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Steady State Simulation of Pyrolysis Gases in an Inductively Coupled Plasma Facility

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Steady State Simulation of Pyrolysis Gases in an Inductively Coupled Plasma Facility

A Thesis Presented

by

Nicholas C. Martin

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The Faculty of the Graduate College

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Abstract

An important step in the more efficient use of PICA (Phenolic Impregnated Carbon Ablator) as a Thermal Protection System (TPS) material for spacecraft is the understanding of its pyrolysis mechanics. The gases released during pyrolysis and their subsequent interaction with the reactive plasma environment is not yet well understood. The surface recession of PICA as it ablates during testing only makes the study and characterization of the chemical reactions more difficult. To this end, a probe has been designed for this study to simulate, in steady state, the pyrolysis gases within the UVM 30kW Inductively Coupled Plasma (ICP) Torch Facility. This probe, which is an extension of previous work done at UVM, has been used to inject Carbon Dioxide, Hydrogen, and a mixture of the two into pure Argon and dilute Nitrogen, Oxygen, and air plasmas. During testing, spatially resolved, pointwise, line of sight emission measurements were taken in the boundary layer region. These results were then compared to temporally resolved PICA emission data taken in a previous study. After the correct temporal PICA scan was found the data sets closely matched. This indicates that the gas-injection probe is a viable method to simulate pyrolysis in a steady state environment. The key pyrolysis species of CN, NH, OH, Hydrogen Alpha ($H_\alpha$), and Hydrogen Beta ($H_\beta$) were spatially traced along the stagnation line for the pure Hydrogen and mixture injection cases. These measurements show evidence of spatial relationships between NH and $H_\alpha$ as well as between OH and $H_\beta$. They also show that all of the molecules tend to follow the same general trend spatially. The work done for this study has both reintegrated gas-injection capability into the UVM facility as well as laid the groundwork for future gas-injection testing within the facility. Spatial emission analysis techniques currently being developed at UVM will provide a more resolved picture of the interactions occurring in the boundary layer once completed.
Acknowledgements

I would like to sincerely thank everyone who helped me along the way up to this point. A special thank you goes to Dr. Doug Fletcher and Dr. Jason Meyers for all of their guidance and support over the last two years. You have both helped me grow as both a student and a researcher.

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Chapter 1

Introduction

1.1 Objective

Other than launch, one of the most difficult portions of space and planetary exploration and research is the successful entry or re-entry of the spacecraft into a planetary atmosphere. These spacecraft must be able to survive extremely harsh conditions as they enter atmospheres at blistering speeds. The fastest Earth entry velocity for a man made spacecraft was recorded during the Stardust mission. The Stardust probe entered the atmosphere at 12.9 km/s. For reference, the Apollo lunar missions reentered at 11.0 km/s and the reentry speed from low earth orbit is about 7.8 km/s. This high entry velocity also caused the spacecraft to experience the highest heating rates for any Earth returning vehicle [6]. Dealing with these intense thermal loads requires advanced thermal protection system (TPS) materials. These materials, despite their high performance, come with significant mass penalties for the spacecraft. For example, the Apollo heatshield accounted for nearly 13.7% of the capsule’s total mass, and the Galileo spacecraft’s more aggressive Jupiter entry conditions meant
that the TPS material accounted for nearly 50% of the mass of the vehicle [2,12].

As mass is a major factor and constraint in any space flight mission, low mass TPS materials have become a major research topic at NASA and other spaceflight institutes. In 2012, NASA’s Entry, Descent, and Landing Roadmap included the need for a TPS material that was low mass as well as qualified for a wide range of reentry conditions [1]. An important facet of the development of new TPS materials is ground based testing in order to obtain a better understanding of how the material will react in high heating conditions before committing to expensive flight tests. One method of ground based testing is to use an Inductively Coupled Plasma (ICP) torch. The focus of this study is the steady state simulation of the pyrolysis mechanism of the TPS material PICA (Phenolic Impregnated Carbon Ablator) in an ICP torch facility.

