atmosphere. As the laser continues to heat the plasma it also consequently heats the surrounding air. Thus as the plasma rises in temperature so does the surrounding atmosphere, which then begins to interact with the plasma causing a skewing in the resulting emission. This affect is suppressed by the inert argon atmosphere and radical formation due to the air does not occur. From the PC composition charts and the score plots the influence of air does play an important role in the NIR ns regime.

A quantitative measurement or ROC curve evaluating the variance criterion as a discriminator was done by measuring the Euclidean distance between the model and test scores. In theory, the distance from a sample compared against itself should be smaller than the distance to other samples. It was unknown as to how the clustering would affect the ability to differentiate between very similar samples (samples which may lie on top of each other).
Figure 58: Receiver Operator Characteristic curves for the atmosphere in the NIR regime.

From Figure 58, the ROC plots show that the air and argon have similar areas under the curve. This means that using the PCA technique, there is a 83-84% of obtaining a true positive before a false positive, or in this case correctly identifying the sample with itself before identifying it with another. On the scale, where 100% is the optimal technique, the 83% and 84% rank fairly well.

An analogous atmospheric study was conducted with a UV excitation and sampling source. There was still an observable difference between the spectra due to the atmosphere as shown in Figure 59.
The argon again appeared to suppress the atmosphere recombination and as a result the atomic emission from the carbon appeared to be higher in the argon, while the CN band was much lower. In the air atmosphere the inverse was found to be true. The relationship between C, N, and CN emission has been studied and modeled by various research groups\textsuperscript{155, 214}. The loadings and their respective eigenvalues were explored in order to determine how this relationship was reflected in the PCA analysis.

Table 14: Percentage of data represented by each PC for air and argon atmospheres excited by 266-nm.

<table>
<thead>
<tr>
<th></th>
<th>Variance In Air Data (%)</th>
<th>Variance In Argon Data (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>89.7</td>
<td>89.6</td>
</tr>
<tr>
<td>PC2</td>
<td>8.0</td>
<td>8.7</td>
</tr>
<tr>
<td>PC3</td>
<td>1.5</td>
<td>0.9</td>
</tr>
<tr>
<td>PC4</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>PC5</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>PC6</td>
<td>0.2</td>
<td>0.0</td>
</tr>
</tbody>
</table>
From Table 12, PC1 was found to represent approximately 90% of the data. Again, if the user has selected that 90% of the variance is sufficient to describe enough of the data then only PC1 is necessary. However, 99% of overall variance can be described with the first three PCs. Also indicated in Table 12, there is a small difference in the amount of variance described in PC2 (0.7%) and PC3 (0.8%). In contrast with the air regime, the argon regime had a higher amount of variance described in PC2, while PC3 contributed more to the overall variance in the air regime. Again the rule of one was used, with the third PC being kept in the argon as it was approximately 1%.

Figure 60: Principal component composition for 266-nm in air and argon atmospheres.

Indicated in Figure 59, PC 1 had a similar composition in both atmospheres. The coefficients of the loadings were the following: C (0.237), CN (0.453), C2 (0.138), H (0.449), N (0.448), and O (0.563) for the air; alternatively PC1 in argon had the following coefficients: C (0.243), CN (0.422), C2 (0.075, H (0.449), N (0.385) and O (0.638). For both atmospheres, the CN, H, N had similar values with argon relying a little less on the nitrogen by 0.06, the main reliance was on oxygen. While the carbon had fairly similar values of 0.237 and 0.243 for air and argon respectively, the air had almost double the reliance on C2 in comparison with argon.
It was observed that overall the PC compositions appeared to be more equally distributed throughout the six variables. Again the main differences lie in the compositions of PC2 and PC3. In the air atmosphere the structure of PC2 showed a reliance on CN (0.551) and O (-0.721), whereas in argon a strong dependence was placed on CN (0.545), H (0.457), and O (-0.685). The PC3 in air had a reliance on CN (-0.654) and N (0.59), alternatively in the argon the H and N were the major contributors of the PC with values of -0.686 and 0.611, respectively. Therefore, in argon the hydrogen (0.457) played more of a role than in the air (0.28) in separating the groups based on variance.

As previously mentioned, the equivalence in the coefficients indicates that there was no strong preference in alignment for these CN, H, and N variables. The similar loading coefficients however, were thought to play a role in generating an analytical stable model regardless of the atmosphere. This would allow for the same loadings to be used in both an air and argon environment (and possibly other environments as well). In addition to the similar loadings, the amount of variance represented by each PC would need to be similar as well as a similar grouping in the scores plots. This was examined in the scores plots, which are shown below in Figure 61 and Figure 62.
From the scores plot there is a slight difference between the air and argon plots, but both appear to be randomly scattered. PC1, PC2, and PC3, all contribute to separating the polymers from the
other groups. The air appears to separate all of the samples from one another, with the help all the PCs. In the argon the separation does not appear quite as drastic. A quantitative measure of the clustering is shown in Table 15 and Table 16.

Table 15: Radii of centroids for the different organic groups and distances between the groups in an air atmosphere sampled and excited by 266 nm.

<table>
<thead>
<tr>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitros</td>
<td>0.173</td>
<td>0.210</td>
<td>0.039</td>
<td>N/A</td>
<td>0.026</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitros</td>
<td>0.084</td>
<td>0.000</td>
<td>0.114</td>
<td>0.082</td>
<td>0.217</td>
</tr>
<tr>
<td>Oxys</td>
<td>0.031</td>
<td>0.114</td>
<td>0.000</td>
<td>0.034</td>
<td>0.130</td>
</tr>
<tr>
<td>PAHs</td>
<td>0.012</td>
<td>0.082</td>
<td>0.034</td>
<td>0.000</td>
<td>0.157</td>
</tr>
<tr>
<td>Cyanos</td>
<td>0.147</td>
<td>0.217</td>
<td>0.130</td>
<td>0.157</td>
<td>0.000</td>
</tr>
<tr>
<td>Polymers</td>
<td>0.181</td>
<td>0.264</td>
<td>0.151</td>
<td>0.183</td>
<td>0.144</td>
</tr>
</tbody>
</table>

Table 16: Radii of centroids for the different organic groups and distances between the groups in an argon atmosphere sampled and excited by 266 nm.

<table>
<thead>
<tr>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitros</td>
<td>0.168</td>
<td>0.086</td>
<td>0.036</td>
<td>N/A</td>
<td>0.057</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitros</td>
<td>0.050</td>
<td>0.000</td>
<td>0.028</td>
<td>0.044</td>
<td>0.085</td>
</tr>
<tr>
<td>Oxys</td>
<td>0.022</td>
<td>0.028</td>
<td>0.000</td>
<td>0.021</td>
<td>0.068</td>
</tr>
<tr>
<td>PAHs</td>
<td>0.019</td>
<td>0.044</td>
<td>0.021</td>
<td>0.000</td>
<td>0.080</td>
</tr>
<tr>
<td>Cyanos</td>
<td>0.063</td>
<td>0.085</td>
<td>0.068</td>
<td>0.080</td>
<td>0.000</td>
</tr>
<tr>
<td>Polymers</td>
<td>0.227</td>
<td>0.277</td>
<td>0.249</td>
<td>0.236</td>
<td>0.235</td>
</tr>
</tbody>
</table>
The overall clustering distance of 0.231 a.u. and 0.260 a.u. was calculated for air and argon, respectively. The polymers in both regimes are separated from the rest of the organics but the argon had a further average separation distance of 0.249 a.u., in comparison with the separation distance of 0.186 in air. Under argon the cyanos appears to be grouped with the nitros and oxys, as the group clustering (0.168 a.u. for nitros and 0.086 a.u. for oxys) was larger than the separation between the centroids (0.85 a.u. for nitros and 0.065 a.u. for oxys).

For both atmospheres, the polymers and PAHs had the strongest clustering with the smaller grouping distances. In air the polymers had a cluster radius of 0.026 a.u. and the PAHs had a cluster radius of 0.039 a.u.; whereas in the argon the polymers had a cluster radius of 0.057 a.u. and the PAHs had a radius of 0.036 a.u.. The overall scattering appears to be more confined in the air regime. In the air, the largest cluster distance was the oxys at 0.210 a.u., and in the argon the largest cluster distance was for the nitros at 0.168 a.u.. The argon environment does well in separating the polymers from the other organic groups and clustering the oxys together (0.086 a.u. in argon versus 0.086 a.u. in air). However based on the group clustering the argon does not seem to offer any great advantage over the air regime.

It was unclear how well the PCA technique would work in the identification of the test scores in comparison with the model scores. If the scattered samples were far enough apart from each other such as the polymers an advantage may have been gained, as the closest neighbor would in theory be the identical test sample. However, if the clustering distance is much greater than the centroid distance to another group as is the case for the nitros and oxys, there is a greater opportunity for misclassification which would have lowered the effectiveness of the PCA technique. The ROC plots which evaluate the PCA technique in the UV are shown below.
From Figure 63, the air regime has a comparable area under the curve (0.80) to that of argon (0.77). The small increase in the area under the curve may not seem important, but a single misclassification or missed detection of an explosive could have costly consequences.

5.3.4 Conclusions about Atmospheric Background

In conclusion, the air and argon environments yield similar results. The first principal component had a similar composition for both the air and argon regime. In the argon the polymers and the cyano were clearly separated from the nitros, oxys and pahs. Inside the nitros, oxys and pahs group the pahs were congregated closer together. In the air regime, the polymers were clearly separated from the other organic groups. In both conditions the variance could definitively be used to separate polymers from the rest of the organics.

With the massive scattering based on the large distance in the clustering in the nitros, pahs, and oxys groups and the small distance between the centroids of the groups it appeared that PCA technique would have a difficult time when comparisons were made from a test set of data.
Surprisingly, the ROC plots for both the air and argon revealed that the PCA technique had an relatively comparable chance of selecting the correct sample before selecting an incorrect sample, respectively. While not excellent (above 90%), the PCA does give a measure that a true classification would have to match and surpass. According to this method and data set the argon only gives a slight advantage over the air. This was surprising as the argon should have allowed for the variance to be based on emission strictly from the sample, without skewing from the air recombination. This was apparently not the case as both regimes relied heavily on the CN, but not the C or the N,

5.3.5 Results Comparing Laser Wavelengths

After studying the impact that the atmosphere had on organic detection and discrimination when excited by a near infrared (NIR) laser pulse, the source was changed to an ultraviolet (UV) pulse at 266 nm and the effects were studied. The study conducted under the 266-nm was done under the same conditions as those taken at 1064 nm.

Basic organic spectroscopy has shown that in the UV region (~200-300 nm) organic molecules have strong absorption regions. It was hypothesized that the excitation and sampling by a UV source may provide better groupings due to the possibility of more efficient heating. In general, the plasma has an absorption coefficient that is dependent on the excitation wavelength. For wavelengths below the transitions involving the ground state, known as resonance lines, the plasma and the surrounding atmosphere are highly absorbent. The UV wavelengths fit in such a regime, which results in a strong radiative transport mechanism, on which the formation of plasma structure is reliant. In fact, the radiative transport is often many times larger than the
intrinsic thermal conduction, making it the dominant heat-transfer process for regions in the plasma that are strongly ionized\textsuperscript{87}.

For the wavelengths above the resonance lines, the absorption of the excitation wavelength is smaller for the plasma and surrounding atmosphere. More of the laser light is allowed to escape, as the absorption length for the light is often larger than the characteristic dimensions of the plasma (such as the length and diameter). This in comparison with the NIR, would make the UV wavelength much more efficient in heating the organic samples, resulting in more emission from the sample and not the surrounding atmosphere\textsuperscript{215}.

A comparison between the 266-nm and 1064-nm pulses for LIBS using plastics and one explosive was explored by Wang \textit{et al.}\textsuperscript{167}. Their results showed that the NIR wavelength coupled better into the plasma after it had been formed, which yielded greater signal intensities with less signal variation. However, a more consistent plasma generation was yielded when using a UV beam, which the group hypothesized, could be due to the absorption of UV by the samples.

It should be noted that the studies cited above were not conducted on residues nor in a single shot regime. Therefore, it was necessary to verify that the conclusions were consistent in the single shot regime, and on a silicon substrate.
Figure 64: Comparison of Fluoranthene spectra in different atmospheres for the NIR (top six spectra) and the UV (bottom six spectra) regimes.
The spectra shown in Figure 64 are nearly identical, and due to the nature of residues any differences may be attributed to a number of factors including the inhomogeneity of the residue, the shot-to-shot variation, etc. From the spectra alone it would be difficult to determine any significant variances in the spectrum due to the wavelength. A better interpretation of the differences due to the change in the wavelength could be gained through examining the loadings of the PCs, and the amount of variance accounted for by each PC. The loadings of the NIR and UV PCs in air were first examined. It was hypothesized that the skewing effects on the data due to atmospheric recombination may result in similar PC compositions.

Figure 65: Principal component composition for the NIR and UV in an ambient air atmosphere.

Figure 65 illustrates that while not clearly evident in the spectra, there is a difference in the PC loadings based on the NIR and UV regime. While the NIR tends to have PC compositions that have strong contributions from one or two variables, the UV has a more equal distribution of the contribution from the variables. The first PC in the NIR has a strong dependence on O (0.839) which is followed by a dependence on H (0.405) and N (0.290). In the UV, however, the first PC has a fairly even distribution over the CN (0.453), H (0.449), N (0.448), and O (0.536), with the
O being slightly higher by approximately 0.086. In the second PC, both the NIR and UV have strong contributions from the CN (0.659 for air and 0.551 for argon) and O (-0.439 for air and 0.563 for argon), but the NIR had an additional strong contribution from H (0.605). The CN (-0.703 for air and -0.654 for argon) continues to play a major role in the composition of the third PC, but while the NIR also depended on H (0.684), the UV was dependent on N (0.590). Overall the PC composition in the UV is distributed over all of the variables, in contrast with the NIR where the CN, H, and O are the main contributors.

Another contrast between the wavelengths was found in comparing the eigenvalues or amount of variance represented by each eigenvector.

Table 17: Comparison of the amount of variance represented by each eigenvector in the air atmosphere.

<table>
<thead>
<tr>
<th></th>
<th>Variance in Air Data (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>266-nm</td>
</tr>
<tr>
<td>PC1</td>
<td>89.7</td>
</tr>
<tr>
<td>PC2</td>
<td>8.0</td>
</tr>
<tr>
<td>PC3</td>
<td>1.5</td>
</tr>
<tr>
<td>PC4</td>
<td>0.4</td>
</tr>
<tr>
<td>PC5</td>
<td>0.2</td>
</tr>
<tr>
<td>PC6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

In the NIR the first PC represents 93.3% of the overall variance in contrast with the 89.7% in the UV. Which results in the PC1 playing a greater role in the NIR than in the UV, and thus the O contribution in the NIR helps to describe a larger portion of the data. The second PC played more of a role in the UV with its 8.0% contribution than in the NIR which only had a 5.7%
contribution, but both loadings were strongly dependent on the CN and O variables. It is only at
the third PC contribution that the approximate overall variance becomes equivalent. The NIR
starts off with the higher amount of variance and by the third PC the cumulative variance is
99.8%, while in the UV it takes the third PC in order to reach 99.2% of the variance. Hence for
an accurate comparison of the data set between the two regimes 3 PCs are necessary.

Using three PCs to describe the data resulted in the score plots shown below.

Figure 66: Comparison of the score plots of the organic samples in an ambient air atmosphere.
In comparison, the PC1 in the 1064 nm regime serves to separate the polymers and the cyano. In comparison, using the 266-nm as an excitation and sampling source results in PC1 separating the samples to a much greater. PC2 and PC3 appear to further separate the 266 nm to a greater extent than in the 1064 nm regime. This however, may not be true as the scale of PC3 has changed between the two regimes. Quantitative measurements of the radii between the clusters and within the cluster are shown in Table 18.

Table 18: Radii of centroids for the different organic groups and distances between the groups in an air atmosphere sampled and excited by 266 and 1064 nm, respectively.

