Plasma Temperature Measurements in the Context of Spectral Interference

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PLASMA TEMPERATURE MEASUREMENTS IN THE CONTEXT OF SPECTRAL INTERFERENCE

by

BRANDON SEESAHAI

A thesis submitted in partial fulfillment of the requirements for the Honors in the Major Program in Photonic Science and Engineering in the College of Optics and Photonics and in the Burnett Honors College at the University of Central Florida Orlando, Florida

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ABSTRACT
The path explored in this thesis is testing a plasma temperature measurement approach that accounts for interference in a spectrum. The Atomic Emission Spectroscopy (AES) technique used is called Laser Induced Breakdown Spectroscopy (LIBS) and involves focusing a laser pulse to a high irradiance onto a sample to induced a plasma. Spectrally analyzing the plasma light provides a "finger print" or spectrum of the sample. Unfortunately, spectral line broadening is a type of interference encountered in a LIBS spectrum because it blends possible ionic or atomic transitions that occur in plasma. To make use of the information or transitions not resolved in a LIBS spectrum, a plasma temperature method is developed. The basic theory of a LIBS plasma, broadening mechanisms, thermal equilibrium and distribution laws, and plasma temperature methods are discussed as background support for the plasma temperature method tested in this thesis. In summary, the plasma temperature method analyzes the Full Width at Half the Maximum (FWHM) of each spectral line for transitions provided from a database and uses them for temperature measurements. The first implementation of the temperature method was for simulated spectra and the results are compared to other conventional temperature measurement techniques. The temporal evolution of experimental spectra are also taken as a function of time to observe if the newly developed temperature technique can perform temporal measurements. Lastly, the temperature method is tested for a simulated, single element spectrum when considering interferences from all the elements provided in an atomic database. From stimulated and experimental spectra analysis to a global database consideration, the advantages and disadvantages of the temperature method are discussed.
## TABLE OF CONTENTS

Introduction .................................................................................................................................................. 1

CHAPTER 1 Laser Induced Breakdown Spectroscopy (LIBS) ................................................................................. 3
    1.1 LIBS Introduction, History, and Applications ......................................................................................... 3
    1.2 LIBS Plasma Concepts ........................................................................................................................... 4
    1.3 Spectral Acquisition from LIBS Setup ..................................................................................................... 7
    1.4 Spectral Analysis ...................................................................................................................................... 8
    1.5 Line Broadening Mechanisms and Spectral Profiles ............................................................................... 9

CHAPTER 2 Plasma Temperature and its Measurement ....................................................................................... 14
    2.1 Plasma Temperature Introduction .......................................................................................................... 14
    2.2 Thermodynamic Equilibrium and Distribution Laws ............................................................................. 14
        2.2.1 Boltzmann Population Distribution Law .......................................................................................... 14
        2.2.2 Maxwellian Velocity Distribution Law ............................................................................................. 16
        2.2.3 Saha Ionization Equilibrium .......................................................................................................... 17
        2.2.4 Photon Energy Distribution Law ..................................................................................................... 18
        2.2.5 Local Thermodynamic Equilibrium (LTE) ...................................................................................... 18
    2.3 Measuring Plasma Temperature ............................................................................................................. 20
        2.3.1 Boltzmann Plot Method .................................................................................................................. 20
        2.3.2 Saha-Boltzmann Plot Method ......................................................................................................... 24
        2.3.3 Multi-Element Saha-Boltzmann Plot ............................................................................................... 26

CHAPTER 3 Plasma Temperature of Known Samples ......................................................................................... 32
    3.1 Broadening as an Interference ............................................................................................................... 32
    3.2 Plasma Temperature Methods .............................................................................................................. 33
        3.2.1 Attribution to a Single Transition .................................................................................................... 34
        3.2.2 Attribution to Multiple Transitions .................................................................................................. 34
        3.2.3 Example of 4 Temperature Methods from Simulated Spectrum .................................................. 35
    3.3 Experimental Application of Sharing of Intensities ................................................................................ 38
        3.3.1 Aluminum Sample ............................................................................................................................ 38
3.3.2 Copper Sample ........................................................................................................ 46
3.4 Summary .................................................................................................................... 54

CHAPTER 4 Plasma Temperature with Global Database (Simulated Spectra) ............... 56

4.1 Global Database ........................................................................................................ 56
4.2 Filtering ...................................................................................................................... 59
  4.2.1 Temperature Filter .............................................................................................. 59
4.3 Matching Factor (MF) ............................................................................................. 61
  4.3.1 MF as a Filter ................................................................................................... 63
4.4 Summary .................................................................................................................... 65

Overall Conclusion .......................................................................................................... 67

APPENDIX A: WAVELENGTH CALIBRATION ............................................................... 70
APPENDIX B: SPECTRAL RESPONSE CALIBRATION ............................................... 79
APPENDIX C: SAMPLE MATLAB CODE ................................................................. 83
REFERENCE ..................................................................................................................... 87
LIST OF FIGURES

Figure 1: Plasma Life Cycle from a nanosecond laser pulse. .................................................. 5
Figure 2: Spectrum dependence on lifetime of LIBS plasma from a nanosecond laser pulse
(intensity is not drawn to scale). The blue curve is the plasma intensity as a function of time...... 6
Figure 3: Stark broadening and shift resulting from split energy levels.................................. 11
Figure 4: Gaussian, Lorentzian, and Pseudo-Voigt Fit for a spectral line............................... 13
Figure 5: Simulated Aluminum spectrum from 250-400 nm at 3.0 eV with N_e = 10^{24} m^{-3}. The
upper and lower energy level transitions are shown and the Al III peaks that are formed as a
result........................................................................................................................................... 23
Figure 6: a) The relative population of electrons in Al III with respect to the upper energy level.
b) The intensity of an emission line with respect to the upper energy level. c) Boltzmann Plot. 23
Figure 7: Boltzmann, Saha-Boltzmann, and Multi-Element Saha Boltzmann plots for a simulated
Aluminum and Calcium spectrum at 1.5 eV............................................................................... 30
Figure 8: Al II transitions within the FWHM of an Al II peak.................................................... 33
Figure 9: Simulated Aluminum Spectrum at 1.5 eV with Al II detected peaks. ......................... 36
Figure 10: Boltzmann plots for Al II when methods A, B, C, and D are implemented............... 36
Figure 11: Experimental Setup ................................................................................................ 38
Figure 12: Aluminum Spectrum taken at 5 mJ laser energy...................................................... 40
Figure 13: Aluminum Spectrum taken at 20 mJ laser energy.................................................... 40
Figure 14: Method C and D Boltzmann Plots for an experimental Aluminum Spectrum........... 41
Figure 15: Plasma Temperature vs. Delay time for Al I when laser energy is 5 mJ and 20 mJ. 41
Figure 16: Energy Level Transitions for the Aluminum spectrum at 400 ns when laser energy is 5
mJ and 20 mJ .......................................................................................................................... 45
Figure 17: Copper Transitions within the FWHM of each spectral line.................................... 46
Figure 18: Process for including population density of species for plasma temperature
measurements................................................................................................................................. 50
Figure 19: Saha-Boltzmann Plots for Cu using method C and D.............................................. 52
Figure 20: Simulated Aluminum spectrum from 250 nm to 400 nm at 0.7 eV and its Boltzmann
plot from method C .................................................................................................................. 56
Figure 21: Global Transitions within the FWHM of peak 1...................................................... 58
Figure 22: Global Transitions within FWHM of peak 1 after temperature filter. ...................... 60
Figure 23: The gA transitions within the range of the simulated Aluminum spectrum. Green are
the detected gA transitions and blue are from the database. The green transitions are from the
database as well........................................................................................................................ 61
Figure 24: Global Transitions within FWHM of peak 1 after temperature filter and MF is used in
method C..................................................................................................................................... 62
Figure 25: Experimental and Real intensity values for a deuterium and halogen lamp. .......... 81
# List of Tables

Table 1: The typical orders of magnitude for plasma and instrumental broadening [36] ............ 12  
Table 2: Summary of the Boltzmann, Saha-Boltzmann, and Multi-Element Saha Boltzmann plots ......................................................................................................................... 31  
Table 3: Intensity, wavelength, and FWHM for each detected peak emitted by Al II ............. 36  
Table 4: Ions that obtain most of the total intensity compared to Al I for peak 1 ................. 58  
Table 5: Ions that obtain most of the total intensity compared to Al I for peak 1 ............... 60  
Table 6: Ions that obtain most the total intensity compared to Al I for peak 1 ............... 63  
Table 7: Ions that obtain most the total intensity compared to Al I for peak 8 .................... 64  
Table 8: Center $\lambda = 240$ nm wavelength calibration ....................................................... 72  
Table 9: Center $\lambda = 310$ nm wavelength calibration .......................................................... 73  
Table 10: Center $\lambda = 365$ nm wavelength calibration ...................................................... 74  
Table 11: Center $\lambda = 420$ nm wavelength calibration ...................................................... 75  
Table 12: Center $\lambda = 485$ nm wavelength calibration ...................................................... 76  
Table 13: Center $\lambda = 555$ nm wavelength calibration ...................................................... 77  
Table 14: Center $\lambda = 625$ nm wavelength calibration ...................................................... 78  
Table 15: Lamp and polynomial fit used for each spectral window ..................................... 82
**Introduction**

A spectrum produced from Laser-Induced Breakdown spectroscopy (LIBS) contains spectral lines that are broadened because of plasma broadening mechanisms or from a low-resolution spectrometer. Within its linewidth, a broadened spectral line does not reveal other emitters or transitions that could be resolved unless an atomic database is consulted. Atomic databases display transitions within the linewidth of a spectral line that could occur in plasma. This thesis explores a method that utilizes the transitions not resolved in a LIBS spectrum for plasma temperature measurement.

Before focusing on calculating the temperature of a Laser Induced Plasma (LIP), chapter 1 describes LIBS as an analytical technique along with its history, applications, and instrumentation. Additionally, the concept on how a LIP plasma is produced, the plasma life cycle, and the temporal effect plasma has on an emission spectrum is explained. From a LIBS spectrum, qualitative and quantitative information can be obtained, but can contain error because of spectral interferences. Chapter 1 focuses on instrumental and plasma broadening mechanisms as the main source of spectral interference and discusses the spectral profiles that can explain a broadened spectral line in a LIBS spectrum.

Chapter 2 introduces the concept of temperature along with the distribution and equilibrium laws that govern the system of species in plasma. From these distribution and equilibrium laws, temperature methods such as the Boltzmann, Saha-Boltzmann, and Multi-elemental Saha Boltzmann plots are derived to calculate the plasma temperature.
Using the temperature methods mentioned in chapter 2, the concept of using a different plasma temperature approach that accounts for emitters within a broadened spectral line is introduced. The plasma temperature method is tested on simulated and experimental spectra and the results are discussed.

Finally, a global database is used to analyze a single element spectrum with the plasma temperature method. This test shows the performance of the plasma temperature method if an unknown sample is considered and how unreasonable emitters can be filtered out to improve results.
CHAPTER 1 Laser Induced Breakdown Spectroscopy (LIBS)

1.1 LIBS Introduction, History, and Applications

In the early 1800s, scientists understood that elements that are excited emit certain colors [1]. Atoms or ions that emit light at certain wavelengths or frequencies result in its own spectrum or "fingerprint" that serves as a tool for identifying that atom or ion [1]. Atomic Emission Spectroscopy (AES) is the study of quantitatively or qualitatively determining the elemental composition or constituents of a solid, liquid, or gas sample [2]. Sources of excitation that cause samples to emit light include the flame, inductively coupled plasma (ICP), direct coupled plasma (DCP), Glow Discharge (GD), Laser Spark (LIBS), microwave-induced plasma (MIP), DC arc, and AC spark [2, 3]. Laser-Induced Breakdown Spectroscopy (LIBS) is a popular technique in AES that involves the formation of laser-induced plasma (LIP) on or in the surface of a sample [2]. The plasma functions as the atomization and excitation source and embodies the spectroscopic information of the sample [2]. Compared to conventional AES techniques, LIBS has advantages in its operational simplicity, the requirements of little or no sample preparation, the speed of spectra acquisition, and ability to analyze all materials [2].

After building the maser (Microwave Amplification by Simulated Emission of Radiation) in the early 1950s [4], Charles Townes published his ideas for the fundamental principles of the laser in 1958 [5]. It was not until 1960 that Teodore Maiman invented the first working ruby laser [6]. The first spectrum obtained using a ruby laser was documented by Franken, however the excitation was induced with the assistance of an electric spark [7]. The birth of LIBS was performed by two French females Debras-Guédon and Liodec and their paper in 1963 showed a laboratory LIBS setup that was used to created plasma from a ruby laser [8]. Debras-Guédon and
Liodec collected spectra from different materials and observed emission lines from 25 elements [8]. In 1964, Runger used a pulsed Q-switched ruby laser to induced a plasma on iron [9]. Based on the laser-induced spectrum, linear calibration curves were performed for nickel and chromium in iron, thereby making this the first spectrochemical analysis using LIBS [9]. Since then, the devices and technology (spectrometer, fiber optics, lasers, detection cameras, spectrum software) that allow suitable spectroscopic analysis by LIBS have been developed and improved upon, thereby providing growth in its application and research. LIBS has applications in environmental monitoring, material sorting, metal analysis, planetary exploration (LIBS on a Mars Rover [10, 11]), toxic substance detection, oil and gas exploration, art restoration, explosive residue detection, biomedical research and etc [12-20].