For this study, a probe holder was designed to simulate pyrolysis by injecting gas into the plasma flow. The holder simulates, in steady state, the latter stages of PICA pyrolysis where the gases exiting PICA have settled to a relatively flow stable rate. The reason for studying this stage of pyrolysis is that it is present during a majority of the entry trajectory, whereas the initial burst of gas lasts only for a few seconds. Spectroscopic measurement techniques were implemented in order to identify and characterize the atomic and molecular species present in the boundary layer surrounding the probe face. The data was then compared to data collected from PICA samples under the same conditions in order to quantify how accurately the steady state simulation replicates PICA pyrolysis. The results can be used along with those of other studies to help improve and validate numerical atmospheric entry models as well as provide more information to help engineers properly size PICA heat shields based on entry conditions.
1.2 Background

As the scope and objectives of future space missions increase in complexity, larger spacecraft will be necessary in order to achieve mission goals. This means that larger bodies will need to be protected during the harsh conditions encountered during planetary entry. These harsh conditions are caused by the hypersonic speeds that are common during atmospheric entry. At these speeds, a bow shock is formed at the leading edge of the vehicle. This shock is formed in order to slow the gas to subsonic speeds so that it can flow around the vehicle. Slowing hypersonic flow to subsonic speeds through a shock causes a massive temperature increase across the shock, known as shock-heating. The increase in temperature is caused by the kinetic energy of the flow being converted into thermal energy. These high temperatures in turn cause the gas to dissociate and ionize, producing a plasma. The plasma conditions encountered by the spacecraft cause severe aero-thermodynamic heating [20]. This heat must be carefully and completely dealt with in order to prevent destruction of the vehicle or damage to the delicate instrumentation inside. Thermal protection systems are therefore implemented to protect the spacecraft. Currently, there are two categories of TPS materials that are used to protect spacecraft during atmospheric entry: non-ablative TPS and ablative TPS. Figure 1.1 shows these two materials as well as their different cooling methods.

Non-ablative thermal protection systems are primarily used in conditions with lower heat fluxes such as Earth reentry. They rely on the re-radiation of thermal energy that the material absorbs during entry. These materials are generally characterized by a high emissivity and have low catalytic surfaces. They are also very poor
heat conductors [12]. An advantage gained with these materials is reusability. The non-ablative thermal protection tiles of the space shuttle were made out of silica and could be reused after every mission.

Ablative TPS materials are not reusable but can survive much harsher conditions than reusable materials. They have been used by NASA for over 40 years and have been the material of choice for all NASA planetary entry probes. Ablative materials have two primary methods of coping with the intense heat of atmospheric entry: phase change and mass loss. The material is generally made up of reinforced composite that uses an organic resin as the binder. This resin is what produces the pyrolysis gases as the material is heated. Ablative thermal protection system materials have been used for the Gemini, Apollo, Stardust, Mars Science Laboratory, and Orion missions [12].

Phenolic Impregnated Carbon Ablator (PICA) is a type of ablative TPS material. It was developed in the 1990's at NASA Ames Research Center. PICA was the chosen heatshield material for the Stardust and Mars Science Laboratory missions. It is also
used by SpaceX for their Dragon capsule [16].

The base material of PICA is a low density, rigid, carbon fiber insulation called FiberForm®, which is impregnated with a commercial phenolic resin. Only a brief description of the cooling mechanisms of PICA will be given here. Further explanations can be found in references [12, 25, 27]. The first method of cooling for PICA is ablation. This method involves the material itself melting and/or vaporizing and being removed from the heatshield. This process carries away heat and exposes new material so the process can begin again. The second method is pyrolysis. As the resin is heated by the high temperature environment surrounding the spacecraft it begins to pyrolyze, producing the pyrolysis gases. The gas absorbs some of the heat as it travels through the material and is ejected into the boundary layer surrounding the vehicle. This creates a buffer layer between the plasma and the spacecraft, leading to a reduction in convective heating.