<table>
<thead>
<tr>
<th>Radius of clusters for 266 nm</th>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.231</td>
<td>0.173</td>
<td>0.210</td>
<td>0.039</td>
<td>N/A</td>
<td>0.026</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distance between centroids of clusters for 266 nm</th>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group</td>
<td>0.000</td>
<td>0.084</td>
<td>0.031</td>
<td>0.012</td>
<td>0.147</td>
<td>0.181</td>
</tr>
<tr>
<td>Nitros</td>
<td>0.084</td>
<td>0.000</td>
<td>0.114</td>
<td>0.082</td>
<td>0.217</td>
<td>0.264</td>
</tr>
<tr>
<td>Oxys</td>
<td>0.031</td>
<td>0.114</td>
<td>0.000</td>
<td>0.034</td>
<td>0.130</td>
<td>0.151</td>
</tr>
<tr>
<td>PAHs</td>
<td>0.012</td>
<td>0.082</td>
<td>0.034</td>
<td>0.000</td>
<td>0.157</td>
<td>0.183</td>
</tr>
<tr>
<td>Cyanos</td>
<td>0.147</td>
<td>0.217</td>
<td>0.130</td>
<td>0.157</td>
<td>0.000</td>
<td>0.144</td>
</tr>
<tr>
<td>Polymers</td>
<td>0.181</td>
<td>0.264</td>
<td>0.151</td>
<td>0.183</td>
<td>0.144</td>
<td>0.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Radius of cluster for 1064 nm</th>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.403</td>
<td>0.156</td>
<td>0.101</td>
<td>0.028</td>
<td>N/A</td>
<td>0.134</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distance between centroids of clusters for 1064 nm</th>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group</td>
<td>0.000</td>
<td>0.065</td>
<td>0.076</td>
<td>0.008</td>
<td>0.084</td>
<td>0.327</td>
</tr>
<tr>
<td>Nitros</td>
<td>0.065</td>
<td>0.000</td>
<td>0.047</td>
<td>0.059</td>
<td>0.149</td>
<td>0.390</td>
</tr>
<tr>
<td>Oxys</td>
<td>0.076</td>
<td>0.047</td>
<td>0.000</td>
<td>0.069</td>
<td>0.150</td>
<td>0.399</td>
</tr>
<tr>
<td>PAHs</td>
<td>0.008</td>
<td>0.059</td>
<td>0.069</td>
<td>0.000</td>
<td>0.090</td>
<td>0.334</td>
</tr>
<tr>
<td>Cyanos</td>
<td>0.084</td>
<td>0.149</td>
<td>0.150</td>
<td>0.090</td>
<td>0.000</td>
<td>0.251</td>
</tr>
<tr>
<td>Polymers</td>
<td>0.327</td>
<td>0.390</td>
<td>0.399</td>
<td>0.334</td>
<td>0.251</td>
<td>0.000</td>
</tr>
</tbody>
</table>
Both score plots show that the polymers are separable from the other organic groups, however the NIR (~0.344 a.u.) appears to separate the two polymers by a greater distance than the UV (0.186 a.u.) by approximately 0.158 a.u.. The NIR appears to have separated out the cyano from the remaining groups, however according to the centroid measurements (barring the polymer centroid measurement) the NIR on average has a distance of 0.130 a.u. from the nitros, oxys, and PAHs. Alternatively, the UV separates the cyanos from the oxys, nitros, and PAHs by an average distance of 0.168 a.u.. According to the tables, the UV has a wider scattering between groups. In the NIR, the distance from the nitros to the oxys is 0.047, and the distance from the nitros to the PAHS is 0.059 a.u.. In the UV, the distance between the nitros and oxys is 0.114 a.u., and the distance between the nitros and PAHs is 0.082 a.u..

Overall, the NIR and UV have similar cluster distances for the nitros, PAHS, and oxys. There is a drastic difference in the clustering distance of the polymers, where the NIR has a distance of 0.134 a.u. in comparison with the UV’s distance of 0.026 a.u.. In fact, while the UV data appears to be scattered, it is done so over a small range as the overall group cluster radius was 0.231 a.u.. Alternatively, the NIR had a large overall group cluster radius of 0.403 a.u., which was mainly due to the distinctive polymers. Based on the larger overall group cluster radius and the comparable distances between the group centroids the NIR air regime would be preferable over the UV air regime.

The ROC curves for the air atmosphere show that while the areas are comparable, the NIR regime has a slightly higher area under the curve. This may be due to the greater separation in the clusters.
In the argon environment, where atmospheric effects were suppressed the loadings that were found are shown below in Figure 68.

From other studies$^{216-219}$ it has been shown that any of the signals detected in the argon atmosphere could be attributed to the sample alone. This being the case, any differences in the
loadings could be attributed to the laser coupling interaction with the plasma. The first PC in the NIR was mainly dominated by the contribution of the O variable which had a coefficient value of 0.856, while the in UV, the O variable which had a coefficient value of 0.638 had a slightly larger contribution relative to the C (0.243), CN (0.422), H (0.449), and N (0.385) variables. However, from the coefficients the loading in the UV was reliant on five of the six variables, where the C variable whose coefficient of 0.243 was much lower than the other variables coefficient. The second PC for both wavelengths was very similar in composition with major contributions from the CN (0.461 for air and 0.545 for argon), H (0.779 for air and 0.457 for argon), and O (-0.413 for air and -0.684 for argon) variables. A slight difference in emphasis was placed on the major contributing variable which was the O (-0.684) variable for the UV and the H (0.779) variable for the NIR.

The CN (0.789 for air and 0.318 for argon) and H (-0.474 for air and -0.686 for argon) variables also make key contributions to the third PC in both wavelength regimes along with the N (0.361 for air and 0.611 for argon) variable. A further examination of the PC compositions revealed that the major contributors to the loadings in both wavelengths are CN, H, N and O variables. This meant that the variance was fairly diversified, but the C and C2 variables were not as varied, which is possible as carbon is inherent to most of the samples and the emission would not be as varied the argon atmosphere. In the NIR the coefficients for C variable for PC1, PC2, and PC3 are 0.100, 0.004, and 0.068, respectively, while in the UV the coefficients are 0.243, -0.111, and 0.040, respectively. For the C2 variable, the coefficients for PC1, PC2, and PC3 in the NIR are 0.032, 0.059, and 0.118, respectively, and for the UV the coefficients are 0.075, 0.103, and 0.187, respectively.
In order to explore the differences in the argon grouping, the clustering tables were examined and compared.

Table 19: Radii of centroids for the different organic groups and distances between the groups in an argon atmosphere sampled and excited by 266 and 1064 nm, respectively.

<table>
<thead>
<tr>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>266 nm</td>
<td>0.260</td>
<td>0.168</td>
<td>0.086</td>
<td>0.036</td>
<td>N/A</td>
</tr>
<tr>
<td>1064 nm</td>
<td>0.399</td>
<td>0.111</td>
<td>0.092</td>
<td>0.008</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Similar to the air results, the overall cluster radius was larger in the NIR than the in the UV by approximately 0.139 a.u.. Again the polymers were the major difference radii of the clusters as the NIR had a radius of 0.105 a.u. in comparison to the UV which had a radius of 0.057 a.u..

In regards to the distance between the clusters there are no large disparities in the
distances between the nitros, oxys, and PAHs. The NIR separated the cyano from the nitros, oxys, and PAHs slightly better than the UV, where the NIR had an average distance of 0.095 a.u. in comparison with the UV’s average distance of 0.078 a.u..

A quantitative measure of the PCA technique in the argon environment resulted in the NIR having a higher ROC curve area than the UV.

The difference (7%) between the argon ROC plot areas was slightly higher in than the difference in the air regime. More specifically, the PCA appeared to have a more difficult time in selecting the correct sample before the incorrect sample.

5.3.5.1 Conclusion Concerning the Laser Wavelength

Comparisons of the wavelengths illustrate the differences between the NIR and UV regimes. In the NIR, the PC loading compositions were mostly dominated by one or two variables. This made it possible to ascertain which variables had a significant impact on the
variance. The UV regime however had contrary results to the NIR, as the loadings were distributed over all of the variables. In terms of quantitative studies, the area under the ROC curves was higher by 3% for the NIR in air then the UV. In the argon the difference was more pronounced as the NIR was higher by 7%. With the higher ROC curve area the NIR would be the preferable regime to conduct the LIBS analysis. However, according to this data set the UV does offer the advantage of fairly stable PC loadings, which may play a role if a single model that could be used in different studies is necessary. More studies with different data sets are necessary to determine if the analytical stability is repeatable.

The difference between the two wavelength regimes may be attributed to the photon absorption processes. In the NIR regime the photon absorption of the laser energy is dominated by the inverse Bremsstrahlung process which not only heats the sample but the surrounding atmosphere as well. While the UV regime does have some inverse Bremsstrahlung heating occurring, the UV regime is dominated by multi-photon ionization. This reduces the amount of air entrained into the plasma which decreases the skewing effects due to radical formation. In addition, as previously discussed, the UV wavelength has much more efficient ablation of the organic samples, which results in more emission from the sample.

5.3.6 Femtosecond LIBS on Organic Residues

The femtosecond regime was selected as a parameter of study due to its advantages over the nanosecond regime. Studies have shown that femtosecond LIBS yields lower temperature plasmas and as a result there is reduced background continuum emission and minimal air entrainment\textsuperscript{220, 221}. These properties make it an ideal sampling and excitation source for LIBS. A
further study conducted by De Lucia Jr. et al.\textsuperscript{171}, noted that the due to the lower laser fluences necessary for femtosecond LIBS, there is less substrate interrogation.

Conducting LIBS in the femtosecond regime introduced new challenges that needed to be addressed. Utilizing the same optics system which had been optimized for the Echelle, it was difficult to collect a sufficient number of photons in order to generate an adequate signal-to-noise ratio. An example of a typical femtosecond LIBS spectrum is shown below in Figure 70.

![Figure 70: Typical femtosecond spectrum acquired by an echelle spectrometer focusing on the CN window.](image)

In order to address this issue with signal collection, the Czerny-Turner was utilized with larger fibers as shown in Figure 71. Enlarging the linewidth of the spectrometer was done at the loss of spectral resolution. However, with a 600 ln/mm grating the loss of spectral resolution was negligible, and if it had been problematic a higher resolution grating would have been utilized.
While this improved signal collection efficiency, as well as resolution, it introduced the problems discussed in section 5.2.3. However, keeping the errors in mind, the sample set was examined, with the polymers were excluded as there were still problems collecting adequate useable signal. The PCA model categorized the organic samples as shown below in Figure 72.
Figure 72: Score plots for air and argon excited and sampled in the femtosecond regime.
There was no apparent natural grouping by the selected classes in either the air or argon atmosphere. In air, the samples are widely spread apart, but there does appear to be two main clusters of data. The separation in the clusters appears to be mainly due to PC1 and PC3. The clusters contain samples from all groups with the exception of cyanos. In the argon, PC2 and PC3 appear to the one nitro, oxy, and PAH from the main cluster. In order to determine quantitative measurements the cluster radii tables were calculated.

Table 20: Radii of centroids for the different organic groups and distances between the groups in an air and argon atmosphere sampled and excited by 800 nm, respectively.

<table>
<thead>
<tr>
<th>Radius of cluster in air</th>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.476</td>
<td>0.336</td>
<td>0.484</td>
<td>0.120</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distance between centroids of clusters</th>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Group</td>
<td>0.000</td>
<td>0.046</td>
<td>0.038</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>Nitros</td>
<td>0.046</td>
<td>0.000</td>
<td>0.080</td>
<td>0.090</td>
</tr>
<tr>
<td></td>
<td>Oxys</td>
<td>0.038</td>
<td>0.080</td>
<td>0.000</td>
<td>0.034</td>
</tr>
<tr>
<td></td>
<td>PAHs</td>
<td>0.044</td>
<td>0.090</td>
<td>0.034</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Cyanos</td>
<td>0.102</td>
<td>0.137</td>
<td>0.106</td>
<td>0.073</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Radius of cluster in argon</th>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.575</td>
<td>0.555</td>
<td>0.323</td>
<td>0.290</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distance between centroids of clusters</th>
<th>Group</th>
<th>Nitros</th>
<th>Oxys</th>
<th>PAHs</th>
<th>Cyanos</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Group</td>
<td>0.000</td>
<td>0.053</td>
<td>0.081</td>
<td>0.235</td>
</tr>
<tr>
<td></td>
<td>Nitros</td>
<td>0.053</td>
<td>0.000</td>
<td>0.100</td>
<td>0.257</td>
</tr>
<tr>
<td></td>
<td>Oxys</td>
<td>0.081</td>
<td>0.100</td>
<td>0.000</td>
<td>0.311</td>
</tr>
<tr>
<td></td>
<td>PAHs</td>
<td>0.235</td>
<td>0.257</td>
<td>0.310</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Cyanos</td>
<td>0.193</td>
<td>0.236</td>
<td>0.149</td>
<td>0.353</td>
</tr>
</tbody>
</table>
The original assumption that the air was more widely spaced was a misconception as the overall group cluster radius in the argon is larger than the radius in the air by 0.099 a.u.. Also from Table 20, the cluster radii for the nitros and PAHs were larger than in the air by 0.219 a.u. and 0.17 a.u., respectively. Only the oxy cluster radius was smaller in the argon environment by 0.161 a.u. It is true that there is no clustering in the air environment, as all of the cluster radii are larger than the distance between the groups. This is not the case in the argon regime as the PAHs should be separable from the oxys, and the cyano should not be included in the PAHs group. According to the argon portion of Table 20, the inner cluster radius for the PAHs is 0.290 a.u., but the between the PAHs centroid and the oxys centroid is 0.310 a.u. Since this calculation is based on the centroid it is possible that some oxys may lie in the PAHs. In the case of the cyano, however, this should not be the case as there is only one cyano.

Without the labels false groupings would probably have been assumed. From the lack of natural grouping it was necessary to examine the PC composition the amount variability that each PC represented and it respective composition.

![PC Composition for Femtosecond](Air) ![PC Composition for Femtosecond](Argon)

Figure 73: Femtosecond PC loadings for the air and argon atmospheres.

Based upon the PC composition, the data acquired in both atmospheres for the femtosecond regime appeared to be very similar. PC1 and PC2 in both the air and argon regime rely heavily
on the CN and the O variables in their constitution. PC1 had coefficients of -0.276 in air and -0.672 in argon for the CN variable, and coefficients of 0.944 in air and 0.714 in argon for the O variable. PC2 had coefficients of 0.912 in air and 0.697 in argon for the CN variable, and coefficients of 0.315 in air and 0.700 in argon for the O variable. Whereas a more distinguishing factor is in the constitution of PC3, where air favors the C₂ variable (-0.715) slightly more than the H (-0.414) and the N (-0.452), and the argon favors the H variable (-0.647) over the C₂ (-0.479) and the N (-0.534) variables. One could assume that the model constructed has analytical stability in as far as similar loadings, and could thus be used for both atmospheres with slight misclassifications. However, due to the collection of data using the Czerny-Turner it is uncertain as to what may have caused this stability. Using the Czerny-Turner and the current grating it is not possible to collect emission from all of the variables in a single window. This means multiple shots have to be collected, and since the residue is not homogenous it is not possible to justifiably stitch a spectrum together as the laser shot-to-shot stability and the amount of residue collected may not be equal for each window. This inherent instability could lead to bias in the data.

It is unclear if there was any skewing in the data as a consequence of any unfair weighting being placed on any of the variables. This may have occurred if the case described in the Section 5.2.3 occurred. Introduction of the possible matrix effects such as laser interaction with varying amounts of residue adds to the complexity of this detection and characterization problem. While the loadings appear very similar, the score plots show a different spread in the data. This variability may have been attributed to the eigenvalues shown in the table below.
The first PC in air accounts for over 92% of the overall variance, while in argon the first PC accounts for slightly less than 84% of the variance. In fact, according to Table 21, in the argon regime the first two PCs are necessary to account for approximately 98% of the data.

In order to observe the effects of the random piecing together (as described in section 5.2.3), a ROC curve was generated. While the PC components appeared to be more analytically stable than those in the nanosecond regime the ROC curve yields a more accurate quantitative representation of the analytical ability of PCA technique.

<table>
<thead>
<tr>
<th></th>
<th>Variance in Air Data (%)</th>
<th>Variance in Argon Data (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>92.2</td>
<td>83.8</td>
</tr>
<tr>
<td>PC2</td>
<td>7.4</td>
<td>14.6</td>
</tr>
<tr>
<td>PC3</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>PC4</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>PC5</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>PC6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
The ROC plots show that PCA technique could use some improvement. While not quite at the point of complete randomness, the models generated were far below those in the nanosecond regime. In the air regime, the NIR had an area of 0.83 while the UV had an area of 0.80 in contrast to the femtosecond’s area of 0.63. In the argon regime, the NIR’s area of 0.84 and the UV’s area of 0.77 are still quite higher than the femtosecond’s area of 0.68.

5.3.6.1 Conclusions for Femtosecond LIBS

The femtosecond regime does show promise, but do to the manner in which the data was collected, further studies are necessary. Alternative methods of collecting the signal in a single shot with a high signal-to-noise ratio need to be explored. From the current manner of collection, it is difficult to determine if the PC loadings which seem to show similar results in both atmospheres is true result or an artifact of this study. The ROC plots for both the air and argon have lower areas under the curves in comparison with the NIR and UV of the same atmosphere.
5.4 **Overall Conclusions**

In an effort to construct an optimal LIBS technique for the sensing and detection of organic residues on a non-metallic surface, it was necessary to study many influential parameters. An attempt was made to control as many factors as possible in the experimental setup in order to offer controlled conditions for single shot analysis. There were factors, however, such as the laser pulse-to-pulse stability, the differences in laser coupling with the organic analyte, residue inhomogeneity on the substrate, and the amount of analyte that is ablated, which could not be controlled. This was made evident in an outlier that was observed in the 1064 air regime. As all the data was handled in the same manner, the outlier was attributed back to the LIBS event which may have sampled an area with a high concentration of analyte, causing the spectrum to appear different from the rest of its respective group. Given this background, variations of the characteristic atomic lines (C, H, N, and O) and molecular bands (CN and C₂) in the LIBS plasma were collected, studied, and utilized to build analytical models. These models were then evaluated through the use of ROC curves to understand their effectiveness in classifying the organic residues.