1.2 LIBS Plasma Concepts

Plasma is considered the fourth state of matter and is defined as a collection of atoms, free electronics, and ions [1, 21]. The life cycle of a plasma induced from a nanosecond laser pulse is shown in Figure 1 below. A nanosecond laser pulse is described because the pulse width of the laser used for the experiments in this thesis is in the order of nanoseconds.
5

The focused laser irradiance must reach the breakdown threshold of the sample to generate plasma [2]. Prior to breakdown, when the laser is incident on the sample, photoionization occurs since the electromagnetic energy is sufficient to remove electrons from the neutral atoms composing the sample (Figure 1a). The optical field also causes the initial free electrons created from photoionization to gain energy and accelerate. Collisional or impact ionization then occurs because the accelerated electrons have enough energy to collide with other neutral atoms and free additional electrons. This ongoing process of ionization or free electron creation is called avalanche or cascade ionization. Once the electron density reaches
approximately $10^{18}$ electrons / cm$^3$, breakdown officially occurs and a plasma is formed on top of the sample surface (Figure 1b) [3, 22].

After the plasma initiates, it expands and contains the emission signals of the ablated neutral atoms and ions (Figure 1c). As the plasma cools, ions and electrons recombine to form neutrals (Figure 1d). Molecules are also formed during plasma cooling. The plasma reaches the end of its lifetime once there is not a frequency of pulses incident on the sample. When the plasma disappears, a crater remains on the surface of the sample, showing a sign of ablation (Figure 1e).

Figure 2: Spectrum dependence on lifetime of LIBS plasma from a nanosecond laser pulse (intensity is not drawn to scale). The blue curve is the plasma intensity as a function of time.
The temporal effect plasma has on a spectrum is shown above in Figure 2 with the blue curve representing plasma intensity. After a nanosecond laser pulse hits a sample and plasma forms, a background continuum dominates over the neutral and ionic emission signals. A continuum forms because of photons emitted from electron acceleration and deceleration from collisions, and electron and ion recombination [2]. Being able to capture a LIBS spectrum when the continuum diminishes and the emission signals prominently arise becomes vital for spectral analysis and plasma diagnostics. This is why LIBS systems usually utilize time resolved detection. The parameters used for time resolved detection include the delay time and gate width. The delay time is the time after the plasma forms that the detector will capture signal and the gate width is how long the detector collects signal. Figure 2 shows an Aluminum spectrum taken at a time delay of 500 ns for 500 ns with signs of a continuum signal added to the emission signals. At a time delay of 1000 ns, the continuum subsides and the Aluminum emission lines are clearly resolved.

1.3 Spectral Acquisition from LIBS Setup

The plasma light contains the emission signals relevant to the sample and capturing this signal embodies the basis of a spectrum. Plasma light focused using another lens onto a fiber optic cable allows the plasma light to deliver its spectral information to a spectrometer. A fiber optic cable is not always required. A lens can be used to capture and focus the plasma light to the slit of a spectrometer or any other frequency selective device. Inside a spectrometer is a diffraction grating that separates the plasma light into its wavelength components. The diffracted wavelengths are then detected by a photodetector with an array of photosensitive pixels with each pixel corresponding to a particular wavelength. When the photodetector converts the
intensity of light incident on each pixel into an electrical signal, computer software processes the electrical signal to plot the wavelength light vs. its intensity. Basically, a spectrum shows the spatial distribution of pixels that experienced a certain intensity of incident light. A single laser pulse can produce a spectrum, however, several pulses are used to obtain a set of spectral data, which are averaged to improve signal quality.

1.4 Spectral Analysis

Line assignment is a qualitative analysis of LIBS that explains the existence of certain elements in a sample [1]. Performing elemental analysis on a LIBS spectrum becomes possible through databases. Not only do databases aid in assigning elements to emission lines, but they also provide the energy level transitions that contributed to a peak as well as the probability of that transition occurring. Databases used in LIBS include the Kuruz, National Institute of Standards and Technology (NIST), and Kelly Atomic Line database [23-25]. A list of other atomic databases that can be used in plasma spectroscopy is given in the following reference [26].

Furthermore, the quantitative information that can be obtained by analyzing a LIBS spectrum include the physical parameters of plasma such as electron density and plasma temperature. The electron density in plasma can be determined from a spectrum by knowing the Stark broadening linewidth of a spectral line. The electron density is useful for plasma temperature measurements by the Saha-Boltzmann method (section 2.3.2 and 3.3.2) and for using the McWhirter criterion to prove that plasma is in Local Thermodynamic Equilibrium (LTE) (section 2.2.5) [2]. After less than a microsecond after plasma formation, a typical value for electron density is around $10^{24}$ electrons / m$^3$ when operating LIBS at atmospheric pressure
At around 5 to 10 μs after plasma formation, the electron density is approximately $10^{22}$ m$^{-3}$ [1]. Lastly, plasma temperature is a parameter that can be determined from a spectrum and is the focus of this thesis. Plasma temperatures are typically measured up to 3.0 eV [13].

1.5 Line Broadening Mechanisms and Spectral Profiles

Without considering the effect of plasma broadening mechanisms, an electron transition from an upper energy level to a lower energy level in a motionless atom results in its spectral intensity having a small line width induced from natural broadening. However, when dealing with plasmas, broadening mechanisms contribute to a spectral line having a larger line width. The sources of plasma line broadening include Doppler and Collisional or Pressure broadening.

Natural broadening occurs because of the Heisenberg uncertainty principle, but is negligible in plasma spectroscopy [27-29] because spectral lines broadened by only natural broadening has a full width at half maximum (FWHM) much smaller than plasma and instrumental broadening contributions [1, 28]. Doppler broadening is one of the major broadening mechanisms in plasma and is the cumulative result of the Doppler effect occurring for a system of species [1, 30]. The Doppler effect occurs when a system of species with a velocity distribution have different motions with respect to an observer or detector, which leads to an emitted frequency to be detected in a frequency range [28, 29, 31]. For instance, an emitter moving away from an observer causes a detection of a lower frequency and an emitter moving toward an observer will cause a detection of a higher frequency [31]. The difference in the lower and higher frequency results in the line width of the detected signal [31]. The equation for the Doppler width depends on the temperature of the system and the atomic mass of the emitting species [1, 29].
where $M$ is the atomic mass of the element and $\lambda_0$ is the central wavelength of the spectral line.

Collisional or pressure broadening is the other major line broadening mechanism in plasma, and is caused when atom or ion emitters collide with either neutral or charged particles [29, 30]. Neutral emitters that collide with different neutral atoms results in Van der Waals broadening and collisions between an excited atom and an identical neutral atom in the ground state results in resonance broadening [28-30]. Van der Waals broadening occurs from the dipole interaction between an excited atom and another neutral atom that is in the ground state with an induced dipole [32, 33]. Resonance broadening occurs between identical neutral atoms with an upper and lower energy level having an electric dipole transition to the ground state [33, 34]. The stark effect is another main contributor to not only spectral broadening, but also to the shift of an emitted wavelength [1, 30, 35]. Stark broadening occurs when emitters collide with charged particles such as ions or electrons [1, 35]. The electric field from an ion or electron also causes the energy levels of an atom to split into sublevels that all contribute to their emission. A shifted wavelength occurs because electron transitions occur between the sublevels of the two electronic main levels [1, 35]. The figure below shows an example of the effect Stark broadening and shift has on a spectral line. If an electron transitions between energy levels that is not split, a delta function is measured at 785 nm. If an atom or ion is in an electric field, the energy levels will split into sublevels and cause a broadened peak that is shifted from 785 nm to be measured. Overall, the major broadening mechanisms in plasma are Doppler and Stark broadening [1, 30].
Spectral line broadening can occur from the instrument used for spectroscopic analysis. Larson mentioned that instrumental perturbations can effectively broaden spectral lines more than Doppler and collisional or pressure broadening combined [28], which can be the case when a low-resolution spectrometer is used for spectral analysis. However, having a high-resolution spectrometer does not completely eliminate spectral line broadening. The instrumental resolution can be as high as possible, but plasma broadening is still a major contributor to interferences. The typical orders of magnitude of Natural, Doppler, Stark, Resonant, Van der Waals, and Instrumental broadening are shown in the table below [36].
<table>
<thead>
<tr>
<th>Broadening Mechanism</th>
<th>Magnitude (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>(10^{-1})</td>
</tr>
<tr>
<td>Doppler</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>Stark</td>
<td>(10^{-2}) to (10^{0})</td>
</tr>
<tr>
<td>Resonant</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>Van der Waals</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>Instrumental</td>
<td>(10^{-1}) to (10^{-3})</td>
</tr>
</tbody>
</table>

Table 1: The typical orders of magnitude for plasma and instrumental broadening [36].

Doppler broadening results in a Gaussian line profile and collision broadening provides a Lorentzian profile [1, 37]. A compromise between both the Lorentzian and Gaussian profiles is needed since a spectral line obtained from a LIBS plasma contains a line width developed from both Doppler and collision broadening. Convoluting both profiles provides the Voigt profile, but implementing it in analysis is difficult [37]. Although computer software can still execute the voigt fit, computational time is much longer, especially when spectral lines are asymmetric. Combining both profiles is made possible by the pseudo-voigt approximation, which multiplies each profile by a factor and sums up their relevant contributions [37]. Since the pseudo-voigt approximation takes less computational time than the voigt fit, it is a more practical implementation for uniting the Lorenzian and Gaussian fitting capabilities into one fit.
The figure above shows an example of the Gaussian, Lorentzian, and Pseudo-Voigt fit on an experimental copper peak. The Gaussian fit shown in blue shows a good representation of the spectral line intensity, but fails to fit the line wings or the baseline. The Lorentzian fit shown in pink unfortunately over shoots the intensity of spectral line, but provides a better representation of the spectral line wings or baseline than the Gaussian fit. The red fit shows a compromise between the Gaussian and Lorentzian with the Pseudo-Voigt fit. Figure 4 shows that the Pseudo-Voigt fits the spectral line a lot better than the Gaussian and Lorentzian. When the coefficient of determination ($R^2$) is closer to 1, a fitting function best represents a data set. The pseudo-voigt fit in Figure 4 has a coefficient of determination closer to 1 when compared to the Gaussian and Lorenzian fit.
CHAPTER 2 Plasma Temperature and its Measurement

2.1 Plasma Temperature Introduction
Laser-Induced Plasma (LIP) temperature is a quantitative value obtained through spectral analysis that controls the electron density, the population density of ions and neutrals, and the degree at which complex processes occur inside plasma [13]. The complex processes that occur in LIP include photoionization, collisional ionization, radiative and three-body recombination, collisional excitation and de-excitation, radiative decay, photoexcitation, and Bremsstrahlung process [13, 38]. Completely characterizing the entire plasma system while these complex processes are occurring is difficult, especially when considering the inhomogenous and transient nature of LIP [13, 38]. To simplify plasma characterization, thermodynamic conditions are assumed so that a plasma can be described by the population density of species (electrons, ions and neutrals), and temperature [13, 38, 39]. Plasma is in the thermodynamic equilibrium (TE) state when the rate at which a process occurs equals the rate of its opposite process by collisional energy transfer. When a plasma is in TE, a set of equilibrium laws governed by a single temperature describes the plasma: Plank, Maxwell and Boltzmann distributions, and Saha equilibrium [13, 38].

2.2 Thermodynamic Equilibrium and Distribution Laws

2.2.1 Boltzmann Population Distribution Law
When plasma is in thermodynamic equilibrium, the relative population between two energy levels in an atom, ion, or molecule follows a Boltzmann distribution [1, 38, 40, 41].

\[ N_2 = \frac{N_1 g_2}{g_1} e^{-\frac{\Delta E}{k_BT_{exc}}} \]  \hspace{1cm} (2)
Where $N_2$ and $N_1$ are the population density in the upper energy level and the lower energy level respectively, $g_2$ and $g_1$ are the statistical weights for the respective energy levels, $\Delta E$ is the energy difference between the upper and lower energy level, $T_{\text{exc}}$ is the excitation temperature and $k_B$ is the Boltzmann constant.