The introduction of gas into the superheated and reactive plasma environment surrounding a vehicle entering an atmosphere adds much more complexity to the atmospheric entry problem. There are many more mechanisms and reactions that need to be fully understood before an accurate model can be produced to properly predict heating rates and material recession. The overarching goal behind the work presented in this thesis is to help validate and improve these models. Once models are proven accurate, future heatshields can be sized more appropriately and mass can be saved to use elsewhere. This could lead to more instruments being used on missions or smaller and cheaper rockets being used to launch the spacecraft.
1.3 Previous and Existing Work

Several numerical codes are currently used to model and predict the behavior of PICA and other ablative TPS materials during flight conditions. These codes, when used together, have the ability to model the flight conditions that a vehicle would experience during atmospheric entry as well as how the thermal protection system would respond to those conditions. One of these codes is the Data-Parallel-Line-Relaxation (DPLR) code developed at NASA Ames. This code is a full three-dimensional computational fluid dynamics (CFD) Navier-Stokes solver that is MPI-based and parallel. It contains general models for finite-rate reaction kinetics, thermal and chemical non-equilibrium, accurate high-temperature transport coefficients, and ionized flow physics. A large section of the code is also dedicated to generalized realistic surface boundary conditions and 'hooks' that enable efficient coupling with TPS material response codes [33].

A code used to model TPS materials, specifically those that ablate and pyrolyze, is the Fully Implicit Ablation and Thermal response program (FIAT) that was also developed at NASA Ames. This code simulates one-dimensional transient thermal energy transport in a multilayer stack of TPS materials. It has the ability to model surface ablation as well as in-depth decomposition of the material [17].

While both codes help to give engineers more direction in terms of designing the heatshield for spacecraft, their complete accuracy has not yet been fully validated. There is still plenty of room for improvement in terms of simulation accuracy. This is especially true when it comes to the boundary layer. Many issues can be attributed to the level of fluid material coupling that is present in the codes. A higher-level
model could be produced if the surface qualities and the ablation/pyrolysis species
from the material response code were used as the surface boundary condition for the
fluid flow simulation code [10]. The non-equilibrium state of these boundary layers
is much more difficult to model and the incomplete understanding of the pyrolysis
process only adds to the difficulty [25].

Several testing campaigns and measurement techniques have been run and devel-
oped in order to try and improve computational codes. Tests have been conducted
at NASA Ames’ Aerodynamic Heating Facility (AHF) and Interaction Heating Fa-
cility (IHF) in order to better understand the pyrolysis and ablation characteristics
of PICA. Testing has also been done to study the effective heat of ablation, in-
depth temperature response, and thermal conductivity for PICA and its substrate
FiberForm® [5,7,25,26]. All of this information is vital to helping numerical simula-
tions produce more accurate results.

In addition to test campaigns, spectroscopic methods have also been developed
and implemented to observe and characterize pyrolysis gases as well as the chemical
reactions they cause in the boundary layer [22,32]. These spectroscopic methods
have been implemented at UVM’s ICP facility in previous studies. The initial goal
of these studies was to attempt to characterize the pyrolysis gases. A brief study was
also conducted on simulating the pyrolysis gases using a gas injection probe [25,27].

Emission results from the first study [27] are shown in Figures 1.2, 1.3 and 1.4.
(a) PICA and FiberForm® in Argon at 6s.  

(b) PICA and FiberForm® in Argon at 60s.

**Figure 1.2:** Previous PICA and FiberForm® emission results in Argon [27].

(a) PICA and FiberForm® in Argon/air at 6s.  

(b) PICA and FiberForm® in Argon/air at 60s.