In order to optimize the LIBS setup it was necessary to select an Echelle spectrometer over a Czerny-Turner spectrometer. The advantage of collecting the whole spectrum in a single shot ensured that amount of residue collected for all the emitters was equivalent. Therefore any operations conducted on the spectrum affect the entire set of variables simultaneously. In regards to the laser, with the Echelle only the shot-to-shot stability has to be observed, and this can be accounted for through the use of normalization. However, the pulse-to-pulse stability of the laser
in itself affects the ablation parameters, which drive the plasma temperature, electron density, and the laser coupling with the sampling, which are necessary for characterizing the plasma.

The major disadvantage to using the Echelle was the poor throughput, which lead to a poor signal-to-noise and as a consequence poor analytical performance, specifically in the case of femtosecond LIBS. Simple solutions to this problem would be either to increase the amount of energy used, or engineer a better optical collection system. If neither of the two solutions successfully improve the signal-to-noise then it would be necessary to use another spectrometer system capable of collecting single shot data.

In the nanosecond regime while not great, the signal-to-noise ratio was high enough to allow for the Echelle to be used successfully. In both the 266-nm and the 1064-nm irradiation cases, LIBS was successfully used to detect the organic residues. The detection, however, was simplified by the fact that silicon did not interfere with the residue’s signature as mentioned above. In order to verify that the detected signature was not just due to air, equivalent studies were conducted under an argon environment. This suppressed the air, and any signature other than the silicon lines could be associated with the organic residue. However, according to the metric utilized for the ROC curves, the argon environment did not show vast improvements over the air environment.

The ROC curves show that the analytical models constructed for each atmosphere performs reasonably well, giving approximately an 80% chance of selecting the correct sample before an incorrect sample. There was a slight difference in the area under the ROC curves based on the wavelength. The NIR regime was better for identifying single variables that significantly impact the variance, while the UV regime appeared to use similar PCs in order to perform its
groupings hence giving stability in the algorithm. More studies need to be conducted with both an optimized setup and more samples in order to verify that the results can be repeated.

While PCA was shown to give reasonable results, the main issue with the technique is determining the number of relevant PCs, as the amount of variation described is highly dependent on the problem. Another issue is the variance criterion itself, improvements can be made to the algorithm if class information is included. This however would require a more robust supervised classification technique. Therefore classification techniques that would better address the LIBS data and correctly identify the samples of interest should be explored.
6 ADDRESSING CURRENT DISCRIMINATION AND CLASSIFICATION ISSUES WITH LIBS THROUGH CHEMOMETRIC TECHNIQUES

6.1 Motivation

The parameters affecting LIBS’s ability to sense and detect organic residues have been studied and characterized. Exploration with the different organic samples has helped to develop a better understanding of LIBS’s limitations. This chapter explores LIBS’s potential to accurately identify and classify explosive-like and non-explosive organic residues, in a single shot regime, on a non-metallic substrate. In addition, an alternative chemometric technique has been introduced to compensate LIBS’s weakness towards the detection and discrimination of organics deposited on an organic background.

6.2 Experimental Setup

The experimental setup utilized for these studies was similar to the setup described in Chapter 5, with a few modifications. In the nanosecond studies, the sample chamber was changed to allow the laser to directly interrogate a sample without having to pass through a quartz window. The revised sample chamber as shown in Figure 75 continued to allow for the sample to be placed in a full argon environment. This was accomplished by allowing a continuous flow of argon into the chamber for at least three minutes prior to sample interrogation. The air was displaced due to the heavier vapour pressure of argon, and to keep the air from refilling the chamber the argon flow was continued throughout the sampling process.
Figure 75: Sample chamber constructed for the nanosecond studies.

Another modification made to the nanosecond regime setup was the incorporation of a photodiode which was used to monitor the laser pulse energy as shown in Figure 76.

Figure 76: Experimental setup with new additions.
From previous studies, it was observed that the outer cavity frequency conversion crystals did not yield stable pulse-to-pulse energies. In this study, the stability of the laser at different wavelengths was characterized and the results are shown in Table 22.

<table>
<thead>
<tr>
<th></th>
<th>1064 nm (NIR)</th>
<th>532 nm (VIS)</th>
<th>266 nm (UV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Value (mJ)</td>
<td>5.09</td>
<td>5.25</td>
<td>5.66</td>
</tr>
<tr>
<td>Minimum Value (mJ)</td>
<td>4.91</td>
<td>4.67</td>
<td>4.8</td>
</tr>
<tr>
<td>Average Value (mJ)</td>
<td>4.99</td>
<td>4.99</td>
<td>5.15</td>
</tr>
<tr>
<td>Standard Deviation (µJ)</td>
<td>30</td>
<td>85</td>
<td>150</td>
</tr>
<tr>
<td>RMS Stability (%)</td>
<td>0.6018</td>
<td>1706</td>
<td>2.918</td>
</tr>
<tr>
<td>PTP Stability (%)</td>
<td>3.656</td>
<td>11.78</td>
<td>16.69</td>
</tr>
</tbody>
</table>

* PTP: point-to-point
* RMS: root mean square stability

The laser statistics show that as the wavelength shift towards the UV regime, the stabilities increase representing larger variances between the energy pulses. By monitoring the pulse energy, only spectra that were within 5% of 5 mJ were kept for analysis, resulting in an irradiance of 8.86*10^8 W/cm². While this may have increased the number of shots needed for sampling it reduced the laser’s shot-to-shot fluctuation in the data set.

In the femtosecond regime, a different sampling chamber was utilized as shown in Figure 77.
This chamber allowed for the sample of interest to be placed in either an ambient air or argon environment. An ambient argon atmosphere was achieved by pumping the system down to approximately 100 Torr. The chamber was then backfilled with argon, and another purging and backfilling cycle was completed.

In addition to changing the sample chamber, the collection optics, the spectrometer, and the iCCD camera were changed as well. The collection optic was replaced with a 45 mm effective focal length (EFL) triplet lens. The lens was used to focus the collected light directly onto the spectrometer slit. The spectrometer, while still of a Czerny-Tuner design had a focal length to a 500 mm focal length with a 150 lines/mm. The iCCD camera was an Andor iStar camera, and with this configuration it was possible to collect a spectrum ranging from 240-900 nm in a single shot. This setup addressed the main problem observed in the femtosecond section of Chapter 5 however a new problem was introduced.
The main drawback to the new detection system was the fact that in order to achieve such a wide spectral window, a sacrifice had to be made in the spectral resolution. The figure below displays a typical spectrum collected by the new detection system.

![Spectrum Figure](image)

Figure 78: Example of a LIBS spectrum collected by the new detection system.

With such low resolution (0.56 nm), it was important that the peaks from the substrate and the sample be sufficiently spaced to allow for the sample line to be resolved.

6.3 **Organic Samples**

The organic samples and their respective solvents selected for this study are shown in Table 23.
Table 23: Organic samples along with their respective solvents, classifications, and categories, respectively.

<table>
<thead>
<tr>
<th>Organic Solute</th>
<th>Solvent</th>
<th>Classification</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-cyanonaphthalene (cn)</td>
<td>acetonitrile</td>
<td>cyano</td>
<td>NE</td>
</tr>
<tr>
<td>2,3-dinitrotoluene (2,3-dnt)</td>
<td>acetonitrile</td>
<td>nitro</td>
<td>E</td>
</tr>
<tr>
<td>2,4-dinitrotoluene (2,4-dnt)</td>
<td>acetonitrile</td>
<td>nitro</td>
<td>E</td>
</tr>
<tr>
<td>3,4-dinitrotoluene (3,4-dnt)</td>
<td>acetonitrile</td>
<td>nitro</td>
<td>E</td>
</tr>
<tr>
<td>anthracene (anth)</td>
<td>acetonitrile</td>
<td>pah</td>
<td>NE</td>
</tr>
<tr>
<td>fluoranthene (fluor)</td>
<td>acetonitrile</td>
<td>pah</td>
<td>NE</td>
</tr>
<tr>
<td>benzophenone (bp)</td>
<td>acetonitrile</td>
<td>oxy</td>
<td>NE</td>
</tr>
<tr>
<td>phthahlic acid (pa)</td>
<td>ethanol</td>
<td>oxy</td>
<td>NE</td>
</tr>
<tr>
<td>1,2,4,5-benzenetetracarboxylic acid (btca)</td>
<td>ethanol</td>
<td>oxy</td>
<td>NE</td>
</tr>
<tr>
<td>caffeine (caff)</td>
<td>ethanol</td>
<td>occns</td>
<td>NE</td>
</tr>
<tr>
<td>ammonium nitrate (an)</td>
<td>methanol</td>
<td>occns</td>
<td>E</td>
</tr>
</tbody>
</table>

Similar to Chapter 5, the samples were broken into different groups: nitrogenated samples (nitros), oxygenated samples (oxys), polyaromatic hydrocarbons (pahs), cyanides (cyanos), and other compounds containing nitrogen (occns). In addition, these samples were further divided into the broader classifications: explosive-like (E), and non-explosives (NE). For these studies a library was constructed using five spectra from each organic residue, resulting in 55 spectra in total.

6.4 Analysis Beyond PCA

After PCA has been used as a data reduction technique, an additional analytical chemometric technique is necessary for the discrimination of organics. A definitive study which focused on improving the sensitivity and selectivity of LIBS for residue explosive detection and included organic residues on a metallic substrate conducted by Gottfried et al.\textsuperscript{174}, has suggested the use of Partial Least Square-Discriminant Analysis (PLS-DA). While the study reported the ability to discriminate various explosive organic residues from each with a 100% accuracy, the
study only included three explosives, and all the explosives were on an aluminum substrate. In order to accomplish this however, 20 ratios and nine summed intensities were needed for the discrimination. While the results are encouraging, it must be reiterated that only three organics were used and the residues were on an aluminum substrate. With more organic residue samples it is unclear if the accuracy would continue to be as high as is shown by the study conducted by Lazic et al. \(^{175}\)

6.5 **Linear Discriminant Analysis (LDA)**

In this study, different chemometric algorithms were examined in order to offer alternative paths to PLS-DA, as alternative method may yield better or more insightful results. A simple linear discriminant analysis (LDA) was selected as the first classification technique to be applied to the organic residue data set. The linear discriminant analysis is very similar to the PCA, but unlike PCA class information is maintained and utilized throughout the analysis making it a true classification technique.

Using the experimental setup explained above, the organic samples were excited and sampled by a near-infrared (1064 nm and 800 nm), visible (532 nm), and ultraviolet (266 nm) sources under both an air ad argon environment. The NIR argon data set was selected as a trial case for the LDA as it had the highest ROC curve area. It was determined that if the LDA was not successful for the best case scenario, then an alternative analysis technique would be necessary.

PCA was utilized as the first step of the LDA process in order to reduce the amount data as well as remove noise and redundancy from the data set as explained in Chapter 4. The amount of variance represented by each of the PC loadings is shown in Table 24.
Table 24: Variance in data represented by principal components.

<table>
<thead>
<tr>
<th>Principal Component</th>
<th>Variance in Data (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC 1</td>
<td>82.33</td>
</tr>
<tr>
<td>PC 2</td>
<td>16.49</td>
</tr>
<tr>
<td>PC 3</td>
<td>0.93</td>
</tr>
<tr>
<td>PC 4</td>
<td>0.22</td>
</tr>
<tr>
<td>PC 5</td>
<td>0.03</td>
</tr>
<tr>
<td>PC 6</td>
<td>0.00</td>
</tr>
</tbody>
</table>

To be sure that a majority of the data could be reproduced, the first three principal components which represented 99.75% of the data were selected. Again the rule of one was used with the caveat that PC3 is close to the value of one. Using three PCs, scores for the samples were obtained, and the samples were then divided into two classes: explosive-like (E) and non-explosive (NE).

Before proceeding in the LDA process it was necessary to determine whether the covariance matrices of the two classes were equivalent. The resulting covariance matrices are shown in Figure 79, and the covariance matrices for the explosive-like and non-explosives were calculated, respectively.

Figure 79: Covariance matrices of the explosive-like and non-explosive samples.
Table 25: Covariance matrices for the explosive-like and non-explosive samples, respectively.

<table>
<thead>
<tr>
<th></th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
<th>PC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explosive-like</td>
<td>0.0535</td>
<td>0.0145</td>
<td>0.0093</td>
<td>0.0131</td>
</tr>
<tr>
<td>Non-Explosive</td>
<td>7.8157</td>
<td>-0.0081</td>
<td>-0.0052</td>
<td>-0.0073</td>
</tr>
<tr>
<td></td>
<td>0.0145</td>
<td>0.7038</td>
<td>0.0157</td>
<td>-0.0451</td>
</tr>
<tr>
<td></td>
<td>-0.0081</td>
<td>1.1780</td>
<td>-0.0087</td>
<td>0.0252</td>
</tr>
<tr>
<td></td>
<td>0.0093</td>
<td>0.0157</td>
<td>0.0303</td>
<td>-0.0001</td>
</tr>
<tr>
<td></td>
<td>-0.0052</td>
<td>-0.0087</td>
<td>0.0716</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>0.0131</td>
<td>-0.0451</td>
<td>-0.0001</td>
<td>0.0136</td>
</tr>
<tr>
<td></td>
<td>-0.0073</td>
<td>0.0252</td>
<td>0.0001</td>
<td>0.0138</td>
</tr>
</tbody>
</table>

Figure 79, displays within-group scatterplot ratios where the ellipses shown represent an 85% confidence interval and help to visualize the covariances between PCs. As explained in Chapter 4, because the length, width, and tilt of the ellipses for most pairs of variables vary significantly across the groups, the assumption of equal covariance matrices has not been met\(^{202,205}\). In order to take into account the variation of covariance, the development of the discriminant analysis to the second order is necessary. This results in the linear analysis becoming a quadratic discriminant analysis.

### 6.6 Quadratic Discriminant Analysis (QDA)

Since the data obtained from the PCA process could not be accurately modeled with a linear relationship, a quadratic model was selected. It was necessary to conduct PCA analysis similar to the NIR argon case above. Before applying the quadratic model, it was necessary to explore the data sets and determine a cut-off for the amount of variance, and the number of PCs necessary to achieve this desired variance. A variance of 90% was selected as the cut-off value for the data. In Figure 80, the cumulative variance for the different wavelengths in the two environments is shown. The 90% cut-off and the number of PCs necessary to reach this value are show by the projections in Figure 80.
Figure 80: Number of PCs necessary to represent 90% of the variance in the data for air and argon, respectively.

As seen from Figure 80, the NIR (ns) argon represents the best case for reaching the selected level of variance in the least amount of PC needed in both cases. The second best case is that of the VIS (ns) in argon. While, these cases may have needed the least amount of PCs, the effectiveness of the classification using the QDA model needed to be studied and evaluated.

6.6.1 QDA Results Based on Variance

The results of the quadratic discriminant analysis based upon Figure 80 are shown below in Table 26.
Table 26: Classification results of the Quadratic Discriminant Analysis model.

<table>
<thead>
<tr>
<th></th>
<th>Classification Matrix</th>
<th>Jackknifed Classification Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atmosphere</td>
<td>E (%)</td>
</tr>
<tr>
<td>UV (ns)</td>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>100</td>
</tr>
<tr>
<td>VIS (ns)</td>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>95</td>
</tr>
<tr>
<td>NIR (fs)</td>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>100</td>
</tr>
<tr>
<td>NIR (ns)</td>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>100</td>
</tr>
</tbody>
</table>

Only the VIS wavelength in air had trouble discriminating all of the explosives, with its 95% classification.

As pointed out before, the classification matrix may give a false sense of confidence and needs to be compared against the jackknife method. The results of the classification with a Jackknife technique are on par with classification matrix, and thus give a better idea as to how the model will classify an unknown sample. Even with the jackknife results the explosive classification can still be as high as 95%. The UV (ns), VIS (ns), and NIR (fs) studies conducted in argon reached this high level of discrimination for the explosives, but fell below their counterparts in the overall correct classification. It should be noted that the argon studies have lower correct identification of the non-explosives in comparison with the explosive case. This indicated that the air does play a beneficial role in the discrimination process.

Overall, the jackknife technique shows that it is possible to classify the organic residues in categories of explosive-like and non-explosive data. Based on the total classification, the NIR (fs) in air had the highest rate of correct classification, followed closely by NIR (ns),
VIS (ns), and UV (ns) in the air regime. In order to more accurately gauge these cases an overall confusion matrix was examined.