Including the partition function, $U(T)$, in the Boltzmann equation provides the probability that an atom is in a certain energy state. The partition function is the sum of the population of all the possible energy levels for a particular atom, ion, or molecule and is a function of temperature [40].

\[
\sum_{m=0}^{m_{\text{max}}} N_m = N
\]

where $m_{\text{max}}$ is the number of excited levels (0, 1, 2, 3..etc.)

\[
U(T) = \sum_{0}^{m_{\text{max}}} g_m e^{-\left(\frac{E_m}{k_B T_{\text{exc}}}\right)}
\]

\[
\frac{N_2}{N} = \frac{g_2}{U(T)} e^{-\left(\frac{E_2}{k_B T_{\text{exc}}}\right)}
\]

The intensity of a spectral line emitted by a species is then expressed as [41]:

\[
I_{em} = A_{21} h \nu_{21} N_2 \text{ [W]}
\]
Where the subscripts 2 and 1 are assigned to an upper energy state and a lower energy state respectively, \( A_{21} \) is the transition probability, or the Einstein coefficient for the spontaneous emission process, \( h \) [J*s] is the Plank’s constant, \( \nu_{21} \) is the frequency of the emitted light, and \( N_2 \) [unitless] is the population of electrons in the upper energy level. Substituting \( N_2 \) from the Boltzmann equation (3) into the intensity of a spectral line equation (4) provides a connection between the population of excited states and the intensity of a spectral line [40].

\[
I_{em} = A_{21} h \nu_{21} N \frac{g_2}{U(T)} e^{-\left(\frac{E_2}{k_B T_{ex}}\right)}
\]

\[
h \nu_{21} = \frac{hc}{\lambda_{21}}
\]

\[
I_{em} = \frac{hc}{\lambda_{21}} g_2 A_{21} N \frac{N}{U(T)} e^{-\left(\frac{E_2}{k_B T_{ex}}\right)}
\]  

(5)

2.2.2 Maxwellian Velocity Distribution Law

The velocity of each species in a TE plasma follows the Maxwellian velocity distribution law [40, 42].

\[
f(v) = n \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\left(\frac{mv^2}{2k_B T}\right)}
\]

(6)

Where \( n \) is the population density, \( m \) is the mass, \( T \) is the kinetic temperature, and \( v \) is the average velocity of a particular species. Each species (electrons, ions, and molecules) can have
their own temperature, but in TE, these temperatures are equal. For instance, the different temperatures include the electronic temperature, Te, which defines the temperature of the electrons and $T_H$, which defines the temperature of heavy particles or molecules. $T_H$ can be equal to the molecular vibrational temperature ($T_{vib}$) and rotational temperature ($T_r$) because of the energy exchange between translational and rotational-vibrational states of molecules [13]. Additionally, heavy particles that are different species of neutrals and ions in the plasma can have a different temperature or $T_H$.

### 2.2.3 Saha Ionization Equilibrium

The Saha equation describes the population density of atoms in a certain stage of ionization. Consider a neutral atom being singly ionized in a system at equilibrium.

$$A + M \rightleftharpoons A^+ + e^- + M$$

The ionization equation above shows that the rate at which ionization ($\rightarrow I$) occurs as a result of collisions equals the rate at which recombination ($R\leftarrow$) occurs [42] and the variable $M$ indicates another atom involved in 3rd body collision energy transfer. The Saha equation is shown below for a system of a neutral atom and an ion in its first degree of ionization [27].

$$S(T) = \frac{N_e N_{A^+}}{N_A} = \frac{2U_{A^+}(T)}{U_A(T)} \left( \frac{m_ek_BT_{ion}}{2\pi\hbar^2} \right)^{3/2} e^{-\left(\frac{E_{\infty}-\Delta E}{k_BT_{ion}}\right)}$$

(7)

Where $N_e$, $N_{A^+}$, and $N_A$ are the population densities for the electron, ion, and neutral respectively. $E_{\infty}$ is the ionization energy of the neutral atom, $\Delta E$ is a plasma correctional factor for $E_{\infty}$, which can be calculated by the equation $\Delta E = 3z^2e^2\left[\frac{4\pi N_e}{3}\right]^{1/3}$ [13]. The correction for
the ionization energy accounts for the interactions in the plasma. \( U(T) \) is the partition function, \( m_e \) is the electron mass, \( T_{ion} \) is the ionization temperature, and \( \hbar \) is the reduced Plank constant.

### 2.2.4 Photon Energy Distribution Law

Finally, the energy density of photons in vacuum is described by the Plank function below. In other words, the Plank function describes the spectral content of a black body [13].

\[
W(\nu) = \frac{8\pi \hbar \nu^3}{c^3} \left( e^{\frac{\hbar \nu}{k_B T_{ph}}} - 1 \right)^{-1} \left[ \frac{J \ast s}{m^3} \right]
\]

(8)

where \( T_{ph} \) is the photon temperature [K], c [m/s] is the speed of light, and \( \nu \) [1/s] is the frequency of the photon.

### 2.2.5 Local Thermodynamic Equilibrium (LTE)

When the plasma is in thermodynamic equilibrium, the entire system can be described by a single temperature, \( T = T_{ex} = T_e = T_h = T_{vib} = T_{rot} = T_{ion} = T_{ph} \). LTE is a better description than thermodynamic equilibrium because a laser induced plasma (LIP) is inhomogeneous, transient, and does not exhibit the behavior of an ideal blackbody [13, 38]. Deviations from the Plank function occur because photons escape from the plasma, which creates an imbalance between emission and absorption in the blackbody equilibrium. This also leads to a photon temperature not being able to equilibrate with the other temperatures. Since the overall plasma cannot be described by the TE state, LTE is assumed in small volumes of the plasma and not for the plasma as a whole. As long as the energy transferred in the plasma from collisional processes is greater than the energy lost by the photons, then the Boltzmann population distribution, the Maxwellian velocity distribution, and the Saha ionization equation
can still accurately represent the plasma under the LTE approximation [13, 38]. Consequently, the temperature, although different from the photon temperature, can be identified as the excitation temperature and be calculated by evaluating the relative population of the different energy levels. The different types of temperature methods will be discussed in detail later.

The most used condition used to evaluate if a plasma is in LTE is the McWhirter criterion, which requires that the rate of collisional processes be at least one order of magnitude higher than the rate of radiative processes [13, 35, 38]. The expression for the McWhirter criterion is shown below.

\[
N_e > N_{cr} = (1.6 \times 10^{12})\frac{1}{T^2(\Delta E)^3}
\]

Where \(N_{cr}\) is the critical electron density in cm\(^{-3}\), \(T\) is the plasma temperature in K, and \(\Delta E\) (eV) is the largest energy gap between the upper and lower energy levels for an emitter in the plasma. For instance, a hydrogen plasma having the largest energy level transition from 13.6 eV to the ground state [23] and a plasma temperature of 3.0 eV would have a critical electron density value of 7.51e17 cm\(^{-3}\) or 7.51e23 m\(^{-3}\). Therefore, the electron density in the plasma must be greater than 7.51e17 cm\(^{-3}\) to support the existence of LTE. Although the McWhirter criterion has a weakness in assuming that the plasma is homogenous and stationary, failing this criterion means that LTE does not hold at all [13, 38, 43].
2.3 Measuring Plasma Temperature

2.3.1 Boltzmann Plot Method

Excitation temperature can be deduced by the ratio of the intensity of two spectral lines emitted from the same species. If two spectral lines emitted by the same ion are labeled 1 and 2, then the excitation temperature can be found by the equations below [44, 45].

\[
\frac{I_1}{I_2} = \frac{g_1 A_1 \lambda_2}{g_2 A_2 \lambda_1} \exp \left[ -\frac{(E_1 - E_2)}{k_B T_{ex}} \right] \tag{10a}
\]

\[
\ln \left( \frac{I_1 \lambda_1}{g_1 A_1} \right) - \ln \left( \frac{I_2 \lambda_2}{g_2 A_2} \right) = -\frac{(E_1 - E_2)}{k_B T_{ex}} \tag{10b}
\]

\[
T_{exc} = \frac{E_1 - E_2}{\ln \left( \frac{I_1 \lambda_1}{g_1 A_1} \right) - \ln \left( \frac{I_2 \lambda_2}{g_2 A_2} \right)} k_B \tag{10c}
\]

The relative intensity of two spectral lines emitted by the same element or ion is the oldest method for plasma temperature determination [35, 46]. The benefits provided by this method are that it is the simplest and fastest approach for temperature determination because of the prerequisite of only two emission lines with a reasonable difference in upper level energy. Temperatures can also be calculated for samples that do not emit a rich spectrum and only contains a few emission lines that are within the spectral range of the instrument [35]. However, the two-line ratio method is highly sensitive to errors [35]. From equation (10c), the relative error of temperature is shown by the equation below when considering that \(y = \ln(I\lambda/gA)\) [35, 47].
Graphically, the two-line method is similar to plotting \( \ln \left( \frac{I_{1} \lambda_{1}}{g_{1} A_{1}} \right) \) and \( \ln \left( \frac{I_{2} \lambda_{2}}{g_{2} A_{2}} \right) \) with respect to their upper energy levels \( E_{1} \) and \( E_{2} \) and taking the slope of the line \( -\frac{1}{T k_{B}} \) to extract the temperature. Although the minimum requirement for a temperature measurement are two emission lines, the Boltzmann plot presents a more accurate temperature measurement because it takes into account multiple emission lines. Rearranging equation (5) and taking the natural log will provide the Boltzmann plot equation [13].

\[
\frac{\Delta T_{ex}}{T_{ex}} = \frac{k_{B} T_{ex}}{E_{2} - E_{1}} \frac{\Delta \left( \frac{y_{1}}{y_{2}} \right)}{\frac{y_{1}}{y_{2}}} \tag{11}
\]

If \( \ln \left( \frac{I_{2} \lambda_{2}}{g_{2} A_{2}} \right) \) is plotted with respect to the energy of the upper level, \( (E_{2}) \), for each spectral line associated to a particular ion or neutral, then the fitted slope will be equal to \( -\frac{1}{T k_{B}} \), thus providing the temperature. If the data points display a strong linearity, then this proves that the Boltzmann distribution correctly represents the population of excited levels and that LTE approximately describes the plasma [13, 35, 39]. Since more emission lines are taken into
account in the Boltzmann plot, errors in line assignment or intensity values calculated for the emission lines are easily diagnosed by inspecting the linear correlation of points [45]. For instance, if a Boltzmann plot contains points in a linear formation except for one outlier, then the outlier indicates an error in either the intensity calculated for that transition or in its line assignment parameters (element or transition probability). The Boltzmann plot method is also depleted from its accuracy for spectrum with relatively few emission lines and when there is not a large upper energy level spread of data points [35].

Equations (3), (5), and (12) are shown graphically below for Al III that is taken from a 250-400 nm simulated Aluminum spectrum at a plasma temperature of 3.0 eV and an electron density of $10^{24}$ m$^{-3}$. The simulation for Aluminum is generated from a LabView code written by Dr. Matthieu Baudelet. To create a spectrum using the code, the spectral range, electron density, plasma temperature, element, elemental concentration, highest ionic stage, and peak width must be entered into the user interface. This code does not take into account plasma broadening mechanisms and only broadens spectral lines with a width inputted by the user. Lastly, the peaks for a particular element are formed by reading from the Kurucz database.
For both Figure 6a and 6b respectively, there is an exponential decay in electron relative population and line emission intensity from the lower energy levels to the upper energy levels. Figure 4a shows that when the plasma is in LTE, there is a greater relative population of electrons at the lower energy levels than the higher energy levels. Figure 6b shows that high
intensity line emissions result from transitions initiating from the lower energy levels because of the large relative population of electrons of these levels. Figure 6c depicts graphically that the natural logarithm of the intensity multiplied by $\frac{\lambda_{21}}{g_2 A_{21}}$ for each spectral line provides a negative linear relationship to the energy of the upper level. The negative reciprocal of the slope of the line fit was found to be $T = 2.92$ eV, which has a small error of 2.67 % when compared to the correct plasma temperature of 3.0 eV.

2.3.2 Saha-Boltzmann Plot Method

By combining the intensity equation that includes the Boltzmann distribution (Eq. 5) with the Saha equation (Eq. 7), a ratio of the intensity of two spectral lines emitted by the same element, but at two subsequent ionization stages can be used to measure temperature [45].

$$\frac{I_z}{I_{z+}} = \frac{g_z A_z \lambda_{z+}}{g_{z+} A_{z+} \lambda_z} \frac{2(2\pi m e k_B)^{3/2}}{\hbar^3 n_e} T^{3/2} \exp \left[- \frac{(E_z - E_{z+} + E_\infty - \Delta E)}{k_B T_{ion}} \right]$$  (13)

The parameters with the subscript $z$ corresponds to a species at an ionization stage $z$. The parameters with the subscript $z+$ correspond to the same species at the next degree of ionization. $E_\infty$ is the ionization potential of the lower ionized stage and $\Delta E$ is the correction to the ionization potential that accounts for interactions in the plasma.

To improve the accuracy of the temperature measurement, the Saha-Boltzmann plot can be used to take into account multiple emission lines from neutrals and ions, or from an ion at different ionization stages. The equation for the Saha-Boltzmann plot is shown below [13].
The temperature measurement is found from fitting a linear relation to the points on the Saha-Boltzmann plot and setting the slope equal to $-\frac{1}{T k_B}$.

The subscript "21" indicates a transition from an upper energy level 2 to a lower energy level 1. The superscript $z$ is the degree of ionization of the atom and superscript 0 indicates parameters for neutral atoms only. The Saha-Boltzmann plot equation contains the same format as the Boltzmann plot equation (Eq. 12) except for the extensions indicated by the subscript " * " [13].

\[
\ln\left(\frac{I_{21}^{z} z_{21}}{g_{2}^{z} A_{21}^{z}}\right)^* = -\frac{1}{T k_B} E_2^{z*} + \ln\left(\frac{h c N_0}{U_0 (T)}\right)
\]  

\[
y = mx + b
\]

Equation (15) shows that the Saha-Boltzmann plot equation has a larger spread of upper level energies accessed by the added correctional ionization energy term, unlike in the Boltzmann plot equation [13]. For example, if $z = 3$, then added to the energy of an atom in the third ionization stage is the corrected ionization energy of the first and second ionization stage. If only a neutral atom is taken into account, than the extensions in equations (15) and (16) are not necessary and the Boltzmann plot method is retrieved [39]. The Saha-Boltzmann plot method is

\[
x = E_2^{z*} = E_2^{z} + \sum_{k=0}^{z-1} \left( E_{\infty}^k - \Delta E_{\infty}^k \right)
\]
more accurate than the Boltzmann plot method because a line fit is made from emission parameters taken from two species, an ion and a neutral, or ions at different ionization stages for a single temperature measurement [39]. The disadvantage of the Saha-Boltzmann plot method is the necessary knowledge of an additional parameter, the electron density, whereas the Boltzmann plot does not have this requirement [48]. Since the y-coordinate equation for the Saha-Boltzmann plot includes the temperature factor $T^{5/2}$, then an iterative method is used to determine the temperature. An initial guess of the plasma temperature is used in equation (15) so that a line fit on the Saha-Boltzmann plot can provide a second temperature value. This second temperature value is then plugged back into the Saha-Boltzmann plot equation to find a third temperature value. This process is repeated until convergence [45].

2.3.3 Multi-Element Saha-Boltzmann Plot

Even for a plasma containing multiple elements, it is possible to have one linear fit on a Saha-Boltzmann plot consisting of multiple elements if a relation between the concentration in the sample, and the total population density in the plasma for each element is made [48]. The concentration of an element in the sample is considered under the assumption that the stoichiometry in the plasma is equal to that in the sample [48]. The total population density of an element $\alpha$ and its ion is defined by the equation below, assuming that the population of elements ionized to stages greater than one is too low to be considered [48].

$$N_\alpha = N^0_\alpha + N^1_\alpha$$  \hspace{1cm} (17)

where $N^0_\alpha$ is the population density of neutral atoms, $N^1_\alpha$ is the population density of first degree ions, and $N_\alpha$ is the total population density for that element. The subscript $\alpha$ is for a particular
element. The population density ratio of ions and neutrals from the Saha equation (Eq. 7) is substituted into equation (17) to provide the relation shown in equation (18) below [48].

\[
S_{\alpha}^{10} = \frac{N_{\alpha}^{0}}{N_{\alpha}^{1}} = \frac{2U_{\alpha}^{1}(T)}{N_{e}U_{\alpha}^{0}(T)} \left( \frac{m_{e}k_{B}T}{2\pi\hbar^{2}} \right)^{3/2} e^{-\frac{(E_{\alpha}^{0} - \Delta E_{\alpha}^{0})}{k_{B}T}}
\]

\[
N_{\alpha}^{1} = S_{\alpha}^{10} N_{\alpha}^{0}
\]

\[
N_{\alpha}^{0} = \frac{N_{\alpha}}{1 + S_{\alpha}^{10}}
\]  (18)

Assuming that the stoichiometry of the plasma matches that of the sample, then the following relationship between the elemental concentration in the sample and the population densities in the plasma is made [48].

\[
N_{\alpha} = \frac{c_{\alpha}}{100} N
\]  (19)

where \(N_{\alpha}\) is the total population density for a particular element, \(N \, [cm^{-3}]\) is the total population density for all the elements, and \(c_{\alpha} \, (\%)\) is the molar concentration for a particular element. Making the appropriate substitutions using equations (18) and (19) will provide the relevant modification to the Saha-Boltzmann equation to plot multiple elements [48].
The modification made to the Saha-Boltzmann plot equation is the additional equation that includes the elemental concentration of the sample, the partition function of the neutral element, and the ratio of ions to neutrals for each element. Adding the factor is important in aligning points from different elements into a single line fit [48].

Equation (20) shows that for each element, the x coordinate of the Saha-Boltzmann plot includes the ionization energy of an element added to the energy of the upper level in order to provide a correction for ionic lines. The same iterative process used to determine a suitable representative temperature for

\[ y = mx + b \]

\[ y = \ln \left( \frac{I_{21}^{z_1} \Lambda_{21}}{g_{z_2} A_{21}^z} \right)^* = -\frac{1}{k_B T} E_{2,\alpha}^{z^*} + \ln \left( \frac{hcN_0^0}{U^0(T)} \right) \]  

(20)

\[ \ln \left( \frac{I_{21}^{z_1} \Lambda_{21}}{g_{z_2} A_{21}^z} \right)^* = \ln \left( \frac{I_{21}^{z_1} \Lambda_{21}}{g_{z_2} A_{21}^z} \right) - z \ln \left[ 2 \left( \frac{m_e k_B}{2 \pi \hbar^2} \right)^{3/2} \frac{T^{3/2}}{N_e} \right] - \ln \left( \frac{C_0}{100 T_{00}(T)} \left( \frac{1}{1 + S_{10}} \right) \right) \]  

(21)

Defining:

\[ x = E_{2,\alpha}^{z^*} = E_{2,\alpha}^z + z E_{\infty,\alpha}^0 \]  

(22)

\[ B^z(T, N_e) = z \ln \left[ 2 \left( \frac{m_e k_B}{2 \pi \hbar^2} \right)^{3/2} \frac{T^{3/2}}{N_e} \right] \]

\[ D_\alpha(T, N_e) = \ln \left( \frac{C_0}{100 T_{00}(T)} \left( \frac{1}{1 + S_{10}} \right) \right) \]

The modification made to the Saha-Boltzmann plot equation is the additional \( D_\alpha(T, N_e) \) equation that includes the elemental concentration of the sample, the partition function of the neutral element, and the ratio of ions to neutrals for each element. Adding the \( D_\alpha(T, N_e) \) factor is important in aligning points from different elements into a single line fit [48]. Equation (22) shows that for each element, the x coordinate of the Saha-Boltzmann plot includes the ionization energy of an element added to the energy of the upper level in order to provide a correction for ionic lines. The same iterative process used to determine a suitable representative temperature for
the plasma using the Saha-Boltzmann plot is used for the multi-element Saha-Boltzmann plot because the y-coordinate equation is dependent on an input temperature.

While the Saha-Boltzmann plot involves a single element at different ionization stages, a multi-element Saha-Boltzmann plot embraces a line fit on points created by different elements at different ionization stages. The multi-element Boltzmann plot equation takes the same form as the Saha-Boltzmann equation except for the added $D_a(T, N_e)$ and the adjustment made to the energy of the upper level. Additionally, the multi-element Boltzmann plot gives a more accurate temperature measurement than the Saha-Boltzmann plot because more emitters are taken into account to form a linear fit. The disadvantage of the multi-element Saha-Boltzmann plot is the required knowledge of more parameters such as the elemental concentration and the electron density. These parameters allow emission lines from multiple elements at different ionization stages to be projected onto a linear fit.

The figure below shows a summary of the Boltzmann, Saha-Boltzmann, and Multi-Element Saha Boltzmann plot for a simulated Aluminum Calcium spectrum from 300 nm to 400 nm at a plasma temperature of 1.5 eV. Three Boltzmann plots are created for Al I, Al II, and Ca II. A Boltzmann plot for Ca I cannot be created because Ca I peaks are not detected. With knowledge of the electron density, $N_e = 10^{24}$ m$^{-3}$, a Saha-Boltzmann plot is created for Al I and Al II. The Saha-Boltzmann plot allows for the Al I and Al II Boltzmann plots to adapt to a single line fit. Furthermore, with knowledge of the concentration of Al and Ca along with the electron density, a multi-element Saha-Boltzmann plot is created for Al I, Al II, and Ca II. The multi-element Saha-Bolzmann plot is shown to created a single line fit of the Al I, Al II, and Ca
II Boltzmann plots. The table below summarizes the function of the Boltzmann, Saha-Boltzmann, and Multi-Element Saha Boltzmann plots as well as their advantages and disadvantages.

Figure 7: Boltzmann, Saha-Boltzmann, and Multi-Element Saha Boltzmann plots for a simulated Aluminum and Calcium spectrum at 1.5 eV.
Table 2: Summary of the Boltzmann, Saha-Boltzmann, and Multi-Element Saha Boltzmann plots.

<table>
<thead>
<tr>
<th>Function</th>
<th>BP</th>
<th>SBP</th>
<th>MESBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Function</td>
<td>Plot by species</td>
<td>Plot species of different ionization stages</td>
<td>Plot different elements from different ionization stages</td>
</tr>
<tr>
<td>Disadvantage</td>
<td>Fewer Points and energy level spread</td>
<td>Prior knowledge of electron density. Requires iteration of temperature.</td>
<td>Prior knowledge of electron density and elemental concentration. Requires iteration of temperature.</td>
</tr>
<tr>
<td>Advantage</td>
<td>No Prior knowledge of plasma or sample except qualitative composition.</td>
<td>Larger energy level spread and more points to fit a linear slope than BP.</td>
<td>Larger energy level spread and more points to fit a linear slope than BP and SBP.</td>
</tr>
</tbody>
</table>
CHAPTER 3  Plasma Temperature of Known Samples

3.1  Broadening as an Interference

Interference can be defined as a signal or mechanism that masks or distorts real information and it can be produced in a LIBS spectrum from the broadening of spectral lines. The concept of interference is shown visually in Figure 8 below, which shows an Al II peak from a simulated Aluminum and Calcium spectrum from 300 nm-400 nm at 1.5 eV. Within the full width at half the maximum intensity (FWHM) of the Al II peak are all the Al II transitions that are in the Kurucz database [24]. For this study, the FWHM is chosen as the conventional range to analyze transitions within a broadened peak. The Al II transitions are plotted in orange as stems by normalized gA values vs. wavelength. Idealistically, a spectrum with perfect resolution would show the stem lines shown in orange. However, shown in blue, a wide line with a peak intensity and a broadening quantified by its FWHM is resolved. Therefore, broadening brings interference in the spectrum because it blends all of the other possible Al II transitions that occur in plasma.

The peak wavelength of the broadened peak is 358.69 nm. For line assignment, the transition in the database used to explain this peak would have characteristics of an emitted wavelength close to 358.69 nm or a high gA value. For temperatures, the single transition that best represents the spectral line is used to generate a point on a Boltzmann plot. However, there are more Al II transitions that can explain the formation of the Al II peak. These other transitions can occur in the Al & Ca plasma, but are lost in broadening and cannot be resolved. Being able to utilize the extra information of the other transitions within the FWHM of a peak to measure temperature is a path explored in this thesis.
3.2 Plasma Temperature Methods

The analysis of spectra and the determination of temperature will take advantage of four different approaches when utilizing the Boltzmann plot method.

- Attributing the peak to a single transition into the temperature calculation.
  
  A. Closest emission wavelength in the database to the detected peak in the spectrum.

  B. Highest emission probability within the peak's FWHM.

- Attributing the peak to multiple transitions that are within the peak's FWHM into the temperature calculation. Each transition is assigned an intensity according to:
3.2.1 Attribution to a Single Transition
The two different approaches for using parameters from a single transition in the temperature calculation are re-iterated below in detail.

A. Temperature measurements are made by matching the wavelength of the detected peaks in the spectrum to the closest wavelength value found in the database. For example, in Figure 8, the transition circled in green is used to generate a single point in the Boltzmann plot because it emits light at a wavelength closest to the peak wavelength of the spectral line (light orange dash).

B. Temperature calculations are made by only using the transition with the highest $gA$ (transition probability) from the list of transitions within the FWHM of a spectral line. In Figure 8, the transition in the purple rectangular box is used to generate a single point in the Boltzmann plot because it contains the highest $gA$ value.