Table 27: Confusion matrix for the respective laser regimes.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>UV (ns)</th>
<th>VIS (ns)</th>
<th>NIR (fs)</th>
<th>NIR (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atmosphere</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Air</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Argon</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Accuracy (%)</strong></td>
<td>72.73</td>
<td>80.00</td>
<td>63.64</td>
<td>78.18</td>
</tr>
<tr>
<td><strong>True Positive Rate (%)</strong></td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td><strong>False Positive Rate (%)</strong></td>
<td>42.86</td>
<td>31.43</td>
<td>57.14</td>
<td>34.29</td>
</tr>
<tr>
<td><strong>True Negative Rate (%)</strong></td>
<td>57.14</td>
<td>68.57</td>
<td>42.86</td>
<td>65.71</td>
</tr>
<tr>
<td><strong>False Negative Rate (%)</strong></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Precision (%)</strong></td>
<td>57.14</td>
<td>64.52</td>
<td>50.00</td>
<td>62.50</td>
</tr>
</tbody>
</table>

From Table 27, only the VIS (ns) air case generated false negatives (5%). This was due to a failure to classify a 3-4 DNT as an explosive. This failure to classify the explosive may have been similar to the 1064 nm air regime case in Chapter 5, where there was an outlier in the nitros group. As such, this being the case, the Mahalanobis distance may show this sample to be closer to another group in this case the non-explosive, thus causing a misclassification.

The best discrimination case for the peaks was a tie between the UV (ns) argon case and the NIR (fs) air case. These two cases had identical results however; each had its own misclassifications in the non-explosive cases. Studying the false positive cases did show a mutual misclassification of anth, btca, caffe, cn, and pa. The chemical structure for the anth, btca, and pa molecules do not contain nitrogen. The cn molecule does not contain any oxygen, and a single cn bond. The caffeine does contain nitrogen and oxygen atoms, but they are not directly bonded as is the case for the explosive-like samples. These misclassifications would ultimately be traced back to the LIBS sampling of the analyte. There was not enough variance between the respective
spectra in order to differentiate the misclassified samples from the explosive-like. This lack of variance may be attributed to the amount of the analyte that was sampled, hence limits of detection and protocols for measuring the amount of analyte sampled need to be established.

From the covariance matrices shown in Figure 79, it is interesting to note that there is not much separation between the explosive-like and the non-explosives. In fact depending on the PC being studied there seems to be an overlapping region in which both classes are contained. A further examination of the misclassification of the non-explosives was examined based on the wavelength and the environment.

Table 28: Misclassification of non-explosives in the different wavelength regimes under air and argon environments.

<table>
<thead>
<tr>
<th>Wavelength Regime</th>
<th>UV (ns)</th>
<th>VIS (ns)</th>
<th>NIR (fs)</th>
<th>NIR (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
<td>Argon</td>
<td>Air</td>
<td>Argon</td>
</tr>
<tr>
<td>Misclassified Sample (%)</td>
<td>cn (40)</td>
<td>anth (20)</td>
<td>cn (20)</td>
<td>anth (20)</td>
</tr>
<tr>
<td></td>
<td>anth (100)</td>
<td>bp (80)</td>
<td>anth (60)</td>
<td>bp (100)</td>
</tr>
<tr>
<td></td>
<td>btca (20)</td>
<td>btca (20)</td>
<td>btca (60)</td>
<td>btca (60)</td>
</tr>
<tr>
<td></td>
<td>caff (40)</td>
<td>caff (80)</td>
<td>caff (40)</td>
<td>caff (100)</td>
</tr>
<tr>
<td></td>
<td>pa (20)</td>
<td>pa (100)</td>
<td>pa (60)</td>
<td>fluor (20)</td>
</tr>
</tbody>
</table>

Table 28 illustrates that each wavelength and atmosphere has a different set of misclassified samples and in a varying amounts. The difference in the sample misclassification reiterates the need to understand the amount of analyte necessary for detection. The LIBS spectra were examined for carbon emission (whether atomic or molecular) in order to verify that a sampled area had analyte present. However, as found in Chapter 5, unless the sample of interest had a radically different chemical structure such as the polymers, the variance was not strong enough to fully separate the different groups. Since PCA is the initial step in the QDA process, and the scores from the PCA are utilized in the QDA technique, it may be necessary to find an
alternative data reduction technique. PCA is based on a linear relationship and uses only variance as its criteria for separating the data, a hypothesis which may not be suitable for LIBS.

From the overall results, the two best case scenarios show that it is possible to discriminate explosives with a high success rate and a fairly low (~30%) false positive rate. The false positive rate may improve if the either the PCA performance is improved or a non-linear data reduction technique is utilized. In order to improve the PCA performance however, it is necessary to better understand the interaction of the LIBS’s sampling plasma with the organic analyte, as parameters that influence the plasma have already been explored.

6.6.2 QDA Results Based on the Amount of Information

Further examination of the jackknife technique yielded an interesting pattern. What was at first thought to be the best case scenario, the NIR (ns) argon regime, resulted in the worst overall discrimination rate. However, from the PCA results in Figure 80, only two PCs were necessary in order to represent approximately 99% of variance in the data. The second worst case of discrimination was yielded by the UV (ns) argon regime, which similar to the NIR (ns) argon regime, utilized only two PCs to represent approximately 95% of the variance in the data. Lastly, the VIS (ns) argon regime, was the third worst classification overall, and used three PCs to represent 90% of the variance in the data. This pattern was attributed to the fact that in electing to use only two PCs may not have provided as much information to fit to the model, as if four PCs had been utilized.

This meant that the choice of selecting a cut-off value for the variance may not have been the best way to select the number of PCs, and hence the amount of information provided to the quadratic model. Therefore an alternate method of data selection was explored in order to
explore the effects on the model’s results. The regimes with the worst discrimination were fitted with the quadratic model using the same number of PCs as the rest of the data set and the results are shown in Table 29.

Table 29: Results of QDA technique with the scores from the first four PCs used as data points.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Classification Matrix</th>
<th>Jackknifed Classification Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atmosphere</td>
<td>E (%)</td>
</tr>
<tr>
<td>UV (ns)</td>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>100</td>
</tr>
<tr>
<td>VIS (ns)</td>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>95</td>
</tr>
<tr>
<td>NIR (fs)</td>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>100</td>
</tr>
<tr>
<td>NIR (ns)</td>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>100</td>
</tr>
</tbody>
</table>

The adjusted table represents the quadratic model built by an equal number of data points. It was observed that the UV (ns) argon, VIS (ns) argon, and the NIR (ns) argon regimes were vastly improved in their discrimination with the additional data. In fact, the jackknife yields very promising results in positively discriminating explosive-like samples from other organic samples. The NIR (ns) argon case was still the lowest overall correct total classification.

The misclassification of the non-explosives was again examined to determine if the added information helped to rectify some of the incorrectly identified samples for the three improved cases.
Table 30: The QDA results for the amount of variance compared against the same number of PCs representing an equal amount of data.

<table>
<thead>
<tr>
<th>Wavelength Regime</th>
<th>UV (ns) argon</th>
<th>VIS (ns) argon</th>
<th>NIR (ns) argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>Variance</td>
<td>Equal PCs</td>
<td>Variance</td>
</tr>
<tr>
<td>Misclassified Sample (%)</td>
<td>anth (20) bp (60)</td>
<td>anth (20) btca (80)</td>
<td>cn (60) bp (20)</td>
</tr>
<tr>
<td></td>
<td>bp (80) btca (20)</td>
<td>bp (100) caff (40)</td>
<td>bp (100) btca (100)</td>
</tr>
<tr>
<td></td>
<td>btca (20) caff (20)</td>
<td>btca (60) caff (100)</td>
<td>btca (100) caff (80)</td>
</tr>
<tr>
<td></td>
<td>caff (80) pa (100)</td>
<td>caff (100) pa (100)</td>
<td>caff (100) pa (80)</td>
</tr>
<tr>
<td></td>
<td>pa (100)</td>
<td>pa (100)</td>
<td>pa (100)</td>
</tr>
</tbody>
</table>

With the additional data the QDA results were improved. In this case, the NIR (ns) still failed to correctly classify all the btca samples however the fluor, bp and caff results were improved. None of the fluor samples were incorrectly identified and only one of the bp samples was misclassified. Additionally, only four of the caff samples were incorrectly identified. In the VIS (ns) regime half of the samples were removed from the misclassification list. The btca sample classification apparently became worse when the extra data was added to the model, increasing from three to four misclassified samples. This may have been due to the extra PCs moving one of the samples closer to the explosive-like group. For both the VIS (ns) and UV (ns) regions the anth sample which had been misclassified was no longer incorrectly identified. In addition, the UV (ns) regime was able to reduce the percentage of misclassified samples of the caff and bp samples. It should be noted that the pa sample did not improve in any of the wavelength regimes. The pa was still considered an explosive-like sample even though the molecular structure does not contain any nitrogen, and the extra data does not help differentiate this sample.

It should be noted that with additional data the argon cases now surpass the air cases in the overall correct classification (barring the NIR (ns) argon case). This additional information may have added necessary information to better separate the data. While the argon atmosphere
for most of the wavelengths offers better discrimination and thus fewer false positives, however, if LIBS were to be utilized as a remote detection and sensing technique it would be unlikely that an argon atmosphere would be accessible. Thus the necessity to select the parameters that would yield the fewest false positives in an air atmosphere should be focused upon as the air represents realistic conditions of operation. Therefore emphasis was placed on the air regime for each wavelength, and a confusion matrix was constructed for additional information.

Table 31: Confusion matrix for respective laser regimes with equal number of PCs in an air environment.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>UV (ns)</th>
<th>VIS (ns)</th>
<th>NIR (fs)</th>
<th>NIR (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy (%)</td>
<td>80.00</td>
<td>80.00</td>
<td>80.00</td>
<td>78.18</td>
</tr>
<tr>
<td>True Positive Rate (%)</td>
<td>100.00</td>
<td>95.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>False Positive Rate (%)</td>
<td>31.43</td>
<td>28.57</td>
<td>31.43</td>
<td>34.29</td>
</tr>
<tr>
<td>True Negative Rate (%)</td>
<td>68.57</td>
<td>71.43</td>
<td>68.57</td>
<td>65.71</td>
</tr>
<tr>
<td>False Negative Rate (%)</td>
<td>0.00</td>
<td>5.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Precision (%)</td>
<td>64.52</td>
<td>65.52</td>
<td>64.52</td>
<td>62.50</td>
</tr>
</tbody>
</table>

In terms of explosive-like samples in air, all of the wavelengths excluding the NIR (ns) an 80% accuracy. The VIS (ns) case would not be selected due to the false negative rate. Again the UV (ns) and NIR (fs) have identical rates and precisions. Overall in air, the UV (ns) excitation appears to be the best excitation source to use if one wishes to correctly identify the organic residues with as few false positives as possible in the nanosecond regime. Likewise, the femtosecond regime would give similarly results to those of the nanosecond UV (ns) regime. These two regimes were also the preferred regimes in agreement with Chapter 5.

6.6.3 QDA Conclusions

The supervised classification techniques yield a much more positive outlook towards discrimination and classification of explosive-like and non-explosive residue. These studies were
completed on a non-metallic substrate and completed with a single laser shot. The PCA technique is not totally removed from the process, and is utilized for its strength in the reduction of data. While it may often be the starting point for a supervised technique, it does limit the effectiveness of nonlinear techniques, as PCA itself is based off a linear relationship assumption. A more appropriate data reduction technique would need to take into account data that is nonlinear. While this nonlinear data reduction technique would better suit LIBS data, it would also add a more complexity in the data analysis.

It becomes vital to examine the covariance matrices in order to determine if a linear relationship will correctly model the data set. If the covariances are not equal between PCs, then a nonlinear model becomes necessary. The quadratic model, not restricted to having equal covariance matrices, has a restriction on the number of variables that can be used due to the size of the data population. From the studies conducted here promising results are given, which allow for a high correct explosive-like classification, and a relatively low false positive rate. This criterion is met even in an air for the UV (ns) and NIR (fs) excitation sources.

6.7 Elimination of Substrate Using Target Factor Analysis (TFA)

A key application that would greatly enhance the analytical value of LIBS would be the ability to detect an organic analyte on an organic substrate. Previous chapters in this study have pointed out numerous factors that may introduce complications, which may prevent possible detection. However, an attempt was made to try and avoid these issues utilizing TFA. TFA is a positive step towards achieving discrimination of organics on a similar substrate.
6.7.1 Samples

LIBS was used to analyze three pure organic polymers nitrocellulose (NC), polystyrene (PS), and polyacrylonitrile (AN) shown below in Figure 81, as well as two mixtures: nitrocellulose placed on top of polystyrene, and polyacrylonitrile on placed on top of polystyrene.

These samples were selected in order to explore different variable emission. The chemical structure of the samples should be different enough that the PCA technique should have no problems in separating them. Two sets of experiments were conducted, one set in argon so that the influence of air would be negligible, and the other in air in order to understand the effects of air on the discrimination.

The polymers were made into solution by dissolving them into their respective solvents displayed in Table 32. In addition, Table 32 also displays the amount of material dissolved into the amount of solvent.
Table 32: Organic polymers and their respective solvents.

<table>
<thead>
<tr>
<th>Organic Sample</th>
<th>Abbreviation</th>
<th>Solvent</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose</td>
<td>NC</td>
<td>Methyl Ethyl Ketone</td>
<td>200 mg/3 mL</td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td>AN</td>
<td>Dimethyl Formamide</td>
<td>65 mg/2 mL</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>PS</td>
<td>Toluene</td>
<td>100 mg/1 mL</td>
</tr>
</tbody>
</table>

In order to prepare the pure samples a pipette was used to apply a small amount of the polymer solution to a silicon wafer. A glass slide was used to spread the film in a consistent thickness across the wafer (doctor blading). A second slide was held at angle so that the edge could be run along the top of the first slide, spreading the polymer solution as it was pulled across. Mixtures were prepared by applying a thin line of either nitrocellulose or polyacrylonitrile (1 mm width and a 0.70 µm thickness) via pipette on top of a silicon wafer already prepared with a thin base layer of polystyrene (3.40 µm thickness) as shown in Figure 82.

The two mixtures were used to represent organic analytes placed on organic substrates. Random interrogation of such a sample would ensure a complex spectrum with varying amounts of the nitrocellulose or polyacrylonitrile analyte as well as the polystyrene support.

Before the TFA technique could be applied it was necessary to conduct PCA in order to generate the necessary library. Forty spectra were taken on all of the samples in both air and
argon with a 1064 nm excitation source. The C, CN, C₂, H, N, and O peaks were collected from all of the spectra and the data was normalized from zero to one for each emission. Examples of the spectra are shown below in Figure 83.
Figure 83: Comparison of the AN, NC, and PC spectra to the mixed spectra of AN on PS and NC on PS in air, respectively. The region before the break has been multiplied by a factor of 2.
Figure 84: Comparison of the AN, NC, and PC spectra to the mixed spectra of AN on PS and NC on PS in argon, respectively. The region before the break has been multiplied by a factor of 5.

Due to the variability in the pulse energy the data within two standard deviations of the average emission were retained. An eigenanalysis was then performed on the pure sample peaks in order to further reduce the six variables; the variance is shown in the table below.
In this case the rule of one would not suffice, as all the PCs represent over 1% of the data. Therefore, the first three PCs for each environment were selected, this corresponded with a 93.33% cumulative variance in the air and a 94.84% cumulative variance in argon. The results of PCA analysis utilizing the first three PCs in an ambient air and ambient argon atmosphere are shown below in Figure 85 and Figure 86, respectively.

Figure 85: Principal component scores of the pure organic samples in an ambient air environment using the first three PCs.
In Figure 85, the ambient air atmosphere had a slight separation between the three samples. The most pronounced separation is the NC from both the AN and PS. While the AN and NC separate slightly, there is still a large area of overlap between the samples. In contrast with the air, the argon clearly separates all of the organics from one another. These PCA models were then used to predict scores for two mixed samples of AN on PS, and NC on PS.

6.7.2 TFA Results in Argon

The PCA model shown in Figure 86 was used to predict the scores for two mixed polymer samples. The first of which was AN on a PS background. The following plot shows the results of the predictions.
Figure 87: PCA model applied to the NC on PS sample in an ambient argon atmosphere.

The projected scores for the AN/PS sample overlap both the PS and the AN groupings. There appears to be a stronger bias towards the PS cluster with a few extending into the AN cluster. There are a few points between the AN and PS clusters and some outside of the AN cluster. The scores between the two pure clusters would be attributed to the laser sampling a spot which contained both the AN and PS. The shots outside of the AN may be attributed to AN scores that may have been outside of the model’s range.

The following plot shows the results of the NC/PS sample’s predicted scores.
Similar to the AN/PS behavior, the NC/PS scores overlapped the NC and PS clusters. The scores in this case were more equally distributed among the two clusters. There were still some that were in the middle of both, indicating a mixture of the two analytes.

In order to quantitatively compare the TFA analysis, a linear correlation was calculated from the comparison of the test and resulting vectors. The results are shown below in Table 34:

Table 34: Average correlations between the test and resulting vectors in argon.