3.2.2 Attribution to Multiple Transitions
Methods C and D are the approach taken to utilize several transitions within the FWHM of a broadened peak that are not resolved in a LIBS setup. Multiple transitions are used in the temperature calculation by distributing the intensity of a spectral line to several transitions within the peak’s FWHM. Each transition within the FWHM of a detected peak is given an intensity by the two equations below:

C. The $gA$'s of each transition multiplied by the spectral line intensity.
D. The $gA \times \exp(-E/T)$ of each transition multiplied by the spectral line intensity.
\[ C. \ I_{shared} = I_{peak} \left( \frac{g_A}{\sum g_A} \right) \]

\[ D. \ I_{shared} = I_{peak} \left( \frac{g_A e^{-E/T}}{\sum (g_A e^{-E/T})} \right) \]

Where \( I_{peak} \) is the integrated intensity of the spectral line, \( E \) is the upper energy level of each transition, \( T \) is the plasma temperature, and \( g_A \) is the probability of each transition. For the spectral line given in Figure 8, 6 points would be produced on a Boltzmann plot when using method C or D.

### 3.2.3 Example of 4 Temperature Methods from Simulated Spectrum

An example is provided below to demonstrate how the temperature of an ion is calculated using methods A, B, C, and D. In this example, a simulated Aluminum spectrum with a plasma temperature of 1.5 eV and an electron density of \( N_e = 10^{24} \text{ m}^{-3} \) is analyzed. Methods C and D provide the same Boltzmann plot for this analysis, so only one Boltzmann plot is representative for both methods.
Figure 9: Simulated Aluminum Spectrum at 1.5 eV with Al II detected peaks.

Table 3: Intensity, wavelength, and FWHM for each detected peak emitted by Al II.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Intensity</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>263.81</td>
<td>136</td>
<td>0.14</td>
</tr>
<tr>
<td>281.62</td>
<td>2441</td>
<td>0.10</td>
</tr>
<tr>
<td>346.36</td>
<td>46</td>
<td>0.11</td>
</tr>
<tr>
<td>348.72</td>
<td>64</td>
<td>0.11</td>
</tr>
<tr>
<td>358.69</td>
<td>2239</td>
<td>0.13</td>
</tr>
<tr>
<td>365.51</td>
<td>62</td>
<td>0.13</td>
</tr>
<tr>
<td>370.32</td>
<td>38</td>
<td>0.10</td>
</tr>
<tr>
<td>390.07</td>
<td>239</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Figure 10: Boltzmann plots for Al II when methods A, B, C, and D are implemented.
In a Boltzmann plot, points that are less spread out and well-defined by a least square linear fit will provide a plasma temperature close to the correct value. How well a linear fit best represents a spread of points is quantified by calculating the coefficient of determination $R^2$. A linear fit that best represents a set of data points will provide a coefficient of determination closer to 1. On the other hand, data points that are spread out will cause a linear fit to have a coefficient of determination closer to zero.

The effect methods A, B, and C, and D have on the temperature calculation is shown in Figure 10. Compared to method A, method B provides the same number of points (8 points) that are better defined by a linear fit since the coefficient of determination is closer to one. Method B therefore has a temperature value closer to 1.5 eV. The fact that method B has a coefficient of determination closer to one quantitatively shows that utilizing the most probable transitions within the FWHM of each spectral line increases the accuracy of the temperature measurement.

Compared to method B, methods C and D provided a coefficient of determination closer to 1 and a temperature measurement closer to 1.5 eV. Although only 8 points are depicted visually on the Boltzmann plot, methods C and D actually use 30 transitions in the temperature calculation. Including the transitions within the FWHM of each peak did not cause the points to be spread out, but allowed for a well-defined line fit to provide a precise temperature measurement.
3.3 Experimental Application of Sharing of Intensities

3.3.1 Aluminum Sample

The figure below shows the experimental setup. A laser pulse from a 1064 nm Q-switched Nd:YAG laser (Quantel Brilliant) is guided by mirrors onto a focusing lens (L1), which focuses the laser pulse onto a sample so that a plasma is induced. The laser is pulsed at 10 Hz with a pulse width of 5 ns. The plasma light is captured by another focusing lens (L2) onto a fiber optic cable that guides the plasma light into a spectrometer (Acton SpectraPro 2500i). The spectrometer disperses the plasma light into its wavelength components and converts the light signal into an electric signal. A computer software then reads the electrical signal to provided a spectrum of the ablated sample. Lens 3 (L3) focuses an image of the plasma light onto a CCD camera (C1). The camera is used to make sure that a stable plasma is being formed on top the sample surface. Plasma stability is important for obtaining spectra with high signal intensity and is found by moving the sample stage in the z-axis. This system is calibrated in wavelength and spectral response and is explained in detail in the appendix.

Figure 11: Experimental Setup
The first application of using multiple transition attributions (methods C and D) is shown experimentally for an Aluminum spectrum. A solid 99.9 % pure Aluminum sample is analyzed using LIBS at laser energies 5 mJ and 20 mJ. The Aluminum spectrum is taken as a function of time so that temperature can be measured as a function of time. Shown in Figure 12 and Figure 13 are the temporal evolution of the Aluminum spectrum at 5 mJ and 20 mJ respectively.

Plasma temperature is known to have a swift rise as the laser ablates a sample and creates plasma [13]. As the laser duration ends, the once hot plasma begins to cool since there is not a continual ionization source, which causes a decrease in plasma temperature [13]. Therefore, the overall behavior of a temperature vs. time plot should indicate a high value in temperature from the start of the plasma lifetime, which exponentially decays toward a constant value [13]. A sign that methods C and D works are when a plot is created with reasonable temperature values that exponentially decays as a function of time.
Figure 12: Aluminum Spectrum taken at 5 mJ laser energy.

Figure 13: Aluminum Spectrum taken at 20 mJ laser energy.
Figure 14: Method C and D Boltzmann Plots for an experimental Aluminum Spectrum.

Figure 14 above shows two Boltzmann plots for the experimental Aluminum spectrum taken from a laser energy of 5 mJ and at a delay time of 400 ns. The Boltzmann plot on the left is created when using method C or sharing the intensity of each spectral line according to gA transition values. The Boltzmann plot on the right is created using method D or sharing the intensity of each spectral line according to gA transition values multiplied by exp(-E/T). Sharing according to gA*exp(-E/T) requires a temperature loop until convergence.

As shown in Figure 14, temperature measurements using method C spread the points in the Boltzmann plot leading to a coefficient of determination of 0.4483. On the other hand, the
temperature loop that involves method D converged to a Boltzmann plot that allowed the points to show a linear formation with a higher coefficient of determination of 0.9994. Since method D optimizes the Boltzmann plots by forming a better linearity of points than method C, it is applied for the Aluminum spectra taken at 5 mJ and 20 mJ for all delay times. Therefore, the plasma temperature vs. delay time plot shown below is constructed using method D.

Figure 15: Plasma Temperature vs. Delay time for Al I when laser energy is 5 mJ and 20 mJ.
When the laser energy is 5 mJ, the Aluminum spectrum is captured at every 500 ns and has a lifetime of 4,400 ns. Although the emission signals subside at 4,400 ns, temperature is only measured up to 1,900 ns because the remaining doublet peaks (256.8 nm and 257.5 nm) do not provide a sufficient upper energy level spread for a temperature measurement.

The temporal evolution of the plasma when the laser energy is 5 mJ shows more of a linear decrease than an exponential decrease. If spectra were acquired at increments smaller than 500 ns, an exponential decrease can be outlined. At the time that the data was taken at 500 ns increments, it was not known that more increments were necessary to form an exponential decay. Furthermore, when compared to the 20 mJ T° plot, the T° plot at 5 mJ has a faster decay because the laser energy at 5 mJ creates a colder plasma than a 20 mJ laser pulse.

When the laser energy is 20 mJ, the spectrum is acquired at step sizes of 1000 ns and has a lifetime of 16,400 ns. Increasing the laser energy to four times the amount from 5 mJ caused the plasma lifetime to increase approximately 4-fold. Having a longer plasma lifetime also allowed for temperature to be measured at longer times in order to highlight the exponential decay. Plasma temperature is only measured up until 5,400 ns because the remaining 2 doublet peaks (256.8 nm, 257.6 nm, 265.4 nm, and 266.2 nm) do not provide a sufficient spread in upper energy level to form a Boltzmann plot.

A questionable observation in Figure 15 is that if the laser energy is increased by 4 times the amount from 5 mJ, then the initial plasma temperature measurement at 400 ns should have a notable difference proportional to the difference in laser energy. Figure 16 below shows the energy level transitions for the Aluminum spectrum at 400 ns when the laser energy is 5 mJ and
20 mJ. The upper energy levels used for temperature measurements are shown along with their respective lower energy level. Notice from Figure 16 that the highest energy level populated is around 8.8 eV when the laser energy is at 5 mJ and 20 mJ. The second highest energy level populated is around 5.2 eV. The plasma temperature affects the amount of energy electrons gain to populate a certain energy level by the equation below.

$$T \approx \frac{E_u}{10} \quad (23)$$

The plasma temperature can be estimated to 10 % of the highest upper energy level ($E_u$). In this case, a plasma temperature between 0.5 eV to 0.9 eV is a reasonable range based on the two highest upper energy levels being 5.2 eV and 8.8 eV. When the laser is at 5 mJ and 20 mJ, the plasma temperature measured at 400 ns are 0.67 eV and 0.72 eV respectively, which are within the range mentioned above. Therefore, the initial temperatures measured when the laser energy is at 5 mJ and 20 mJ are reasonable.

Another possible explanation why the $T^0$ plot at 20 mJ is not significantly higher at 400 ns when compared to the $T^0$ plot at 5 mJ is because not all of the 20 mJ of energy is reaching the sample to create a hotter plasma. At high enough laser energies, the electron density in the plasma is greater than the critical electron density, which causes the plasma to behavior like a mirror to the laser beam and prevent the full laser energy from ablating the sample. When the plasma acts as a mirror, plasma shielding is occurring [1, 43]. Measuring plasma temperature before 400 ns could show a significant difference when the laser energy is increased. However,
temperatures were not measured before 400 ns because a continuum spectrum was observed with weak emission signals.

Figure 16: Energy Level Transitions for the Aluminum spectrum at 400 ns when laser energy is 5 mJ and 20 mJ.
### 3.3.2 Copper Sample

The data collection for Copper followed a similar protocol as the Aluminum sample except for a difference in laser energy. The laser energies used for the copper experiment are 7.66 mJ and 15 mJ. Pure Copper (99.9 %) is analyzed using LIBS to obtain Copper spectra as a function of time. Compared to Aluminum, Copper adds in an extra level of complexity that is shown in Figure 17. The Aluminum transitions within the FWHM of each peak that were used for temperature measurement were all Al I. On the other hand, within the FWHM of most copper peaks are Cu I and II transitions.

![Spectrum with gA Transitions (Delay = 400 ns) [7.66 mJ]](image)

**Figure 17: Copper Transitions within the FWHM of each spectral line.**

Simply applying methods C and method D to Cu spectral lines do not provide the appropriate proportion of the total intensity to the Cu I and II transitions. For instance, when
applying method C to measure the temporal evolution of the Cu I temperature, the Boltzmann plots were not linear. In addition, when applying method D, the Boltzmann plots for Cu I did not change significantly to improve linearity as it did with Al I in Figure 14. Cu I temperature measurements could not be optimized using method D because there are a lot of Cu II transitions obtaining proportions of the total intensity.

A key parameter to account for sharing with transitions of different elements or ionization stages is the population density of species. The intensity of a spectral line as shown in equation (5) includes the population density of the species in the plasma. For example, let us consider a single spectral line with two transitions within its FWHM. One transition is Cu I and the other is Cu II. The total intensity of this spectral line takes contributions from both the Cu I and Cu II transitions. However, the intensity of the spectral line also depends on the amount of Cu I atoms that emit light to form this spectral line as well as the amount of Cu II ions. The reason why method D worked well for the Aluminum spectrum without considering the population of Al I is because only Al I transitions were found within each spectral line used for temperatures. On the other hand, different species are contributing to Cu spectral lines, therefore making the knowledge of the amount of each species important for accurate temperature measurement.