<table>
<thead>
<tr>
<th>Test Vector</th>
<th>r (NC/PS)</th>
<th>r (AN/PS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>0.017017</td>
<td>0.337721</td>
</tr>
<tr>
<td>NC</td>
<td>0.734041</td>
<td>0.100218</td>
</tr>
<tr>
<td>PS</td>
<td>0.925094</td>
<td>0.967008</td>
</tr>
</tbody>
</table>

Figure 88: PCA model applied to the NC on PS sample in an ambient argon atmosphere.
Both samples show a correlation greater than 0.9 for the polystyrene. The NC correlation while not quite as high (0.73), was still much greater than the AN correlation (0.02) in the NC/PS sample. The AN sample alternatively, showed a higher correlation (0.34) than the NC (0.10) for the AN/PS sample. The lower AN correlation may be attributed to the scores mainly overlapping the PS and the region between the AN and PS clusters. Both samples however had consistent results with the experiment, showing the effectiveness of the TFA method.

6.7.3 TFA Results in Air

The air scores for the air library were not as clearly separated as those in the argon. Nevertheless, the models were used to predict the mixed samples’ scores.

Figure 89: PCA model applied to the AN on PS sample in an ambient air atmosphere.

The data for the AN/PS sample lie above the library samples which may be attributed to an discrepancy in the test data set. The C emission for the data set was found to be larger than the model’s data even after normalization. As a result the projected scores as shown above fall
outside of the model scores invalidating the model. Further studies are necessary to address if the results can be duplicated, indicating that TFA would not be valid for this scenario. The discrepancy however, was not present in the NC/PS data as shown below in Figure 90.

Figure 90: PCA model applied to the NS on PS sample in an ambient air atmosphere.

The projected scores for the NC/PS appear to be scattered throughout all three groups. This was to be expected as there was no clear separation between the groups. There appear to be some slight outliers that belong to no particular, and may have been outside the model. A better understanding of how well the TFA method works in both cases by examining the correlation between the test and model vectors.
Table 35: Average correlations between the test and resulting vectors in air.

<table>
<thead>
<tr>
<th>Test Vector</th>
<th>( r ) (NC/PS)</th>
<th>( r ) (AN/PS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>0.5181</td>
<td>0.5693</td>
</tr>
<tr>
<td>NC</td>
<td>0.8702</td>
<td>0.3330</td>
</tr>
<tr>
<td>PS</td>
<td>0.7341</td>
<td>0.3536</td>
</tr>
</tbody>
</table>

The correlation in this case for the PS was not nearly as strong as in the argon case, but was still fairly high in the NC/PS sample (0.73). The NC correlation (0.87) actually ranked much higher than the polystyrene in NC/PS. While not as big a discrepancy as in the argon the AN (0.52) was still lower than either of the NC or PS for the NC/PS sample. The relative high score could be attributed to the lack of clear separation in the test model. The correlation for the AN (0.57), however was somewhat higher than the NC or PS for the AN/PS sample. The NC (0.33) was fairly close to the PS (0.35) in the AN/NS which may be attributed to the data being outside the model’s valid limits. With these low scores, the NC and PS most likely would not have been considered to be present in the sample.

6.7.4 TFA Conclusions

From the samples tested, the argon case worked out ideally. The PCA model was able to clearly separate the pure samples, allowing for TFA to determine the contributing constituents of the sample with high correlations. For other constituents that were not included in the sample, a low correlation between the test and sample vector was calculated. In the case where the library samples were not as clearly separated, the technique still has the potential to perform a positive identification. In the case of the air model, a single contributor was found to be identified with a
high correlation. However, the lack of separation in the library may have artificially inflated the correlation of components that were not present in the sample. However, the inflated correlation should still be smaller in comparison constituents that were present.

The advantage of the TFA method as previously mentioned is its ability to identify unique classes of analytes regardless of the contributions from components that are not of interest (impurities and background). This can be accomplished only if the data set contains the unique class of analytes that can be separated through PCA. However, the ability for LIBS to sample and positively identify particular signatures in a mixture, adds a new dimension to LIBS sensing and detection.

6.8 Outcomes

LIBS was used to explore possible identification and classification of organic residues on non-metallic and organic substrates. Even with this optimized setup, PCA still failed to naturally cluster the samples by their identities, groups, or classifications. The PCA was still used as a data reduction technique, which was a beginning point for the supervised classification techniques that were studied. The difference in covariance matrices indicated that a linear technique would not be appropriate method to classify the data.

A quadratic discriminant analysis, which is not subject to the restrictions of the linear discriminant analysis, was explored to determine if explosive-like samples could be discriminated from non-explosives with a high accuracy. The model was fitted to the data in two different methods the first one based on a certain amount of variance, and the second based on the same number of PCs being entered so that the amount of data is equivalent. Each model was cross-validated with a jackknife test which demonstrated that the models built were sound as
long as there was not a large difference between the tests results and the jackknife results. Had a large discrepancy occurred, the model would have contained a bias that would have skewed the results to give a false confidence.

The two best cases were found to be the UV (ns) argon and NIR (fs) air. They both correctly classified a 100% of the explosives, and had an 80% accuracy. With the jackknife test the UV (ns) only correctly identified 95% of the explosive-like samples correctly and had an overall correct classification of 71%, while the NIR (fs) air was only able to classify 85% of the explosives correctly and had an overall 75% correct classification rate. An alternative method was used to construct the quadratic discriminant analysis based on using an equal amount of PCs for every regime. In order to model field conditions the air regime was selected. With these restrictions the UV (ns) and NIR (fs) regimes were preferable as they had identical results. Again both were able to classify 100% of the explosive-like samples correctly, and had an 80% overall correct classification rate.

Based on the results from the quadratic discriminant analysis, both cases were able to discriminate explosives-like residues from non-explosives placed on a non-metallic substrate in a single laser shot. Further improvements can be made, but this is a positive step forward for the LIBS community. Another step forward was taken in the discrimination of an organic mixture. The strength of the TFA technique allows for a library of unique analytes to be created, and as long as PCA can separate the unique analytes, the sample can be searched for possible constituents of the library. The TFA process yielded positive results for both the air and argon atmospheres. An ideal PCA separation occurred in argon, and even with a less than optimal separation in air, correlations of components present in the sample were still fairly high. More
studies need to be conducted on a variety of organic samples on organic substrates in order to
truly validate the process with repetitive results.

As steps are taken to move towards the identification of organic substrates, the
importance of being able to characterize the LIBS plasma comes into play. The current methods
of characterizing LIBS plasmas on organics are not valid, due to the limited emission of organics
in the visible wavelength range. Therefore, alternative methods must be sought in order to
address this critical issue.
7 ORGANIC MASS LIMITED DROPLETS

7.1 Motivation

Data analysis of single shot experiments pointed out the need for further examination of LIBS on organic residues and substrates. Optimizing parameters such as the shot-to-shot stability, signal-to-noise ratio, and the gate delay and gate width were not enough to fully explain all of the processes involved in the plasma generation on organics. A greater understanding of the fundamental LIBS interaction with organics would serve to improve detection methods thus improving the sensing technique. As such, fundamental LIBS experiments that explored the plasma emission of simple organics were conducted. These experiments were designed with the intended purpose of exploring the ambiguity in the resulting spectral emission of LIBS plasmas from both the sample and the surrounding ambient atmosphere of organics. With this goal in mind, it was necessary to create samples with well-known constitutions that could be explored under a variety of controlled atmospheric conditions.

The Laser Plasma Lab has become adept at designing and modeling mass-limited droplets for the purpose of Extreme Ultraviolet Lithography source development and the technology was adapted for use with LIBS. Utilizing the mass-limited target concept allowed for liquid droplets of known size and a known quantity of organic material to be constructed. In addition, the known spherical geometry of the droplet allows for an isotropic expansion of the LIBS plasma plume, which in theory would make observation of the plasma similar from all collection angles. The expansion in the experimental regime could be considered as a pseudo 1 D expansion, and thus can be modeled using a 1-dimensional theoretical code.
7.2 Strategy

Alternative techniques and methods are necessary to characterize LIBS plasmas on non-metallic and organic samples as traditional methods cannot be successfully utilized, due to the limited number of emitters in the visible range. Without atomic emitters of different upper energy levels, the necessary conditions to construct a Saha-Boltzmann plot are unmet and thus temperature calculations become nontrivial. The interdependency between the density and temperature result in arduous calculations for the density, and thus the characterization of the plasma becomes problematic. For these reasons we have employed an alternative strategy for characterizing the plasma emission from organics that includes the use of a theoretical code to model the plasma expansion and predict the plasma parameters such as the electron and ion densities and temperatures.

In this new strategy for examining organics organic signatures, LIBS was conducted on mass-limited droplets doped with simple molecules. Initial studies were first conducted with water droplets doped with copper-sulfate in order to characterize the plasma in a vacuum environment. The vacuum environment was selected as a method of minimizing the skewing effects caused by the radical recombination with the nitrogen and oxygen molecules present in an ambient air atmosphere. In this environment it was first assumed that the spectroscopic signatures obtained are characteristic of the samples alone. The copper lines from CuSO₄ +H₂O were utilized to characterize the plasma through the traditional method of calculating the plasma temperature and electronic density from a Saha-Boltzmann plot and the hydrogen alpha line broadening, respectively. The experiment was then modeled using the MEDUSA code, and the theoretical results were compared with the experimental. If the theoretical results could be shown
to accurately model the experimental results then the code could be used as a method of characterizing plasma emission from samples in which traditional techniques could not be used.

Lastly, organic molecules were qualitatively compared and examined to determine if a distinction between the molecules could be made based on contributions from the CN emission. Spectroscopic signatures taken under both an argon and air environment were compared against spectra taken under vacuum. The use of mass limited droplets may give insight into distinguishing molecules that have a CN bond, and molecules that exhibit CN emission due to atmospheric recombination.

7.3 Experimental Setup

The major components in the organic mass-droplet system were the laser and the vacuum chamber for the LIBS plasma generation. The instrumentation included an Echelle spectrometer (spectrometer port), an energy detector (energy meter) for energy measurements, and a webcam (the imaging port) which was used to observe droplet flow consistency. A picture of the 12 port ¼ cylindrical vacuum chamber and the setup within the chamber is shown below in Figure 91. Further details of the experimental setup, target droplet generation, analytical and theoretical methods used in the experiment are described in the following sections.
7.3.1 Laser

The laser utilized for this study was the same Quantel Brilliant laser described earlier in Chapter 4. The laser was operated at its fundamental wavelength of 1064 nm and a repetition rate of 10 Hz. After passing through a light valve the laser produced a p-polarized pulse of 11.7 mJ per pulse and pulse duration (FWHM) of 6 ns. Other laser parameters are shown in the Table 36 below.
Table 36: Laser statistics for 1064 nm over 500 shots at 10 Hz.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Value (mJ)</td>
<td>11.9</td>
</tr>
<tr>
<td>Minimum Value (mJ)</td>
<td>11.4</td>
</tr>
<tr>
<td>Average Value (mJ)</td>
<td>11.7</td>
</tr>
<tr>
<td>Standard Deviation (µJ)</td>
<td>87</td>
</tr>
<tr>
<td>RMS Stability (%)</td>
<td>0.7447</td>
</tr>
<tr>
<td>PTP Stability (%)</td>
<td>4.306</td>
</tr>
</tbody>
</table>

* PTP: point-to-point
* RMS: root mean square stability

Following the light valve, the beam was directed into the vacuum chamber and the target droplets were placed near the rear of the chamber. The laser beam was focused onto the target droplets using a 25.4 mm diameter, anti-reflection coated 50 mm focal length plano-convex lens, as illustrated in Figure 92.
A knife-edge scan\textsuperscript{222}, was conducted to measure the beam size and the focus through the 50 mm focal lens. The knife-edge scan yielded a beam waist of 232 \( \mu \)m, a focus of 51 mm, and a Rayleigh range of 3 mm. This resulted in an irradiance of \( 3.85 \times 10^9 \) W/cm\(^2\). The laser’s focus was aligned using green alignment Helium-Neon lasers, and the droplets and the observation optics were focused on this point.

7.3.2 Droplet Target

LPL has become adept at designing and modeling mass-limited droplets for EUV source technology\textsuperscript{223-226}. Unlike the high Z tin-chloride droplets constructed for EUV purposes, the
materials selected for droplets in these studies were copper-sulfate pentahydrate (CuSO₄·5H₂O), dimethylamine ((CH₃)₂NH), methanol (CH₃OH), and water (H₂O). The copper-sulfate pentahydrate was selected for its copper component which could be used to characterize the plasma. Water was selected due to its simplicity in chemical structure. The dimethylamine and methanol were selected in order to explore the CN band structure which is inherent in one sample and may occur in both due to recombination.

It was necessary to dope 100 mL of water with 32 g of copper-sulfate pentahydrate, which came in crystal form, to yield a copper-sulfate-water solution. The dimethylamine came in an aqueous solution with 0.89 g of dimethylamine per mL of water. Calculations were done in order to determine the number of atoms present in each of the 40 µm droplets. The results are shown in Table 37.

Table 37: Number of atoms for each of the elements in the respective liquids.

<table>
<thead>
<tr>
<th>Copper Sulfate Pentahydrate Solution</th>
<th>Element</th>
<th>Number of Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.27 * 10¹³</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>2.27 * 10¹³</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>2.82 * 10¹⁵</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>1.50 * 10¹⁵</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Methanol</th>
<th>Element</th>
<th>Number of Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4.98 * 10¹⁴</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>2.00 * 10¹⁵</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>4.98 * 10¹⁴</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dimethylamine Solution</th>
<th>Element</th>
<th>Number of Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>3.55 * 10¹³</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>7.10 * 10¹³</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>4.03 * 10¹⁵</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>1.02 * 10¹⁵</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water</th>
<th>Element</th>
<th>Number of Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.23 * 10¹⁵</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>1.12 * 10¹⁵</td>
<td></td>
</tr>
</tbody>
</table>

Time-resolved spectral measurements were made in the same spectral range as a function of the detection delay. Spectral data was acquired by integrating the individual spectra from 15 to 226
25 shots (dependent on the sample and the environment) in order to acquire a signal-to-noise of at least 1:1.20, which was focused on the hydrogen alpha line as it was necessary for the electron density calculations. The number of integrated spectra ranged from. It was assumed that the mass-limited droplets were homogenous, and thus each droplet was equal in constitution to the next.

For each delay, twenty-five spectra were taken with a gate width of 20, 30, or 40 ns depending on the lifetime of the plasma. The twenty-five spectra were divided into groups of five, where each group was summed to yield a total of five spectra for each delay. The five spectra allowed for calculation of mean line intensities and associated relative standard deviations. The table below displays the specifics for each sample.

Table 38: Number of integrated spectra and gate width for each sample in each environment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Environment</th>
<th>Gate Width (ns)</th>
<th>Number of Integrated Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper- Sulfate Pentahydrate</td>
<td>Vacuum</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Argon</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Water</td>
<td>Vacuum</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Argon</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>Methanol</td>
<td>Vacuum</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Argon</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>Vacuum</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Argon</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

It should be noted that the vacuum regime required the most number of integrated spectra due to the lower emission intensity. Additionally, the long lifetime of the plasma in the argon regime requires a larger gate width in order to cover the temporal range.
7.3.3 Droplet Generation

Capillaries were used to generate liquid droplets of approximately 40 µm in diameter. The liquids were placed in a pressurized reservoir which using compressed nitrogen and maintained at a fluid backpressure of 1000 kPa. The pressurization of the reservoir served to help force the liquid through the capillary.

The capillaries that were used in this study had a 10 µm diameter and were made of glass. A square wave voltage signal was used to drive a piezo-crystal, which in turn resonantly drove the glass capillary allowing droplets to be formed. While frequencies ranging from 10 kHz – 200 kHz could be obtained, a typical frequency of 20 kHz was used for the droplet generation in these studies. To synchronize the laser with the droplets, a portion of the capillary driving signal was directed into a phase-locked loop electronics that triggered the flashlamps of the Brilliant laser. Inherent delays between the flash-lamps, the Q-switch, and the emission of the laser light had to be accounted for in the synchronization system. Full synchronization was accomplished by adjusting the delay between the droplet formation and the flash-lamp trigger. A web-camera monitored the laser interaction with the droplets in order to verify that the laser was ionizing the droplets.

The substantial difference between the laser repetition rate and the droplet repetition rate required that unused droplets be collected in order to preserve the vacuum levels in the chamber. In this study the laser irradiated one droplet in every two thousand droplets leaving 1,999 droplets to be collected by a cryogenic trap. The trap was cooled by liquid nitrogen, and was equipped with an electronic chopper to prevent the formation of ice crystals as shown in Figure 93.

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Water droplets have been characterized in the study conducted by Keyser\textsuperscript{227}. Once the 40 µm droplet had been achieved, an image was recorded by a Logitech web-camera. The droplets were then measured in diameter against the water droplet for consistency of droplet size. The web-camera also served as a method of determining when the droplet had strayed from the laser focus.

7.4 MEDUSA Code Assumptions

The MEDUSA code as introduced back in Chapter 2 was selected to model the hydrodynamic expansion of the plasma. In order to do so however, the code had to make some assumptions that would cause the results to differ from the experimental. The initial assumption of the code begins with a two stream fluid that has free electrons and ions, which as discussed in Chapter 2 is not the initial point of a laser-induced plasma. The plasma is treated as a two component fluid in which one subsystem or fluid describes the electrons and the other the ions. The laser-plasma coupling physics, electron, and radiation transport as shown in Chapter 2 are incorporated and treated in the code.
MEDUSA assumes that there is charge neutrality between the two fluids which requires that both systems share the same velocity. This allows for a single equation of motion to describe both systems:

\[ \rho \frac{du}{dt} = -\frac{dp}{dx} \]  \hspace{1cm} (7.4.1)

where \( \rho \) is the mass density, \( u \) is the fluid velocity and \( p = p_e + p_i \) is the hydrodynamic pressure.

The electrons and ion fluids are further governed by an energy equation in which the absorbed laser energy is partitioned into both hydrodynamic and kinetic states. The energy equation is described as:

\[ C_v \frac{dT}{dt} + B_T \frac{d\rho}{dt} + p \frac{dV}{dt} = S_{e,i} \]  \hspace{1cm} (7.4.2)

where \( C_v = (\partial U/\partial T)\rho \) is the specific heat per unit volume, \( B_T = (\partial U/\partial \rho)_T \) describes the variation of internal energy due to the interaction between particles within the same subsystem, and \( U = pV/(\gamma - 1) \) is the internal energy per unit mass, and \( S_{e,i} \) is the rate of energy input per unit mass for either the electrons or ions respectively. The \( S_e \) term represents the electron energy source and is composed of electron-ion energy exchange, Bremsstrahlung, laser absorption, and thermal conduction terms. As only the electrons absorb the laser light they exchange energy with the ions through electron-ion collisions making the electron-ion energy exchange term common to both \( S_e \) and \( S_i \). In addition to the electron-ion energy exchange, the ion energy source \( S_i \) is comprised of thermal conduction, and shock heating terms.

In most laser-produced plasmas or unmagnetized plasmas the major energy transport mechanism is diffusive conduction from cold electrons. The thermal electron energy flux is given by:

\[ q_e = -\frac{1}{3} \lambda_e \nu_e k \nabla T_e = -K \nabla T_e \]  \hspace{1cm} (7.4.3)
where $\lambda_e$ is the average mean for electrons in multiple Coulomb collisions with ions which are deflected off at 90° angle and is expressed as:

$$\lambda_e = 1.12 \times 10^7 \frac{T_e^2}{Zn_e \ln \Lambda} \quad (7.4.4)$$

And $K$ is the classical Spitzer-Harm conductivity (ref) which is defined as:

$$K = 2 \times 10^{-4} \frac{T_e^{5/2}}{Z \ln \Lambda} \quad (7.4.5)$$

The Spitzer-Harm conductivity is only valid if $\lambda_e/L \leq 10^{-2}$, where $L = T/(dT/dx)$ is the temperature scale length\textsuperscript{227}. In terms of heat flow ($q$), the Spitzer-Harm conductivity is valid only when $q/q_f \leq 2.4 \times 10^{-2}$, where $q_f$ is associated with all electrons streaming in the same direction and is known as the free streaming limit of the heat flow and is defined as\textsuperscript{138}:

$$q_f = n_e kT_e \left(\frac{kT_e}{m_e}\right)^{1/2} \quad (7.4.5)$$

The Spitzer-Harm conductivity does not properly describe laser plasmas, as most laser produced plasmas have steep temperature and density gradients, and has been shown from numerical solutions to the Fokker-Planck equation to overestimate the heat flow\textsuperscript{138}. MEDUSA accounts for this multiplying the free streaming limit ($q_f$) by an adjustable parameter $f$, known as the flux limiter. This circumvents the overestimation by restricting the heat flux to the harmonic mean:

$$\frac{1}{q_e'} = \frac{1}{q_e} + \frac{1}{f \cdot q_f} \quad (7.4.6)$$

As a flexible parameter $f$ is usually adjusted to match experimental results and is typically given a value of 0.1\textsuperscript{229}.  

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7.5 Experimental Results Compared to Theoretical Results

For the purpose of these studies MEDUSA will be used as a diagnostic tool for acquiring plasma parameters that cannot be calculated by traditional methods as discussed in Chapter 4. The assumed environment in MEDUSA is a vacuum atmosphere and as such to accurately model and represent the LIBS studies, the experiments were also conducted in vacuum. Copper-sulfate pentahydrate was explored as the initial sample, as the copper lines could be used to characterize the plasma, and compare the electron density and electron temperature against those predicted by MEDUSA.

![Graph](image)

*Figure 94: Copper-sulfate pentahydrate taken under a vacuum environment.*

The collection of the LIBS signal began immediately as soon as the laser interacted with the target. However line emission was not detectable in the first 10 ns as shown below, due to the broad continuum emission.
The Cu I lines intensities as a function of time are shown below and the method of measuring the line intensity is given in Chapter 4.

![Graphs of Cu I line emissions as a function of time](image)

Figure 95: Cu I line emissions as a function of time under vacuum.²³⁰

The copper lines peak at approximately 40 ns after the laser pulse has interacted with the sample. The 465 nm copper line had the strongest emission while the 324 nm had the lowest emission. The absence of intensities before the 40 ns can be attributed to the free-free transitions and free-bound transitions that precede the bound-bound transitions which do not emit specific
line emissions that can be used for temperature measurements. The rapid decay after the peak indicates may be attributed to the free expansion of the plasma in the vacuum. The expansion may have been too rapid for measurements in temporal window of detection of 20 ns. The temperature was calculated based on these copper line transitions and are shown below in Figure 95.

![Graph showing electron temperature (eV) vs. time (ns)](image)

Figure 96: Copper-sulfate pentahydrate temperature under vacuum taken at various times.

The temperature from the copper-sulfate pentahydrate reaches peak of 0.81 eV (± 3%) throughout the emission of the copper lines. The copper lines which prevent further temperature calculations are the transitions of 521.8 nm and 324.8 nm lines, as their emission is indistinguishable from the background. As there was no emission from any of the lines at time 0, the graph starts at 20 ns. Exploration of the plasma closer to its initialization should be studied in order to assess the early plasma constituents, but is prevented due to the emission from the continuum (bremsstrahlung and recombination radiation), and the finite gate width of the iCCD camera due to various electronic limitations.
As discussed in Chapter 4, in order to calculate the electron density it was necessary to measure the Stark Broadening of the H$_\alpha$ line (656.6 nm). Using the temperatures and Equation 4.4.3, the electron densities were approximated with the fractional intensity width of hydrogen which had to be determined from the tables listed in Appendix III of Griem’s, *Spectral Line Broadening by Plasmas*. The parameters for determining the electron densities and the densities themselves are displayed in Table 39 and Figure 97, respectively.

Table 39: Electron densities and the parameters necessary for their calculation.

<table>
<thead>
<tr>
<th>Time (ns)</th>
<th>Temp (eV)</th>
<th>Temp Error (eV)</th>
<th>H$\alpha$ Stark Broadening (nm)</th>
<th>Balmer Alpha (2, 3) Electron Density (cm$^{-3}$)</th>
<th>Density error (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.803</td>
<td>0.033</td>
<td>0.4428</td>
<td>0.0186</td>
<td>2.946E+17</td>
</tr>
<tr>
<td>40</td>
<td>0.811</td>
<td>0.040</td>
<td>0.5481</td>
<td>0.0186</td>
<td>4.057E+17</td>
</tr>
<tr>
<td>60</td>
<td>0.794</td>
<td>0.045</td>
<td>0.3648</td>
<td>0.0186</td>
<td>2.203E+17</td>
</tr>
<tr>
<td>80</td>
<td>0.795</td>
<td>0.036</td>
<td>0.3435</td>
<td>0.0186</td>
<td>2.013E+17</td>
</tr>
<tr>
<td>100</td>
<td>0.797</td>
<td>0.049</td>
<td>0.3491</td>
<td>0.0186</td>
<td>2.062E+17</td>
</tr>
<tr>
<td>120</td>
<td>0.790</td>
<td>0.027</td>
<td>0.3504</td>
<td>0.0186</td>
<td>2.073E+17</td>
</tr>
</tbody>
</table>

Figure 97: Experimental electron density for a copper-sulfate pentahydrate plasma.

The maximum density of 4.06*10$^{17}$ cm$^{-3}$ occurs at 40 ns and rapidly decays after this point to a density of 2.07 *10$^{17}$ cm$^{-3}$. 

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MEDUSA was used to model the experimental conditions and the expansion of the plasma in terms of the electron density is shown below in Figure 98.

Figure 98: Electron density evolution as the plasma expands away from the center of CuSO$_4$+5H$_2$O doped water droplet.

The timescale on the right-hand side of the figure represents the time relative to the peak of the laser pulse. The peak electron temperature of 0.81 eV and density of 4.06*10$^{17}$ cm$^{-3}$ which occur at 40 ns were used to match conditions for the MEDUSA predictions. These parameters allowed for the temporal and spatial location of the emission from the plasma to be identified.
Figure 99: Predicted results for the electron temperature and density at 40 ns using MEDUSA. The red lines show the location of the experimental measurements.

From the MEDUSA predictions the emissions from the copper lines occur in the corona of the plasma. The electron density range of $10^{17}$ cm$^{-3}$ occurs at a distance approximately 190 - 280 µm away from the center of the CuSO$_4$+5H$_2$O doped water droplet. The electron temperature was observed in the same interval and the temperatures range between 0.001 to 0.007 eV. In order to achieve an electron temperature of 0.81 eV MEDUSA predicts that the emission would occur at approximately 25 µm from the center of the droplet.

The discrepancy between the electron temperature and electron density location is attributed to the lower LIBS plasma temperature, as MEDUSA was designed to model fusion plasma temperatures which can range from 200 – 300 eV. Fusion temperature and densities are often achieved with intensities of approximately $10^{14}$ W/cm$^2$ whereas plasmas used for LIBS studies on average range from $10^8$ - $10^9$ W/cm$^2$. In addition the experimental temperature was calculated by fitting a Boltzmann distribution to the emission lines that occur after the Planckian emission has ceased to dominate the spectrum. The MEDUSA code alternatively uses a
Planckian model to calculate the temperature and does not include a subroutine which handles ionization temperatures.

7.5.1 Discussion

Comparison of the experimental and the theoretical results show that it may be possible to utilize the MEDUSA code as a diagnostic tool if appropriate assumptions are made. The hydrodynamic expansion calculations tend to follow the same patterns as the experimental results, but fine tuning the simulation may yield more accurate results, as the code was designed to model higher temperature and higher density plasmas. There will be a limit to the accuracy of the code as it does not include important chemical reactions that can extend the lifetime of the plasma emission via recombination.

Another modification that can improve the accuracy of MEDUSA includes either adding a laser ablation component to the code, or feeding in appropriate initial conditions calculated from an ablation code. As discussed in Chapter 2, laser ablation plays a critical role in the formation and expansion of plasma. While MEDUSA does allow for the user to suitably model the laser parameters and target composition, the initial free electrons and ions temperature make it difficult to pinpoint an agreement in the time domain where the simulations complement the experimental results. Additional knowledge and understanding also needs to be gained on the experimental side as to the initial plasma temperatures.

The continuum emission has classically been attributed to the combined effects of Bremsstrahlung (free-free transitions) and radiative recombination (free-bound) transitions\textsuperscript{124,231}. Studies have linked the observed spectral continuum directly to both the electron and ion density and the electron temperature\textsuperscript{231-233}. However, in using this approach towards non-hydrogenic
plasmas this approach is non-trivial due to the lack of cross section data and the approximations necessary to determine correction factors. De Giacomo et al.\textsuperscript{234} have suggested fitting the continuum emission to a Planck-like distribution which does not necessitate theoretical data (cross-sections and correction factors) but does require spectral calibration of the continuum.

As an estimation method for determining initial temperatures Di Giacomo et al. point out that the fitting of a blackbody radiation curve does not imply that the photons produced by the continuum obey the black body theory. The number of photons generated from the Planck-like distribution corresponds to the photons contributing to the real experimental Planck-like curve. A Planck-like curve, defined as the irradiance (\(I_\lambda\)) of a blackbody in a spectral range (\(d\lambda\)) is represented by the following equation:

\[
I_\lambda = W_\lambda d\lambda = \frac{G}{\lambda^5} \frac{1}{\exp(hc_0/\lambda kT) - 1} d\lambda \approx \frac{G}{\lambda^5} e^{\frac{-hc_0}{\lambda kT}} d\lambda \quad (7.5.1)
\]

where \(h\) is Planck’s constant, \(k\) is Boltzmann’s constant, \(c_0\) is the speed of light, and \(G\) includes the instrumental response coefficient. This equation holds in vacuum, and if another gas replaces the vacuum, the right-hand side of the equation is multiplied by the square of the refractive index of the gas. This estimation of the earlier temperatures may give better initialization temperatures for the electrons and ions. Similar to constructing a Boltzmann plot, the logarithmic form of the Planck curve equation is necessary to form a linear relationship:

\[
\ln \left(\frac{I_\lambda \lambda^5}{8\pi hc_0^2}\right) = Q - \frac{hc}{\lambda kT} \quad (7.5.2)
\]
where the constant \( Q \) contains both the \( G \) factor and the spectrometer’s spectral range \( (d\lambda) \). The inversion of the slope of the line yields the temperature of the photons produced from recombination, and the experimental photon number density can be obtained from:

\[
N_{\lambda, \text{exp}} = \frac{4I_{\lambda} \lambda}{h c^2}
\]  

This method of determining the electron temperature and density has a few caveats, the first being that the Bremsstrahlung contribution to the continuum is neglected, and thus the electron temperature and density is due to the radiative recombination. This was due to the necessity of having to calculate the Biberman and Gaunt correction factor. De Giacomo et al.\(^{234}\) illuminate on other important reasons for neglecting the Bremsstrahlung from the Planck technique in their study. Another big caveat to using the Planck method to determine the plasma characteristics from the continuum lies in the limited amount of data and selected elements that have been studied. Currently, this method has only been applied to pure elements including Ti, Si, C, and Al, and has not been expanded to molecules. In addition, studies on these elements have only been conducted in an ambient air atmosphere.

While not covered in this study, it is hypothesized that the MEDUSA code may be able to give an estimate of the plasma behavior over a wide range of atmospheres with a modifications and additional input data. The code is built around a three shell model, and currently the second and third shells could be filled with different gases including argon and air. The hydrodynamic expansion into these regions would be very beneficial as there are more interactions that occur, and without free expansion the lifetime of the plasma is increased as the plasma cannot expand.
as rapidly. In an effort to observe how the atmosphere affects the lifetime of the plasma, copper-
sulfate pentahydrate droplets were explored using LIBS under argon and air atmospheres.

Figure 100: Temperature and density of plasmas for copper-sulfate pentahydrate doped droplets under an ambient argon environment.
The emission from the copper lines lasted approximately 2.5 times longer in argon than that of the vacuum as discussed in Chapter 5. The temperature peaks at the same point as in the vacuum at 40 ns which corresponds a temperature of 0.87 eV.

The electron density calculations for the argon atmosphere show a slight difference in the profile in comparison with the vacuum. The temperature peak at 40 ns does not correspond to the electron density peak, which occurs at approximately 200 ns and corresponds to density of $2.67 \times 10^{18} \text{ cm}^{-3}$. After this point there is a decay that, while as not as rapid as in the vacuum, is still fairly quick. The earlier densities do not have a smooth increasing trend, which was accredited to the rough estimation that was done due to lack of information in the density tables provided by Griem. The tables only have information for temperature in increments of 5,000 K. The temperatures measured were closer to 9,000 K, therefore the densities have some estimation error. The erratic behavior at later times was attributed to the drift in the droplet position as the data showed increasing amounts of droplets which had strayed from the focal point. Correction to the droplet position was necessary and had to be done manually adding to the error.
Figure 101: Electron temperature and electron density of plasmas for copper-sulfate pentahydrate doped droplets under an air environment.

The air atmosphere has the longest plasma emission relative to the other atmospheres. Similar to the other atmospheres the temperatures remains constant around 0.8 eV, with the
maximum temperature of 0.83 eV occurring at 40 ns. Again, however, it is the electron density that distinguishes the air atmosphere from the others. The air regime does not have as rapid a decay as the vacuum or argon, but has more of an exponential decay that occurs over a period of approximately of 400 ns. At 140 ns the electron density in the air reaches a peak value of $5.0 \times 10^{18} \text{ cm}^{-3}$, and 440 ns later decreases to an approximate value of $1.0 \times 10^{18} \text{ cm}^{-3}$ where it remains constant within the error.