Figure 18 below shows how the population density for Cu I and Cu II are accounted for in the algorithm for temperature determination. Input population density values, one for Cu I and the other for Cu II, are inserted into the algorithm as well as an input temperature. The intensity
of each spectral line are shared among the transitions within their FWHM according to the equation shown below.

\[ I_{\text{shared}} = I_{\text{peak}} \left( \frac{g \alpha e^{\frac{E}{T_{\text{in}} N}}}{U(T)} \right) \sum \left( \frac{g \alpha e^{\frac{E}{T_{\text{in}} N}}}{U(T)} \right) \]  \hspace{1cm} (24)

Equation 24 shows that all the parameters that explain the intensity of a spectral line are used to share the intensity of a spectral line, which includes the population density of species and the partition function. Once the sharing of intensities are accomplished, a Boltzmann plot is produced. Figure 18 below shows that Boltzmann plots are produced for Cu I and Cu II, which provide the output temperature and the y-intercept for these emitters. The population density for Cu I and Cu II are calculated from the y-intercept of the Boltzmann plots by the equation shown below.

\[ N = \frac{U(T)e^b}{hc} \]  \hspace{1cm} (25)

Where b is the y-intercept, hc is the Planck's constant times the speed of light, and U(T) is the partition function.

Once output temperatures and population densities are measured, these output parameters become the new input in the algorithm until convergence. Unfortunately, when the algorithm converges, problems are encountered in the results, even when different combinations of copper peaks are used. For instance, either the Boltzmann plot for Cu I converges to a negative
temperature or the temperatures for Cu I and Cu II do not significantly improve to the point where they have a similar value that proves the existence of LTE. Including the sharing of intensities with the population density and the partition function did not improve the temperature measurement for Cu I and Cu II.

The next alternative is to combine the Boltzmann plots of Cu I and II to form a Saha-Boltzmann plot. Two reasons why the Saha-Boltzmann plot is a better alternative than the Boltzmann plot is because it allows for more points to be utilized in a line fit and requires the knowledge of the electron density in the plasma. The electron density plays a role in accounting for the weight the Cu I and II transitions contribute to a spectral line because it should be approximately equal to the population density of Cu II ions.
Figure 18: Process for including population density of species for plasma temperature measurements.
The electron density is calculated based on an iterative procedure similar to how the population density of species was calculated based on the Boltzmann plot method in Figure 18. The electron density is calculated based on the y-intercept of the Saha-Boltzmann plot and is shown by the equation below.

\[ N_e = 2 \left( \frac{m_e}{2\pi\hbar^2} \right)^{3/2} \frac{(k_B T)^{3/2}}{e^{\ln\left(\frac{I_{21}A_{21}}{g_{21}^2A_{21}^2}\right)} - b} \]

\[ N_e = (6.024 \times 10^{27} \text{ eV}^{-3/2} \text{ m}^{-3}) \frac{(k_B T)^{3/2}}{e^{\ln\left(\frac{I_{21}A_{21}}{g_{21}^2A_{21}^2}\right)} - b} \quad (26) \]

The values for \( \ln\left(\frac{I_{21}A_{21}}{g_{21}^2A_{21}^2}\right) \) are all the y-values used in the Saha-Boltzmann plot, so this can be rewritten as \( \ln(y) \). If there are eight y-values in the Saha-Boltzmann plot then equation (26) will calculate eight electron density values, which are then averaged to provide one value for electron density.

In the algorithm, method D requires an input temperature and equation (15) in the Saha-Boltzmann equation requires an input electron density and temperature. Therefore, both an input temperature and electron density are inserted into the algorithm. The intensity of each spectral line is shared according to method D to produce a Saha-Boltzmann plot. From the Saha-Boltzmann plot, the slope provides an output temperature and the y-intercept is used to calculate an output electron density using equation (26). The output values for both temperature and electron density function as the new input and this process is repeated until convergence.
Unfortunately, when tested on the copper peaks at 218 nm, 220 nm, 262 nm, 282 nm, and 296 nm at a delay of 400 ns, the algorithm that incorporates both the temperature and electron density loop does not converge.

Another approach to this analysis involves keeping the electron density constant ($10^{22}$ m$^{-3}$) to test whether the temperature loop converges. This electron density is chosen because it is a typical value for when a plasma is in LTE according to the McWhirter criterion [35]. Figure 19 shows two Saha-Botlzmann plots formed from analyzing the copper peaks 218 nm, 220 nm, 262 nm, 282 nm, and 296 nm at a delay of 400 ns. The plot on the left is the converging plot when applying method C to share the intensities. The plot on the right is the result when applying method D to share the intensities. Figure 19 shows that method D has a coefficient of determination closer to 1 when compared to method C. Having a high coefficient of
determination means that the points on the plot can be explained well by a linear fit. From method C to D, Figure 19 clearly shows the points for Cu II moving toward a linear formation, which means method D will provide an accurate temperature reading based on a given electron density.

While method D is shown to make a Saha-Boltzmann plot linear for temperature measurements, the exact electron density is not known for the copper plasma. In the literature, Aguilera and Yalcin used the Saha-Boltzmann plot to measure temperature and determined the electron density through Stark broadening [45] [48]. Therefore, an attempt is made to determine the electron density in the copper plasma through Stark broadening by the equation below [2].

\[ \Delta \lambda_{\text{Stark}} = 2\omega \left( \frac{N_e}{10^{16}} \right) \]  

(27)

Where \( \omega \) is the electron impact half-width that is temperature dependent, \( \Delta \lambda_{\text{Stark}} \) is the FWHM of the stark broadened spectral line, and the value \( 10^{16} \) is in units of \( \text{cm}^{-3} \). The value for the electron impact parameter is found in the literature.

In the case for Cu spectral lines, the tables used to determine the electron impact parameter as a function of temperature are found in the following literature [49, 50]. However, a limitation found in these tables is not presenting the electron impact parameter for a wide range of temperature values, thereby providing a hindrance in calculating temperature as a function of time for the copper spectra. For instance, reference [49] only provides an electron impact value for the Cu peak 324.54 nm at 1.46 eV and for other peaks at 2.068 eV. The temperatures
provided for Cu lines in reference [50] are 0.8617 eV and 1.72 eV. Between the temperatures 0.8617 eV and 1.72 eV, linear interpolation can be used to determine the electron width parameter within that range. When applying Stark broadening for temperature determination, the temperature loop does not converge because the electron density cannot be calculated outside of the range 0.8617 eV to 1.72 eV.

3.4 Summary

In LIBS, the resolution is limited by plasma broadening mechanisms and instrumental broadening. A typical broadened spectral line encountered in LIBS spectra is shown in Figure 8. Within the FWHM of the spectral line are transitions presented from a database to explain that these transitions are not only present in the plasma, but also contribute to the formation of the spectral line. A new method is developed to make use of the transitions not resolved in a LIBS setup for temperature determination. To employ the extra transitions for temperature measurement, the total intensity of a spectral line must be shared according to the proportions shown in the equations for method C and D.

For a simulated Aluminum spectrum, methods C and D improved the temperature measurement for Al II when compared to the conventional line assignment using single transition methods. In experiment, methods C and D are implemented for Aluminum and Copper spectra. For Aluminum, method D provides Boltzmann plots with a better linearity when compared to method C, thereby improving temperature measurement. Method D is also used to model temperature as a function of time for the Aluminum spectra taken at laser energies 5 mJ and 20 mJ. In Figure 15, the temperature vs. time plots at laser energies 5 mJ and 20 mJ both start from a reasonable temperature at 400 ns and decreases over time, which supports the correct
behavior of a cooling plasma. Additionally, the temporal evolution of temperature for Aluminum shows that method D can be used to measure temperature during any dynamic moment in a plasma's lifetime.

The spectra for Cooper is more complex than Aluminum because two different ions (Cu I and II) are being examined for the formation of copper peaks. In the case with Aluminum spectra, only Al I explained the formation of the spectral lines used for temperatures. Since Cu I and Cu II species are involved in creating copper spectra, the population density or the electron density becomes a vital parameter for temperature measurement. After calculating temperatures using the population densities of species in the Boltzmann plots showed to be unsuccessful, the Saha-Boltzmann plot was explored. Temperature measurements lead to enforcing the Saha-Boltzmann plot because it required the knowledge of the electron density to generate its plots. However, issues are encounter for the electron density determination from algorithm iterations not converging and Stark broadening tables not supplying enough information. Fortunately, the copper spectra did show in Figure 19 that temperature measurements can be optimized to produce a Saha-Boltzmann plot with points being well-defined by a linear fit. By holding the electron density constant at a reasonable value, method D created a Saha-Boltzmann with a coefficient of determination closer to one when compared to the Saha-Boltzmann plot created from method C. Therefore, if the correct electron density is known, species of different ionization stages can be used on a single plot to measure temperature while still utilizing the transitions within the FWHM of each spectral line. Overall, the experiments for the aluminum and copper samples showed that method D is a promising approach for plasma temperature measurements.
CHAPTER 4 Plasma Temperature with Global Database (Simulated Spectra)

4.1 Global Database

Figure 20: Simulated Aluminum spectrum from 250 nm to 400 nm at 0.7 eV and its Boltzmann plot from method C.

In the previous chapter, the transitions considered within the FWHM of a spectral line were limited to the known elements contained in the sample. For instance, when analyzing an Aluminum spectrum, only Al I, Al II, and Al III transitions are considered from a database. The approach explored here is given an Aluminum spectrum, what if transitions of all elements from a database are considered and used for temperature measurements. This approach tests the idea of performing temperature measurements using spectra from unknown samples.

An Aluminum spectrum at 0.7 eV from 250 nm to 400 nm is simulated and used for temperature measurements. Figure 20 above shows the Boltzmann plot for this spectrum using method C with only Al I transitions provides a temperature of 0.704 eV. When reading from a global database, the transitions within the FWHM of each spectral line is given an intensity according to method C as well. In this analysis, 90 ions are detected with 540 transitions. The
results show that the temperature of Al I is 0.427 eV, which contains a 39 % error when compared to the correct value of 0.7 eV. The Figure 21 below shows why the temperature of Al I deviates from the correct value.

Figure 21 below shows all the transitions provided from the database that is within the FWHM of the first peak in the Aluminum spectrum. The transitions are plotted by their normalized intensity value that is calculated from sharing the intensities according to method C. The intensity of the peaks in the spectrum are normalized as well. Notice in the figure that the Al I transition only gets 0.268 % of the total intensity. On the other hand, the ions Cr II, Ni III , and Eu II obtain a higher percentage of the total intensity because these transitions contain a high transition probability (gA value). When a global database is not considered, peak 1 only contained one Al I transition within its FWHM, thereby leading to that Al I transition obtaining 100 % of the total intensity. Not only are there 83 transitions within the FWHM of peak 1 that are taking more of the total intensity, but there are high probable ions like Ni III and Cr II that obtain most of it. Having other transitions receive proportions of the total intensity causes all the Al I transitions in the spectrum to be given a low percentage of intensity, thereby causing the temperature of Al I to depart from the value of 0.7 eV.
Figure 21: Global Transitions within the FWHM of peak 1.

Table 4: Ions that obtain most of the total intensity compared to Al I for peak 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>% of Total Intensity</th>
<th>Temperature (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr II</td>
<td>256.8484</td>
<td>30.89 %</td>
<td>4.2655</td>
</tr>
<tr>
<td>Ni III</td>
<td>256.8280</td>
<td>42.06 %</td>
<td>-57.2427</td>
</tr>
<tr>
<td>Eu II</td>
<td>256.8173</td>
<td>4.34 %</td>
<td>0.0067</td>
</tr>
<tr>
<td>Al I</td>
<td>256.7983</td>
<td>0.268 %</td>
<td>0.4273</td>
</tr>
</tbody>
</table>
4.2 Filtering

4.2.1 Temperature Filter

An approach taken to eliminate ion transitions from the sharing of intensities is to apply a temperature filter into the algorithm. For instance, in Table 4, notice that Ni III transition obtains the majority of the total intensity of peak 1, but a negative temperature is measured. Since negative temperatures do not make sense, this ion can be removed from the analysis. In the algorithm, once a set list of ions is generated, method C is applied and the temperature of these ions are calculated. The ions with negative temperatures are removed from the list and method C is applied again to determine the temperature of each species. This is repeated until there are a list of ions with no negative temperatures.

When the negative temperature filter is applied, the total number of ions and transitions detected are reduced from 90 to 61 and 540 to 257 respectively. Furthermore, the transitions within the FWHM of peak 1 are reduced from 83 to 39 transitions. Before the negative temperature filter is applied, Ni III obtained the highest amount of the total intensity of peak 1, but as shown in the figure below, is effectively removed by the filter. Now Cr II is first in line with having the highest proportion of the total intensity. The proportion of total intensity Al I obtained in peak 1 increased from 0.268 % to 0.544 %, therefore showing that other Al I transitions experienced an increase in acquired intensity values. Although the temperature of Al I increased from 0.427 eV to 0.462 eV, the temperature filter did not entirely eliminate unnecessary ions to allow for an immense increase in the measured temperature of Al I.
Figure 22: Global Transitions within FWHM of peak 1 after temperature filter.