### 7.6 Water Plasma

Water is a simple molecule consisting of only two hydrogen atoms and a single oxygen atom, making it an ideal molecule to study and characterize using LIBS. In addition, by comparing the results of the copper sulfate solution to water, an understanding of how the copper-sulfate affects the plasma parameters of the water can be obtained. A LIBS spectrum of water in vacuum is shown below in Figure 102.
The spectrum of water shows very strong hydrogen and oxygen transitions that are identified below in Table 40.

Table 40: Atomic transitions for hydrogen and oxygen.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Configuration</th>
<th>Terms</th>
<th>Emission Line (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>n=2 – n=3</td>
<td></td>
<td>656 nm</td>
</tr>
<tr>
<td>H</td>
<td>n=2 – n=4</td>
<td></td>
<td>486 nm</td>
</tr>
<tr>
<td>H</td>
<td>n=2 – n=5</td>
<td></td>
<td>434 nm</td>
</tr>
<tr>
<td>O</td>
<td>2s^22p^3(^4S^0)3s - 2s^22p^3(^4S^0)3p</td>
<td>^5S^0 - ^5P</td>
<td>777 nm</td>
</tr>
<tr>
<td>O</td>
<td>2s^22p^3(^4S^0)3s - 2s^22p^3(^4S^0)3p</td>
<td>^3S^0 - ^3P</td>
<td>844 nm</td>
</tr>
</tbody>
</table>

Other peaks that appear in the spectrum are artifacts due to the higher orders from the grating in the Echelle spectrometer. From the spectrum, the hydrogen alpha line dominates the spectrum, so much so that the other two hydrogen lines were barely visible. The emission peaks of the
hydrogen and oxygen lines were collected over the lifetime of the plasma in order to determine
their individual lifetimes.

The hydrogen beta (486 nm) and the hydrogen gamma (434 nm) have a similar trend in the rise
and fall over the span of after 100 ns. The hydrogen alpha line (656 nm) had a sharp rise and a
slow decay which lasts over the lifetime of the plasma. It was possible to calculate an electron
temperature and density for the hydrogen peak at 40 ns and both are shown below in Table 41.

Figure 103: Lifetimes of the hydrogen and oxygen transition lines respectively.
Table 41: Electron temperature, density, and the parameters necessary for their calculation for H$_2$O at 40 ns.

<table>
<thead>
<tr>
<th>Temp (eV)</th>
<th>Temp Error (eV)</th>
<th>Temp (K)</th>
<th>Hydrogen alpha Stark Broadening (Å)</th>
<th>alpha (1/2)</th>
<th>Electron Density (cm$^{-3}$)</th>
<th>Density Error (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.041</td>
<td>0.5832</td>
<td>12075.6</td>
<td>8.044710345</td>
<td>0.0186</td>
<td>7.214E+17</td>
<td>4.041E+17</td>
</tr>
</tbody>
</table>

The fluctuation in the error for the hydrogen was found to be higher in comparison with the copper-sulfate pentahydrate as hydrogen is a lighter element and is very sensitive to any perturbations. The oxygen lines follow a similar behavior to that of the hydrogen alpha line with a sharp rise time and slow decay, and while not as strong as the hydrogen transition they are still relatively prominent.

The results from MEDUSA are shown below in Figure 104.

Similar to the CuSO$_4$+5H$_2$O the emission region from the water plasma occurs in the corona of the plasma. It spatially located between 258–320 µm which is further away from the core in comparison with CuSO$_4$+5H$_2$O. In order to verify the MEDUSA predictions it is necessary to experimentally probe the plasma in a series of time-resolved studies and spatially resolve the

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temperatures regions of the plasma. However most plasmas are assumed to be in local thermodynamic equilibrium conditions but verification is necessary as discussed in Chapter 4.

7.7 Application to Organics

The organic samples, methanol and dimethylamine, were studied in order to understand how the spectroscopic signature varies with an atmosphere. In LIBS when a target containing carbon is excited the carbon can react with the nitrogen in the atmosphere and emit characteristic CN line emission. The question of the origin of the CN emission becomes more complex in regards to identifying organics when samples which include inherent CN bonds or just carbon and nitrogen in the sample are explored as well. There are three main routes that have been cited: i) the original compound is fragmented to directly release carbon dimmers and CN molecules, ii) the atomic and ionic constituents in the plume of the original compound reacts with the surrounding atmosphere leading to the production of CN, and iii) the C and N atoms from the original compound recombine in the plasma to produce both C$_2$ and CN$^{235}$. While not solved here, an attempt is made to identify whether a sample containing a CN band can be distinguished from a sample which has CN emission due to radical recombination using these mass limited droplets at low irradiance.

From the previous sections if improvements to the MEDUSA code could be made to improve the accuracy of the theoretical calculations, then the calculated electron density and temperature may be used to better quantitatively characterize the organic samples. However, without MEDUSA calculations, it should still be possible to gain a better understanding of the differences in the samples based on their spectra, and their C, CN, and N emissions. In general,
the C₂ emission would be used, however the band falls in-between two orders of the Echelle spectrometer making it difficult to accurately detect in our case.

7.7.1 Vacuum

The dimethylamine (C₂H₇N⁺H₂O) and methanol (CH₃OH) samples were first studied under a vacuum environment of approximately 5*10⁻¹ Torr. Studies have shown that an enhanced spectrum can be obtained from performing LIBS on a surface at pressures below atmosphere; more specifically, these enhancements can include an increase in the spectra signal-to-noise²³⁶-²³⁸. While the LIBS spectrum taken under vacuum has a lower FWHM line width in comparison with that of atmospheric conditions is often less intense²³⁹. Dreyer et al.²⁴⁰ confirmed that the lower FWHM line width was a result of the decreased electron density as observed by reduced Stark broadening. LIBS spectra of dimethylamine and methanol are shown in Figure 105.
Figure 105: LIBS spectra from methanol and dimethylamine in vacuum.

While time-resolved studies were conducted, it was necessary to take an integrated spectrum in order to verify that the emissions were present in a high signal-to-noise spectrum. The samples are different in their respective spectra, as the methanol appears to have more carbon emission
than the dimethylamine. The carbon emission may be due to the fact that the methanol was a pure sample and was not doped into water. While the dimethylamine as molecule has twice the mole fraction of carbon in comparison with methanol, the number of carbon atoms in the methanol was $4.98 \times 10^{14}$ in comparison with the $7.10 \times 10^{13}$ carbon atoms in the dimethylamine as shown in Table 37. There is an order of magnitude difference between the samples and the methanol has more possible carbon emitters. The oxygen in the dimethylamine is not native to the sample but instead is a result from the water, into which the dimethylamine was diluted. The spectra gave some insight into the differences between the two samples, specifically with the emission of atomic and molecular carbon molecules.

The carbon emission was monitored over the emission of the plasma in order to determine if there was any emission for the dimethylamine. There was a weak carbon emission present in the methanol, but not in the dimethylamine sample. The data was visually inspected to verify the presence of the carbon peaks. The plasma emission times are very different with the methanol lasting approximately a full microsecond longer, however the carbon emission only lasts for approximately 120 ns, after which the emission is indistinguishable from noise. In comparison with the pure water sample (as shown in Figure 103) the lifetime of the dimethylamine solution is even shorter by approximately 200 ns. The decrease in the lifetime may be attributed to the droplet placement stability, which seemed to have more variance with the dimethylamine droplets than with the methanol droplets. Improvements to the positioning system could be made by automating the process, as manual adjustments had to be made in this study.
Due to the CN signature in the methanol but not in the dimethylamine, the nitrogen and CN emission signatures were studied for both samples. The CN signature was expected for the dimethylamine sample as it has nitrogen atoms in the molecule.

![Graphs showing nitrogen and CN emissions for methanol and dimethylamine over time](image)

Figure 106: Nitrogen (left) and CN (right) emissions for methanol and dimethylamine over time in a vacuum environment.

Both samples have N and CN emissions that last for approximately 160 ns. The CN emission follows the same trend as the nitrogen with the strongest emission occurring at 40 ns consistent with peaks in the carbon and nitrogen. The peaks were weak indicating that the CN emission was not very strong. The observance of the nitrogen emission could be interpreted as nitrogen
remaining in the vacuum atmosphere. In order to truly remove the nitrogen from the vacuum, a higher vacuum pressure is necessary.

7.7.2 Argon Atmosphere

A study conducted by Aguilera et al.\textsuperscript{241} found that a higher plasma temperature and electron density could be achieved over a slower decay in an argon environment in comparison with air\textsuperscript{241}. In comparison with the vacuum, more emission from the plasma should be captured as the shortened mean free path should retard the plasma expansion velocities. A LIBS spectrum of both the dimethylamine and methanol is shown below.
Similar to the vacuum regime, the methanol showed a weak atomic carbon emission, while the dimethylamine did not exhibit any atomic carbon. However, in the argon there did not appear to be any other molecular carbon emission. Also both samples appear not to show the H\textsubscript{\beta} line which was present in the vacuum atmosphere. The argon lines are very prominent in both spectra and tend to overshadow the signal from the sample. Due to the high argon signal, it was necessary to
observe the hydrogen line and measure the relative standard deviation (RSD) in order to determine when the emission from the sample had ended. The oxygen lines were observed as well but the proximity of the oxygen line to the broad argon line made it difficult to accurately monitor.

Figure 108: Carbon emission over time for methanol and dimethylamine in an argon environment.

The dimethylamine spectra had a small atomic carbon emission of 250 ns during the lifetime of the plasma emission. The methanol conversely has a strong atomic carbon emission that lasted
approximately 220 ns, but from the spectrum there does not appear to be any recombination with other atoms for any radical formation. It interesting to note that the lifetime of the dimethylamine plasma appeared to last longer than the methanol based of the H\textalpha line emission. According to the hydrogen RSD the plasma emission from the methanol sample did not die out until approximately 1900 ns, while the dimethylamine has plasma emission out to 3000 ns approximately 1 \( \mu \)s longer than the methanol. This may have been a consequence of the reliance on the hydrogen emission to determine when the plasma emission from the sample was completed, as there may have inadvertent towards the dimethylamine. This bias would be due to the dimethylamine solution having approximately twice the amount of hydrogen atoms (4.03 * \( 10^{15} \) atoms) relative to the methanol (2.00 * \( 10^{15} \) atoms).

![Graph](image1.png)

**Figure 109:** Hydrogen alpha emission representative of the sample plasma emission lifetime for methanol and dimethylamine in an argon environment.

The CN and N emissions for the methanol and dimethylamine are shown in the Figure 110.
The CN emission for the methanol had a sharp rise time and reaches its peak at 30 ns, the subsequent decay lasts until 250 ns where it then becomes indiscernible from the noise. In the dimethylamine case, the CN emission reaches its peak at 40 ns and decays until 320 ns where it can no longer be distinguished from the noise. The nitrogen in both cases followed the same rise as the CN emission, however the nitrogen in the methanol lasted until 540 ns and in the dimethylamine the nitrogen remained until 560 ns. The nitrogen emission however, needs to be monitored with a high resolution spectrometer as the nitrogen emission was very close to the argon lines in the NIR region.

Figure 110: Nitrogen (left) and CN (right) emissions for methanol and dimethylamine over time in an argon environment.
7.7.3 Air Atmosphere

The air atmosphere is the most complex of the three regimes in terms of spectral signature and the radical recombination. A study conducted by Arp et al.\textsuperscript{242} indicated that as the pressure is increased the LIBS signal intensity and signal-to-noise ratio is decreased. In addition, the spectra from LIBS show a significant peak broadening, and unlike in the argon atmosphere self-absorption of the emission lines may occur. Also with the introduction of air, comes nitrogen which is inherent to the atmosphere making it difficult to distinguish if the CN band emission is due to atmospheric recombination.

Spectra for the methanol and dimethylamine in air are shown below in Figure 111.
From the spectra of the samples, the dimethylamine does not exhibit any carbon emissions atomic or molecular recombination. This was attributed to the early gate delay as the methanol taken under at a slightly earlier delay does show carbon emissions. This behavior has been constant throughout all of the atmospheres explored. To verify that there was no atomic carbon present throughout the plasma emission the atomic carbon emission was inspected.
Figure 112 shows similar results to the vacuum environment in that there is no atomic carbon emission for the dimethylamine whose plasma emission lasts for approximately 760 ns. In contrast, the methanol does have a strong atomic carbon emission that lasts for approximately 140 ns, in comparison with the emission of the plasma which lasts for 1200 ns. The behavior of the carbon emission is very similar to that of the argon atmosphere, although the initial intensity
count was higher in the argon by approximately 10%. While the atomic carbon may not have been detected for the dimethylamine, there still may have been molecular recombination occurring as was evident in the vacuum and argon environments.

The nitrogen lines were inspected along with the CN band emission in order to determine if there was any molecular structure emission.

![Nitrogen emission for methanol](image1)

![CN emission for methanol](image2)

![Nitrogen emission for dimethylamine](image3)

![CN emission for dimethylamine](image4)

Figure 113: Nitrogen (left) and CN (right) emissions for methanol and dimethylamine over time in an ambient air atmosphere.

In the air regime the nitrogen emissions have a longer time of emission in comparison with the argon and vacuum regime. Both the dimethylamine had nitrogen signatures that lasted out until
700 ns before falling into the noise range. The methanol had signatures of nitrogen that lasted out to approximately 800 ns before the emission was indiscernible from noise. The CN emission from the methanol sample lasted out 360 ns, whereas the dimethylamine only had CN emission out to 180 ns.

7.7.4 Discussion

While not all these experiments were optimized, there are some general trends that warrant further studies. The vacuum regime, proved to have the shortest emission times attributed to the rapid free expansion of the plasma. The ability to lower the gate width in order to gain a more accurate picture of the plasma temperature in the earlier times would be preferable but is restricted due to electronic limitations. In terms of spectra, the vacuum may have had the least intense spectrum in comparison with air and argon, but it had the least noise influenced spectra as shown below in Figure 114.

![Figure 114: Comparison of methanol spectrum taken in an air and vacuum environment.](image_url)
A higher signal-to-noise is obtained from the droplets in the vacuum environment in agreement with Cowpe and Pilkington\textsuperscript{238}. If CN formation is to be studied in the vacuum, a higher vacuum than $10^{-1}$ Torr is necessary in order to remove the remaining nitrogen. However as the pressure is lowered the expansion of the plasma will be faster, and faster diagnostics will be necessary to characterize the emission. While not as clear a signal as the vacuum the argon environment may offer an alternative to vacuum if longer emission times are necessary to study the CN formation.

In agreement, with Aguilera\textsuperscript{241} the argon environment does appear to have the longest plasma emission. It was also the only environment in which there was an atomic carbon emission in the dimethylamine. However droplet stability proved to be difficult to maintain in this environment. The stability challenge can be solved by adding an automated system that tracks the droplet position and instructs motorized stages in order to maintain this position. This reduces the amount of missed shots, and automatically corrects for the drift from the focal position. In addition a more efficient manner of determining the end of the plasma emission is necessary. The dominant argon lines make it difficult to determine whether emission from the sample is still present as the argon lines dominate the spectrum while trying to monitor various lines such as hydrogen, nitrogen, oxygen simultaneously. This may be solved by having a high resolution focusing on these elements in a window which excludes the argon emission.

The air environment as expected had longer nitrogen emission over the plasma emission as atomic nitrogen emission due to the ambient air contributed to the total emission. If adequate suppression of the nitrogen (or careful characterization of the nitrogen) could be obtained in the other environments then an accurate estimation of the role of the atmospheric nitrogen could gained from using the mass-limited droplets as targets. Better characterization of the droplets using a fully calibrated LIBS setup would allow for stoichiometric measurements to be made.
However this would mean monitoring the environmental conditions in addition to the laser conditions for each laser shot. Such monitoring would also help increase the understanding of the CN emission as well.

In the air environment, the atomic carbon had a longer emission lasting approximately 20 ns longer in the air, and the CN emission was comparable to that of the argon environment. There have been many hypothesis put forth as to formation of the CN structure in air whether it be from the C or C₂ molecule. With additional equipment it may be possible to answer this question with the use of the mass limited droplets. In order to do this however the C, C₂, CN, and N lines must all be monitored. Unfortunately, in this experiment due to the Echelle spectrometer, it was difficult to monitor the C₂ emission as it fell between a spectral region in which different orders overlapped. The C₂ emission may have explained why although there was no atomic C emission for the dimethylamine in the vacuum and argon atmospheres but there was still a CN signature.

Another possible change that may be necessary if organics are to be studied is the wavelength of the laser. Baudelet et al. suggested the use of the 266 nm wavelength as an appropriate ablation source. From their study, they concluded that the infrared regime is not a suitable regime in which to study the analysis of organics with molecular emission using LIBS. This was due to high rate of recombination with the atmosphere, and the low efficiency rate producing native molecular fragments that is characteristic of the nanosecond IR ablation regime. Whereas, for the UV laser ablation even at low energy (1-5 mJ) efficient molecular ablation occurs and in addition there is low interference due to atmospheric recombination. This is in agreement with results from Chapters 5 and Chapter 6.
7.8 Conclusions

This was the first attempt by the Laser Plasma Lab to characterize the low temperature and density (in comparison with an EUV plasma) LIBS plasma. In addition, to studying the plasma under a low irradiance regime, the samples studied were constructed from low Z materials. A copper-sulfate pentahydrate solution as well as de-ionized water was utilized to try and establish a link between theoretical results predicted from MEDUSA to the experimental. The successful linking of the results allows for MEDUSA to be used as a diagnostic tool to characterize non-metallic and organic samples which cannot be done using current plasma characterization techniques.