Table 5: Ions that obtain most of the total intensity compared to Al I for peak 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>% of Total Intensity</th>
<th>Temperature (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr II</td>
<td>256.8484</td>
<td>62.75 %</td>
<td>4.6241</td>
</tr>
<tr>
<td>Eu II</td>
<td>256.8173</td>
<td>8.82 %</td>
<td>0.0053</td>
</tr>
<tr>
<td>Al I</td>
<td>256.7983</td>
<td>0.544 %</td>
<td>0.4619</td>
</tr>
</tbody>
</table>
4.3 Matching Factor (MF)

The matching factor answers the question, "For a given spectral range, how well does my spectrum match the transitions in the database for a particular species?" For example, for a spectrum of pure Aluminum, Al I should have the highest MF because the transitions detected in the spectrum best match with the transitions the database is saying should be there. The equation for the matching factor is shown below.

\[ MF = \frac{\sum gA \text{ (detected)}}{\sum gA \text{ (database)}} \]  (28)

Figure 23: The gA transitions within the range of the simulated Aluminum spectrum. Green are the detected gA transitions and blue are from the database. The green transitions are from the database as well.
The figure above shows the same simulated Aluminum spectrum with the detected Al I gA transitions (green) and database transitions (blue). Obviously, the green transitions are included as the transitions found in the database as well. Simply dividing the detected gA values by the gA values in the database provides the MF value for Al I. This adds a layer of statistics toward temperature analysis and can modify the equation for method C as shown below.

\[
I_{\text{shared}} = I_{\text{peak}} \left( \frac{gA \ast MF}{\sum (gA \ast MF)} \right)
\]  

(29)

The MF values should provide weight in giving more proportion of intensity to the ion that has a higher probability of explaining the spectrum.

Figure 24: Global Transitions within FWHM of peak 1 after temperature filter and MF is used in method C.
Table 6: Ions that obtain most the total intensity compared to Al I for peak 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>% of $I_{\text{total}}$</th>
<th>Temperature (eV)</th>
<th>MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr II</td>
<td>256.8484</td>
<td>62.81 %</td>
<td>5.2464</td>
<td>3.189 %</td>
</tr>
<tr>
<td>Eu II</td>
<td>256.8173</td>
<td>8.086 %</td>
<td>0.0072</td>
<td>2.919 %</td>
</tr>
<tr>
<td>Al I</td>
<td>256.7983</td>
<td>8.917 %</td>
<td>0.4631</td>
<td>52.186%</td>
</tr>
</tbody>
</table>

The negative temperature filter is applied and the MF value for each ion is included in method C. A total of 60 ions are still detected with 266 transitions. The calculated MF for Aluminum (52.186 %) is the highest compared to the other elements. For peak 1, the intensity the Al I transition obtained increased from 0.544 % to 8.917 %, which is a higher proportion than Eu II (8.086 %). Therefore, when including the MF in method C, Al I transitions in the entire spectrum received higher intensity values. Unfortunately, the increase in the obtained intensity for Al I transitions only increased the temperature of Al I from 0.462 to 0.463 eV. The small increase in the Al I temperature is attributed to the fact that there are still a large amount of other transitions taking the proportion of the total intensity away from Al I. For instance, in peak 1, there are 36 other transitions taking 91.083 % of the total intensity away from Al I and 62.81 % is given to Cr II.

4.3.1 MF as a Filter

Fortunately, Al I does have the highest MF value and there are 58 out of the 60 ions that have MF values lower than 9 %. In peak 1, although Cr II takes more than half of the total intensity away from Al I, it has a low MF value of 3.189 %. The remaining ion, Su I, has an MF value of 39.6128 %. Since the majority of ions present within the FWHM of each peak has a low
probability of explaining the spectrum, the MF value for each ion can be used as a condition for filtering. The approach taken here is to remove ions with an MF value lower than half the maximum MF value calculated. In this case, applying only the MF filter gives the same results as when both the temperature and MF filter is applied. Furthermore, using the MF value in method C does not tremendously change the temperature of Al I. The results are shown below for peak 8 when the MF value is used in the sharing of intensities.

Table 7: Ions that obtain most the total intensity compared to Al I for peak 8.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>% of $I_{\text{total}}$</th>
<th>Temperature (eV)</th>
<th>MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al I</td>
<td>256.7983</td>
<td>98.78 %</td>
<td>0.7052</td>
<td>52.186%</td>
</tr>
<tr>
<td>Su I</td>
<td>396.1974</td>
<td>1.22%</td>
<td>-</td>
<td>39.6128%</td>
</tr>
</tbody>
</table>

The MF filter did a good job at narrowing down the amount of ions that could explain the spectrum. The remaining ions are Al I and Su I. For Su I, only one transition is detected in this spectrum while there are five transitions that are provided in the database to be within the given spectral range. Temperature cannot be calculated for an ion with one transition, but if this spectrum was taken from an unknown sample, Su I still has a 39.628 % match to the spectrum. Even when using the Su I transition in the sharing of intensities, it only obtains 1.22 % of the total intensity of peak 8, while the Al I transition obtains the majority, 98.78 %. Therefore, the temperature of Al I is not interrupted by considering the Su I transition. The calculated temperature of Al I is 0.705 eV, which is close to the correct value of 0.7 eV.
4.4 Summary

Prior knowledge of a sample is vital for obtaining the correct temperature of certain species. Especially when using the method of sharing the intensity of a spectral line with all the transitions within its FWHM, it is important to know the relevant ions and neutrals. Without having any prior knowledge of a sample, all elemental transitions provided from a database are examined, which distorts the correct temperature measurement for the real species generating the spectrum.

Showing how other elemental transitions can distort or interfere with the temperature of a real species is shown in this chapter for a simulated Aluminum spectrum from 250 nm to 400 nm at 0.7 eV. When applying method C with only Al I transitions, the Boltzmann plot yields a temperature of 0.7035 eV, which is the correct measurement. However, when global transitions are examined, 90 ions are detected that reduce the measured temperature of Al I to 0.4273 eV. The reduction in the temperature of Al I is caused from the multitude of other ions taking proportions of the total spectral line intensity away from Al I transitions.

A filtering method is deduced to eliminate ions that provide a negative temperature. Although the negative temperature filter did reduce the amount of total detected ions from 90 to 61, the temperature of Al I only increased by 0.0346 eV. There is still a vast amount of ions interfering with Al I transitions from obtaining a high proportion of the total spectral line intensity.

To add another layer in understanding whether or not an ion should be used for temperature measurements, the MF factor is developed. The MF factor gives the probability that an ion or species matches a given spectrum. Before ions were filtered based on their MF values,
the MF values were used in the method C formula for the sharing of intensities. Ions with high MF values should obtain a higher intensity by including the MF values in method C, but there is still not a significant improvement in the measured temperature of Al I. Using the MF values for each species as a filter did effectively reduce the large number of ions down to Su I and Al I. In peak 8, even when Su I is used in the sharing of intensities with Al I, the measured temperature of Al I is 0.7052 eV, which is close to the correct value of 0.7 eV.

With prior knowledge that the given spectrum is pure Aluminum, the temperature of Al I is accurately determined. Nevertheless, not knowing anything about the elemental composition of a sample allows other elemental transitions to interfere and cause error in the temperature measurement of Al I. By using statistics such as the MF factor, ions with a low probability of explaining the spectrum are eliminated so that accurate temperature measurements are made for emitters with a high probability of existence.
Overall Conclusion

Method C and D are used to calculate the plasma temperature by utilizing the transitions within the FWHM of a broadened peak. Testing method C on a simulated aluminum spectrum showed to improve the coefficient of determination of the Boltzmann plots when compared to conventional plasma temperature techniques. Furthermore, experimental spectra are taken to test methods C and D for plasma temperature measurements. Aluminum and copper samples that are 99% pure are used to obtain the temporal evolution of spectra so that plasma temperature can be measured as a function of time. For aluminum spectra, method D worked better than method C in aligning the points on the Boltzmann plot to a linear fit and is used to measure the temporal evolution of plasma temperature. The T₀ plot for aluminum at 5 mJ laser energy had a faster decay than the 20 mJ T₀ plot, which shows accuracy in using method D for plasma temperature measurements. At both 5 mJ and 20 mJ laser energy, the initial temperature at 400 ns supports the highest energy level that the electrons are excited to in the aluminum emitters. In summary, for experimental and simulated aluminum spectra, method D is shown to be effective in temperature measurements.

Although applying method D through the Boltzmann plots did not work in providing accurate temperatures for the copper spectra, it did show promising results with the Saha-Boltzmann plot. For a given electron density, method D improved the linearity of the Cu I and Cu II points on the Saha-Boltzmann plot by aligning them to a linear fit. If the electron density of the plasma can be measured as a function of time, then method D can be used to measure plasma temperature as a function of time using the Saha-Boltzmann plot.
When method C is used to analyze a simulated aluminum spectrum and calculate temperatures for all the elements in the atomic database, the temperature of aluminum deviates from the correct value. By using filtering techniques, the emitters that have a higher percentage of matching the spectrum can be narrowed down. Once the emitters are narrowed down, method C calculates an accurate temperature for Al I.

Other testing for methods C and D for temperatures can be applied to samples with multiple elements, such as an alloy. A spectral line detected for an alloy will have transitions from different elements or ions. Testing methods C and D using the Multi-Elemental Saha-Boltzmann plot is an interesting next step because different elements considered to have contributed to a spectral line are used for temperature measurements. For the Multi-Elemental Saha-Boltzmann plot to be used, the concentration of elements and the electron density must be known.

Considering the transitions within the FWHM of each spectral line adds more information to a Boltzmann or Saha-Boltzmann plot that can improve temperature measurements. Especially when prior knowledge of a sample is known, like the electron density and elemental composition, experimental and simulated spectra with spectral line broadening can still be used to accurately determine the plasma temperature. In other words, spectra obtained from spectrometers with poor resolution and from dense plasma can take advantage of the temperature methods discussed in this thesis to improve temperature measurements. Furthermore, using the filtering methods and the matching factor can narrow done essential emitters for temperature measurements when the sample is unknown. Overall, this thesis
encourages the implementation of methods C and D for temperature measurements because of its promising results.
APPENDIX A: WAVELENGTH CALIBRATION
The purpose of the wavelength calibration is to ensure that location of each peak appears at the correct wavelength on the spectra software. If the wavelength of peaks emitted from certain samples are known, then a wavelength calibration can be performed. For instance, it is known that Zinc has a peak at 206.423 nm, but without a wavelength calibration, this peak appears at 205.82 nm. To calibrate this peak, simply use the spectra software to reassign the pixel on the iCCD that detects 205.82 nm to 206.423 nm.

Each spectral window is classified by its center wavelength. From a given center wavelength, the spectral window is approximately $\pm 40 \text{ nm}$. Therefore, a given spectral window is about 80 nm. The samples used to calibrate each spectral window are shown below. An important note is that after around 400 nm, second order peaks start appearing because of second order diffraction. For example, that means that a real peak that appears at 200 nm can also appear at 400 nm. Second order peaks are used for wavelength calibration by multiplying the wavelength of the real peak by 2.
Center $\lambda = 240$ nm

Table 8: Center $\lambda = 240$ nm wavelength calibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NIST Calibration [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>202.548</td>
</tr>
<tr>
<td>Zn</td>
<td>206.423</td>
</tr>
<tr>
<td>Zn</td>
<td>209.994</td>
</tr>
<tr>
<td>Zn</td>
<td>213.856</td>
</tr>
<tr>
<td>Zn</td>
<td>250.199</td>
</tr>
<tr>
<td>Zn</td>
<td>255.795</td>
</tr>
<tr>
<td>Mg</td>
<td>279.5528</td>
</tr>
<tr>
<td>Mg</td>
<td>280.2704</td>
</tr>
<tr>
<td>C</td>
<td>247.856</td>
</tr>
</tbody>
</table>
Center $\lambda = 310$ nm

Table 9: Center $\lambda = 310$ nm wavelength calibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NIST Calibration [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>328.233</td>
</tr>
<tr>
<td>Zn</td>
<td>330.258</td>
</tr>
<tr>
<td>Zn</td>
<td>334.502</td>
</tr>
<tr>
<td>Mg</td>
<td>279.5528</td>
</tr>
<tr>
<td>Mg</td>
<td>280.2704</td>
</tr>
<tr>
<td>Mg</td>
<td>285.2127</td>
</tr>
<tr>
<td>Mg</td>
<td>309.2984</td>
</tr>
<tr>
<td>Mg</td>
<td>309.689</td>
</tr>
<tr>
<td>Ag</td>
<td>328.068</td>
</tr>
<tr>
<td>Ag</td>
<td>338.2887</td>
</tr>
</tbody>
</table>
Center $\lambda = 365$ nm

Table 10: Center $\lambda = 365$ nm wavelength calibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NIST Calibration [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>328.233</td>
</tr>
<tr>
<td>Zn</td>
<td>330.258</td>
</tr>
<tr>
<td>Zn</td>
<td>334.502</td>
</tr>
<tr>
<td>Ag</td>
<td>328.068</td>
</tr>
<tr>
<td>Ag</td>
<td>338.2887</td>
</tr>
<tr>
<td>Pb</td>
<td>357.2729</td>
</tr>
<tr>
<td>Pb</td>
<td>363.9568</td>
</tr>
<tr>
<td>Pb</td>
<td>368.3462</td>
</tr>
<tr>
<td>Pb</td>
<td>373.9935</td>
</tr>
<tr>
<td>Mg</td>
<td>383.23037</td>
</tr>
<tr>
<td>Mg</td>
<td>383.82918</td>
</tr>
<tr>
<td>Al</td>
<td>394.40058</td>
</tr>
<tr>
<td>Al</td>
<td>396.152</td>
</tr>
</tbody>
</table>
Center $\lambda = 420$ nm

Table 11: Center $\lambda = 420$ nm wavelength calibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NIST Calibration [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>383.23037</td>
</tr>
<tr>
<td>Mg</td>
<td>383.82918</td>
</tr>
<tr>
<td>Al</td>
<td>394.40058</td>
</tr>
<tr>
<td>Al</td>
<td>396.152</td>
</tr>
<tr>
<td>Pb</td>
<td>405.7807</td>
</tr>
<tr>
<td>Zn</td>
<td>202.548</td>
</tr>
<tr>
<td>Zn</td>
<td>206.423</td>
</tr>
<tr>
<td>Zn</td>
<td>209.994</td>
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<tr>
<td>Zn</td>
<td>213.856</td>
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<tr>
<td>Ag</td>
<td>222.600</td>
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<td>Ag</td>
<td>224.641</td>
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<td>Ag</td>
<td>224.874</td>
</tr>
<tr>
<td>Ag</td>
<td>227.731</td>
</tr>
</tbody>
</table>
**Table 12: Center $\lambda = 485$ nm wavelength calibration.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>NIST Calibration [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>451.2564</td>
</tr>
<tr>
<td>Al</td>
<td>452.8942</td>
</tr>
<tr>
<td>Al</td>
<td>236.7052</td>
</tr>
<tr>
<td>Al</td>
<td>237.3124</td>
</tr>
<tr>
<td>Al</td>
<td>256.7984</td>
</tr>
<tr>
<td>Al</td>
<td>257.5094</td>
</tr>
<tr>
<td>Ag</td>
<td>241.318</td>
</tr>
<tr>
<td>Ag</td>
<td>243.778</td>
</tr>
<tr>
<td>Ag</td>
<td>244.789</td>
</tr>
<tr>
<td>Mg</td>
<td>516.73216</td>
</tr>
<tr>
<td>Mg</td>
<td>517.26843</td>
</tr>
<tr>
<td>Mg</td>
<td>518.36042</td>
</tr>
</tbody>
</table>

*Note: The values marked with x 2 are multiplied by 2.*
Center $\lambda = 555$ nm

Table 13: Center $\lambda = 555$ nm wavelength calibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NIST Calibration [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>516.73216</td>
</tr>
<tr>
<td>Mg</td>
<td>517.26843</td>
</tr>
<tr>
<td>Mg</td>
<td>518.36042</td>
</tr>
<tr>
<td>Pb</td>
<td>280.1995</td>
</tr>
<tr>
<td>Pb</td>
<td>282.3189</td>
</tr>
<tr>
<td>Pb</td>
<td>283.3053</td>
</tr>
<tr>
<td>Pb</td>
<td>287.3311</td>
</tr>
<tr>
<td>Hg</td>
<td>546.0750</td>
</tr>
<tr>
<td>Hg</td>
<td>576.9610</td>
</tr>
<tr>
<td>Hg</td>
<td>579.0670</td>
</tr>
<tr>
<td>Hg</td>
<td>296.7283</td>
</tr>
</tbody>
</table>

*Note: The values are shown in triplicate for Mg and Hg.*

\[x 2\]
Center $\lambda = 625$ nm

Table 14: Center $\lambda = 625$ nm wavelength calibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NIST Calibration [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>296.728</td>
</tr>
<tr>
<td>Hg</td>
<td>312.567</td>
</tr>
<tr>
<td>Hg</td>
<td>313.155</td>
</tr>
<tr>
<td>Pb</td>
<td>666.02</td>
</tr>
<tr>
<td>Zn</td>
<td>328.233</td>
</tr>
<tr>
<td>Zn</td>
<td>330.258</td>
</tr>
<tr>
<td>Zn</td>
<td>334.502</td>
</tr>
<tr>
<td>Mg</td>
<td>309.298</td>
</tr>
<tr>
<td>Mg</td>
<td>309.689</td>
</tr>
</tbody>
</table>

x 2
APPENDIX B: SPECTRAL RESPONSE CALIBRATION
The purpose of a spectral response calibration is to ensure that the real intensity is being measured from a spectrum. For instance, when an aluminum spectrum is taken using the LIBS setup shown in Figure 11, the intensity of light emitted from the plasma experiences losses as it propagates through the focusing lens (L2), the fiber optic cable, and the mirrors and grating in the spectrometer. Once the plasma light reaches the detector in the spectrometer and the spectrum is displayed on the computer, the real intensity of light emitted from the plasma is not measured.

To correct the intensities measured for any given spectrum, the real and experimental spectrum must be known from a broadband lamp source. Then, the equation below can be used to correct any spectrum taken from the experimental LIBS setup.

\[
S_{CORR}(\lambda) = \frac{r_{REAL}(\lambda)}{r_{MEAS}(\lambda)} \times S_{MEAS}(\lambda)
\]  

(30)

Where \( S(\lambda) \) is the spectrum taken from the LIBS setup for any sample and \( r(\lambda) \) is the lamp spectrum.

In this experiment, deuterium and halogen lamps are used to calibrate spectra from 200 nm to 350 nm and 350 nm to 800 nm respectively. The figure below shows an experimental deuterium and halogen spectrum and their real intensity values as provided by the company Ocean Optics. It is important to note that when taking the experimental spectra for deuterium and halogen, the lamp source must be at the same distance away from the lens (L2) as the plasma.
A polynomial is used to fit both the experimental and real intensity values. The function provided from the polynomial fits are then evaluated for every wavelength ($\lambda$) given in a sample's experimental spectrum so that equation (30) can be applied for the spectral response calibration. For the other spectral windows not shown in Figure 25, the table below summarizes the lamp used and the order of the polynomial fit.
Table 15: Lamp and polynomial fit used for each spectral window.

<table>
<thead>
<tr>
<th>Center λ (nm)</th>
<th>Lamp</th>
<th>Polynomial Order Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>240</td>
<td>Deuterium</td>
<td>6</td>
</tr>
<tr>
<td>310</td>
<td>Deuterium</td>
<td>7</td>
</tr>
<tr>
<td>365</td>
<td>Halogen</td>
<td>7</td>
</tr>
<tr>
<td>420</td>
<td>Halogen</td>
<td>7</td>
</tr>
<tr>
<td>485</td>
<td>Halogen</td>
<td>7</td>
</tr>
<tr>
<td>555</td>
<td>Halogen</td>
<td>7</td>
</tr>
<tr>
<td>625</td>
<td>Halogen</td>
<td>7</td>
</tr>
</tbody>
</table>
APPENDIX C: SAMPLE MATLAB CODE
% Read Kurucz database and calculate gA value
database = dlmread('KURUCZ_DATABASE.txt',' ',1);

new_database=zeros(0,5); % Intialize
% Find parameters for a particular (element.ion) database.
for element=[13.0,13.01,13.02]
k = find(database(:,3)==element);
modified_database = database(k,:);
new_database = vertcat(new_database,modified_database);
end

wavelength = new_database(:,1); % first column = wavelength
A_value = new_database(:,2); % second column = A_value
J = new_database(:,7); % seventh column = J
mA = (2.* J + 1) .* A_value; % mA = 2J + 1

% wavelength, gA, Energy, Element.Ion
database2 = [wavelength, mA, new_database(:,6), new_database(:,3)]; % Database2 with mA values

sort_database = sortrows(database2,1); % Sort wavelengths in database2 in ascending order.

wavelength = sort_database(:,1); % Sort wavelengths in database2 in ascending order.

%% Calculate all wavelengths within the FWHM of a spectral line.
separate = dlmread('Aluminum_Jessica.txt',' ',1); % Reads textfile: Detected Wavelength, Integrated Intensity, and FWHM

wavelength_input = separate(:,3); % Detected wavelength peaks
width = separate(:,4); % FWHM
u = numel(wavelength_input); % Count the number of detected peaks

max_wavelength = wavelength_input + (width./2); % + width from each detected wavelength
min_wavelength = wavelength_input - (width./2); % - width from each detected wavelength

%% Initializing conditions
new=zeros(1,5);
T_new = zeros(1,0);
diff_new = zeros(1,0);

T = 1.0; % Input temperature
T=T'
diff = 1; % Initialize variable diff to start while loop
c = 0; % Initialize counter control variable.

while diff >0.0001 % *desired accuracy*
c = c+1 % Update start temperature value to the temperature calculated
new=zeros(1,5); % Initialize
%% Matching wavelengths within the FWHM of each spectral line to the database
for p =1:u % Loop through each spectral line.

wavelength_range = wavelength(find(min_wavelength(p) < wavelength & wavelength < max_wavelength(p))); % Find "min < wavelength_range < max" from the database

ismem = ismember(sort_database, wavelength_range); % Is the wavelength range a member of the database? Yes, return 1

w = find(ismem==1); % Finds the "1s" and assign the wavelength_range values from the database to variable "w."

boltzmann = sort_database(w,:); % Spit out table from the database of each wavelength range: Wavelength_range, gA_2, Energy, Ion

Energy = boltzmann(:,3); % third column = Energy
Ion = boltzmann(:,4); % fourth column = Ion
gA_2 = boltzmann(:,2); % second column = gA

%% Distribute Intensities to each wavelength in a range according to the gA fraction.
gA_count = numel(gA_2);
h = gA_2 .* exp(-Energy ./ T(c)); % gA * exp(-E/T)
gA_sum = sum(h); % Sum(gA * exp(-E/T))

Intensity = separate(:,2); % Integrated Intensity value for each detected peak

Intensity = Intensity(p); % Loop through each intensity value

fraction_gA = h ./ gA_sum; % Divide each gA value by the sum of the gA for each wavelength range

fraction_Intensity = Intensity .* fraction_gA; % Share the integrated intensity value to each wavelength range

new1 = [wavelength_range, fraction_Intensity, gA_2, Energy, Ion];

%% Table with each wavelength range, Shared Intensity, gA, Energy, Ion

new = vertcat(new,new1); % Contains the wavelength range for each detected peak and the shared intensities for each wavelength range
end

limit = max(new(:,5)); % Find the highest ion number
mol = zeros(1,5); % Initialize

%% Calculate the temperature of each ion
for j = 13.0
    v = find(new(:,5)== j); % Loop through table values of one ion
    brand_new = new(v,:); % Spit out the Wavelength, Intensity, and Energy for each ion
    mol = vertcat(mol,brand_new); % Organizes table by ion
end

%% Assign columns, calculate slope, and Temperature
wavelength_2 = brand_new(:,1);
Intensity_2 = brand_new(:,2);
gA_3 = brand_new(:,3);
Energy_2 = brand_new(:,4);
Ion_2 = brand_new(:,5);

x = Energy_2; % x-values for Boltzmann plot
y = log((wavelength_2.*Intensity_2)./gA_3); % y-values for Boltzmann plot

%% Coefficient of Determination
p = polyfit(x,y,1); % Linear Regression
yfit = polyval(p,x); % Evaluate the linear fit equation at all x.
yresid = y - yfit; % Compute residual values
SSresid = sum(yresid.^2) % Square the residuals and total them
SStotal = (length(y)-1) * var(y);
rsq = 1- SSresid / SStotal; % Coefficient of Determination

b = p(2); % y-intercept
slope = p(1); % Slope of the linear fit.
T_out = -1/slope % Calculated Temperature
T(c+1) = T_out;

diff = abs(T(c)-T(c+1)) % Difference between Initial and calculated temperature
diff_new = vertcat(diff_new,diff) % Concatenate differences for each iteration

T_new = vertcat(T_new,T_out) % Concatenate Temperature output values calculated for each iteration

plot(x,y,'*',x,yfit,'-'); % Boltzmann Plot with linear fit.
title('Al I Br', 'fontsize',12)
xlabel('Energy of the Upper Level (eV)', 'fontsize',12)
ylabel('ln(\lambda*I/gA)', 'fontsize',12)
end
REFERENCES


"Using the van der Waals broadening of spectral atomic lines to measure the gas temperature of an argon-helium microwave plasma at atmospheric pressure " *Spectrochimica Acta Part B: Atomic Spectroscopy*, vol. 64, pp. 167-172, J. Muñoz, M.S. Dimitrijević, C. Yubero, M.D. Calzada.