In its current form MEDUSA was used to identify the region in the plasma from which the emission occurs. Supplementary improvements to the theoretical code, such as the addition of an ablation module, would further help to refine simulations of the hydrodynamic plasma expansion. The ablation module would not only help to better model the laser absorption and heating of the material, but would also serve to give better input temperatures for the free electrons and ions characteristic of a two fluid stream code. The addition of chemical kinetic processes would help to better simulate the plasma cooling yielding times that should better compliment the experimental results.

In the experimental regime, additional diagnostic equipment such as a mass spectrometer and a high resolution spectrometer are necessary in order to improve and better characterize the experiments. A mass spectrometer would be extremely useful at the initialization of the plasma where we are limited in spectral data until the formation of well defined lines. If the mass spectrometer has time resolution capabilities then a more accurate understanding of the
constituent particles (atoms and molecules) generated from the laser ablation can be obtained. In addition, knowledge of the molecular recombination indicative of the sample itself can be gained in an argon and vacuum environment. Insight from the mass spectrometer would help shed light onto any molecular fragments which could be generated from the low irradiance ablation.

While an Echelle can be used to simultaneously monitor line emissions, the amount of light collected is sacrificed for resolution. With a high-resolution spectrometer the amount of light collected is increased and we are able to focus specifically on regions of interest thus increasing the effectiveness of the time resolved study. An added advantage of the high resolution spectrometer is that gratings with high quantum efficiencies for specific wavelength regimes (UV, VIS, IR, etc) can be utilized to increase the signal-to-noise ratio.

Implementation of these improvements to both theoretical and experimental studies will help to provide a better understanding of the fundamental LIBS processes in a low irradiance regime. This could lead to further development of plasma codes specifically for the LIBS plasma regime, as physical and chemical processes can be incorporated into the models. The development of a comprehensive model for LIBS plasma is essential if LIBS is to become a main stream diagnostic technique.

With the use of mass-limited droplets the quantitative ability of LIBS can be further improved. Known concentrations make it possible to do very accurate stoichiometric studies, and with the characterization of more samples the limits of detection for LIBS can be further refined. Another advantage to using the mass-limited droplets is the homogeneity of the sample studied, which is ideal for exploring non-metallic and organic samples.
8 CONCLUSIONS AND FUTURE WORK

8.1 Summary

Discrimination of energetic material from other organic samples is a pressing issue in the field of sensing and detection. As the unlawful use of energetic materials continues to evolve so too must the methods used in the detection of these dangerous chemicals. Currently, the sensing community is in need of a sensing technique capable of sampling all forms of media at a remote distance and can provide a rapid or real-time analysis. Due to its ability to address all of the previous issues, Laser Induced Breakdown Spectroscopy (LIBS) has been put forth as a possible solution. As an emerging technology, there are still many challenges that LIBS must resolve in order to be accepted in the sensing community as viable analytical technique.

One of the main challenges facing LIBS is the detection of trace amounts of organic material or analyte on a non-metallic substrate known as a residue. The amount of analyte is randomly distributed across the surface of the substrate and interrogation of this surface must be completed in a single shot. This matter is further complicated by the atmospheric recombination that occurs. Studies were conducted in order to identify other parameters that affect the ability of LIBS to detect and discriminate the organic residues. This was a prelude to determining if LIBS could be used to successfully detect and discriminate organic residues in a single shot.

The first study presented here explores the parameters such as the laser wavelength, laser pulse duration, and environment that can affect the LIBS detection and discrimination of a variety of organic residues. In order to minimize radical formation an argon environment was selected, and in order to quickly and efficiently explore the interrelationships in the data collected the chemometric technique principal component analysis was selected. Results from
this study show that while the argon does quench radical formation, the air may act in a beneficial manner in causing separation of the organic samples. The results of the atmosphere showed comparable results in discrimination of the organic residues.

An exploration into the laser pulse duration resulted in the femtosecond regime being preferred over the nanosecond regime as the principal components remain constant in their projections for both the air and argon regimes. The lack of change in the PC loadings was attributed to minimal atmospheric interference during the laser ablation process. The duration of the femtosecond pulse which is shorter than the response time of the lattice of a material (on the order of a picosecond) decouples the laser-sample and the laser-plasma interactions, and a negligible amount air is entrained into the plasma. With little atmospheric influence there should be no difference between an air or argon environment.

If a nanosecond laser is selected as the excitation and sampling source then the UV regime is preferable over the NIR regime. The inverse Bremsstrahlung plays a major role in the nanosecond regime specifically for wavelengths above 1 µm. As the inverse Bremsstrahlung heats the plasma it also heats the surrounding the air and interactions between the two occur. This is shown in the PC compositions as only one emitter remained constant, and the projections for one environment cannot be used to describe the other. In the UV regime, only two variables have different PC compositions leading to more stability in comparison to the NIR regime. The stability in the UV regime was attributed to two main factors: i) multi-photon ionization is the dominant heating process instead of the inverse Bremsstrahlung reducing the influence of air, and ii) organic molecules have strong absorption in the UV wavelength regime leading to a more efficient ablation of the organic sample.
Studies were also conducted to determine if LIBS could classify energetic-like compounds from non-explosive organics in a single shot regime and to what accuracy. The covariance matrices for the non-explosive and energetic-like were not equivalent and it was determined that linear discriminant analysis could not accurately describe the LIBS data. It was necessary to extend the linear models to include nonlinear terms. Quadratic Discriminant Analysis indicated that in air the UV (ns) and NIR (fs) were again the best regimes for sampling and exciting the samples in agreement with the results of the parametric studies. Each had an 80% overall correct classification rate and a 100% rate for correctly identifying and classifying energetic-like residues.

Another study examined using an alternative chemometric technique target factor analysis (TFA) for the discrimination of organic signatures from an organic substrate. The TFA approach proved to be highly effective for plasmas in an argon environment, where there was ideal separation of signals from the pure organic samples. In an air atmosphere the separation was not quite ideal however the method still gave successful results. This was first time TFA has been used to classify trace organic signatures on an organic substrate using LIBS.

In an effort to improve the LIBS discrimination capabilities, exploration was done using mass-limited droplets in order to understand the interaction of the LIBS plasma with organics. In addition, an alternative method of characterizing plasmas generated by LIBS on organics was explored. The experiments were modeled utilizing the plasma code MEDUSA as a diagnostic tool, and simulations were compared to experimental data. MEDUSA was used to model and predict the region of the plasma to which the emission used to calculate the experimental density was attributed. Modifications to the source code need to be made in order to adapt it to work with lower temperature and lower density plasmas relative to those used in fusion experiments.
Lastly, the mass-limited droplets were used to explore whether a molecule containing a C-N bond could be differentiated from a molecule only containing carbon. Time-resolved measurements were conducted under a vacuum, argon and air environment in order to determine how the spectrum of the molecules was affected. These were the first time that studies using mass-limited droplets were conducted in the LIBS regime (low temperature and low density plasmas).

8.2 Visions for the Future

While LIBS offers many advantages over other sensing techniques, unless it can convince the analytical community of its validity as quantitative measurement technique, it will fade into the background as a mere scientific curiosity. In order to be comparable to the more traditional methods such as ICP-MS and MS, LIBS must 1) establish protocols that will allow for consistent quantitative measurements, 2) establish a comprehensive theoretical model that can be used to accurately simulate and predict experimental results, and 3) establish a more comprehensive understanding of the combined fundamental physical and chemical processes.

By introducing the mass-limited target regime to the field, we can design specific experiments which explore the fundamental physical and chemical processes. In addition true stoichiometric measurements can be accomplished and a better idea of LIBS limits of detection can be gained. Also in using mass-limited droplets, protocols for establishing standards for the LIBS community can prepared. This would allow for calibration of the various LIBS systems that are in use today, and allow for results from one group to be repeated by another group and the same conclusions can be drawn.
Experiments that deal with fundamental physics and chemistry need to be re-implemented with the idea of answering questions that need to be addressed by the LIBS community. One such question that has been studied, but no solution has been agreed upon, is the formation of the CN band structure. Three different mechanisms have been put forth as different groups have put forth different explanations, and until a definitive study is conducted the ambiguity of this formation will continue to relegate LIBS to the background. Another issue that needs to be revisited is the emission in the earlier portion of the plasma. With the addition of technologies such as mass spectrometers, questions dealing with chemical bond structure being destroyed can be answered. At higher irradiances the assumption of all molecular structure being lost is valid, but this may not hold true at lower irradiances, and some molecular structures may remain. This issue must be addressed if lower irradiance are to be used for excitation and sampling.
Polymers

- Polystyrene
- Polyisobutylene
- Polyacrylonitrile
- Nitrocellulose

OCCNs

- Caffeine
- Ammonium Nitrate
APPENDIX C: COPPER-SULFATE INPUT FILE FOR THE MEDUSA CODE
Pulse width (FWHM) = 6.0 ns Initial Ion temp is 10000K
I = 4.78e9 W/cm^2, Laser wavelength = 1064 nm, In Vacuum
CuSO4*5H2O solid spherical target 40 um dia geom - 3 layer
************************************************
$newrun
xamda1 = 1.06e-6, gauss = 1.0, anpuls = 1.0, toff = 1.0e-1,
plenth = 3.6e-9, pmax = 1.91e4, pmult = 3.0,
ngem = 3, piq(55) = 0.0, teini = 1.0e4, tiini = 1.0e4,
mesh = 500, rini = 20e-6,
RHOAS = 1155, RF1 = 0.98,
XZ = 5.708, XMASS = 11.151, FNE = 1.0,
ZGLAS = 0, DRGLAS = 0, ROGLAS = 0, RF2 = 0.99999,
XZ2 = 0.0, XMASS2 = 0, FNE2 = 0.0,
ZPLAS = 0.0, DRPLAS = 0, ROPLAS = 0, RF3 = 0.99999,
XZ1 = 0.0, XMASS1 = 0, HYDROG = 0.0,
NPRNT = -5000.0, TSTOP = 200.0E-9, NRUN = 1300000,
AK0 = 100.0, AK3 = 0.01, AK4 = 0.01, PONDF = 0.0,
NP3 = 1, NLEMP = F, NLPFE = T, STATE = 3.0,
NLABS = T, NLBRMS = T, FLIMIT = 0.1, SAHA = 1.0,
ANABS = 0.05, FHOT = 0.1, FTHOT = -1.0, RHOT = 1.0,
ICXRL = 0, IFRSTA = 1, ILOSTA = 1, IHISTA = 3,
ISTAGE = 2, IDFLG = 0, ROPMUL = 0.0, ITBFLG = 1, ISTFLG = 0,
IPUFLG = 0, TPON = 2.15E-10, TPOFF = 2.85E-10,
NLP = 1, NUP = 3, RMPD = 0.002, DLAMDA = 1.298E-6,
NLMAX = 2, FLSHORT = 0.001, FLLONG = 0.02,
$END
APPENDIX D: WATER INPUT FILE FOR THE MEDUSA CODE
Pulse width (FWHM) = 6.0 ns Initial Ion temp is 10000K
I=4.78e9W/cm^2, Laser wavelength=1064 nm, In Vacuum
H20 solid spherical target 40 um dia geom - 3 layer
******************************************************************************
$newrun
xamda1=1.06e-6, gauss=1.0, anpuls=1.0, toff=1.0e-1,
plenth=3.6e-9, pmax=1.91e4, pmult=2.0,
geom=3, piq(55)=0.0, teini=1.0e4, tiini=1.0e4,
mesh=500, rini=20e-6,

RHOGAS=997.0479, RF1=0.98,
XZ=3.33, XMASS=6.0, FNE=1.0,
ZGLAS=0, DRGLAS=0, ROGLAS=0, RF2=0.99999,
XZ2=0.0, XMASS2=0, FNE2=0.0,
ZPLAS=0.0, DRPLAS=0, ROPLAS=0, RF3=0.99999,
XZ1=0.0, XMASS1=0, HYDROG=0.0,

NPRNT=-5000.0, TSTOP=200.0e-9, NRUN=1300000,
AK0=100.0, AK3=0.01, AK4=0.01, PONDF = 0.0,

NP3=1, NLEMP=F, NLPFE=T, STATE =3.0,
NLABS=T, NLBRMS=T, FLIMIT=0.1, SAHA=1.0,

ANABS=0.05, FHOT=0.1, FTHOT=-1.0, RHOT=1.0,

ICXRL=0, IFRSTA=1, ILOSTA=1, IHISTA=3,
ISTAGE=2, IDFLG=0, ROPMUL=0.0, ITBFLG=1, ISTFLG=0,
IPUFLG=0, TPON=2.15E-10, TPOFF=2.85E-10,
NLP=1, NUP=3, RMPD=0.002, DLAMDA=1.298E-6,
NLMAX=2, FLSHORT=0.001, FLLONG=0.02,
$END
Pulse width (FWHM) = 6.0 ns Initial Ion temp is 10000K
I=4.78e9W/cm^2, Laser wavelength=1064 nm, In Vacuum
Dimethylamine solid spherical target 40 um dia geom - 3 layer
********************************************************
$newrun
xamda1=1.06e-6, gauss=1.0, anpuls=1.0, toff=1.0e-1,
plenth=3.6e-9, pmax=1.91e4, pmult=3.0,

ngeom=3, piq(55)=0.0, teini=1.0e4, tiini=1.0e4,

RHOGAS=987.511, RF1=0.98,
XZ=2.769, XMASS=4.846, FNE=1.0,

ZGLAS=0, DRGLAS=0, ROGLAS=0, RF2=0.99999,
XZ2=0.0, XMASS2=0, FNE2=0.0,
ZPLAS=0.0, DRPLAS=0, ROPLAS=0, RF3=0.99999,
XZ1=0.0, XMASS1=0, HYDROG=0.0,

NPRNT=-5000.0, TSTOP=380.0e-9, NRUN=1300000,
AK0=100.0, AK3=0.01, AK4=0.01, PONDF = 0.0,

NP3=1, NLEMP=F, NLPFE=T, STATE =3.0,
NLABS=T, NLBRMS=T, FLIMIT=0.1, SAHA=1.0,

ANABS=0.05, FHOT=0.1, FTHOT=-1.0, RHOT=1.0,

ICXRL=0, IFRSTA=1, ILOSTA=1, IHISTA=3,
ISTAGE=2, IDFLG=0, ROPMUL=0.0, ITBFLG=1, ISTFLG=0,
IPUFLG=0, TPON=2.15E-10, TPOFF=2.85E-10,
NLP=1, NUP=3, RMPD=0.002, DLAMDA=1.298E-6,
NLMAX=2, FLSHORT=0.001, FLLONG=0.02,
$END
APPENDIX F: METHANOL INPUT FILE FOR THE MEDUSA CODE
Pulse width (FWHM) = 6.0 ns Initial Ion temp is 10000K
I=4.78e9 W/cm^2, Laser wavelength=1064 nm, In Vacuum
CH3OH solid spherical target 40 um dia geom - 3 layer
************************************************
$newrun
xamda1=1.06e-6, gauss=1.0, anpuls=1.0, toff=1.0e-1,
plenth=3.6e-9, pmax=1.91e4, pmult=3.0,

nggeom=3, piq(55)=0.0, tefini=1.0e4, tiini=1.0e4,
mesh=500, rini=20e-6,

RHOGAS=791.8, RF1=0.98,
XZ=3, XMASS=5.33, FNE=1.0,

ZGLAS=0, DRGLAS=0, ROGLAS=0, RF2=0.99999,
XZ2=0.0, XMASS2=0, FNE2=0.0,
ZPLAS=0.0, DRPLAS=0, ROPLAS=0, RF3=0.99999,
XZ1=0.0, XMASS1=0, HYDROG=0.0,

NPRNT=-5000.0, TSTOP=200E-9, NRUN=13000000,
AK0=100.0, AK3=0.01, AK4=0.01, PONDF = 0.0,

NP3=1, NLEMP=F, NLPFE=T, STATE =3.0,
NLABS=T, NLBRMS=T, FLIMIT=0.1, SAHA=1.0,

ANABS=0.05, FHOT=0.1, FTHOT=-1.0, RHOT=1.0,

ICXRL=0, IFRSTA=1, ILOSTA=1, IHISTA=3,
ISTAGE=2, IDFLG=0, ROPMUL=0.0, ITBFLG=1, ISTFLG=0,
IPUFLG=0, TPON=2.15E-10, TPOFF=2.85E-10,
NLP=1, NUP=3, RMPD=0.002, DLAMDA=1.298E-6,
NLMAX=2, FLSHORT=0.001, FLLONG=0.02,
$END


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88. V. I. Babushok, "Processes Induced by the LIBS Technique," (2005).