**Figure 1.3:** Previous PICA and FiberForm® emission results in Argon/air [27].
These initial tests compared the emission results from PICA and FiberForm® in the same plasma conditions in order to determine the pyrolysis gases. When comparing the 6 second and 60 second plots for the Argon test case (Figure 1.2) CN Violet and C$_2$ Swan are the main features of the PICA emission but are not present in the FiberForm®. CN Red is also visible in the PICA spectra at both times. Figure 1.3 shows the two materials tested in a dilute air condition. For this condition OH is very prominent at both times for PICA but CN Violet and C$_2$ Swan are absent. For FiberForm® CN Violet is present at both times. The absence of CN Violet and C$_2$ Swan was an unexpected result but two possible explanations are that the atomic Oxygen is reacting with the Carbon in the material to produce CO or CO$_2$, or that the recession of the sample in the holder caused the emission to radiate outside the line of sight of the optics. The final condition the two materials were tested in was a Nitrogen condition. Figure 1.4 shows that the emission from the two materials is nearly identical. This could be caused by the strength of the CN lines, due to the amount of Carbon and Nitrogen present during the test [25].
A second study was then initiated based on these results [25]. This study focused primarily on further characterizing key pyrolysis gasses of PICA in the observed spectrum on a temporal basis. The key pyrolysis species spectra focused on were CN Violet, NH, OH, and Hydrogen alpha ($H_\alpha$). Select results for each of the four test conditions (pure Argon; and dilute air, Oxygen, and Nitrogen) can be seen in Figures 1.5 - 1.8. A dilute condition is one in which the main test gas is buffered by the addition of Argon into the flow.

The bottom chart in each figure shows the evolution of the traced key species over time and the top chart is a total emission snapshot at a certain point in time. From these charts the general trend of the intensity of the pyrolysis gases can be seen. In all four conditions the species intensity rises sharply upwards when the sample is inserted into the plasma. The intensity then declines until it reaches a relatively steady state level. This level is then held nearly constant throughout the test. The constant level of pyrolysis gases shown in the figures below is the level which this study aims to simulate.

![Figure 1.5: PICA in pure Argon for 480 seconds [25].](image-url)
Figure 1.6: PICA in dilute Nitrogen for 120 seconds [25].

Figure 1.7: PICA in dilute Oxygen for 120 seconds [25].
One item of note are that the pure Argon and dilute Nitrogen tests (Figures 1.5 and 1.6 respectively) produce roughly the same spectra although in different intensities. Additionally, for the dilute Oxygen condition (Figure 1.7) the presence of OH dominates the spectra and the CN levels are much lower than in the other conditions. A Sodium line also appears strongly in this data. Finally for the dilute air case (Figure 1.8) three of the key species are present. This shows that the air condition is indeed a mixture of the Nitrogen and Oxygen conditions. These results provide an emission baseline for PICA that can be used as a comparison for future tests as well as a guide for computer and gas injection simulations.

Studies of injecting gas into a plasma flow have also been undertaken. Two of these studies can be found in references [29,34]. The focus of the first study [34] was how gas injection affected the stagnation point heat transfer to the probe face. It was found that a higher gas injection rate led to lower surface heat fluxes under both sub and supersonic plasma conditions. The second study [29] was able to verify, to some
degree, the results of the first study mentioned. In this study the three injection flow regime assumption of film, cone, and separated cone (Figure 1.9) were verified. It was found that the film flow regime provided the best reduction in heat flux to the probe; and that moving further into the cone and separated cone regimes actually reduced the effect of the gas injection as a cooling mechanism.

Figure 1.9: *Left:* Film regime. *Center:* Cone regime. *Right:* Separated cone regime. [29].

The three injectant flow regimes are described as follows [27,29]:

- **Film regime:** The injectant gas flows out of the sample with a low velocity and low momentum. The plasma flow causes the gas to turn and envelop the sample, creating a buffer layer of cool gas along the surface. This film helps to block and transport away the heat from the plasma leading to a lower heat flux.

- **Cone regime:** The injectant gas has a greater velocity and more momentum. It therefore penetrates into the plasma before being turned, creating a cone shape. The gas is now less effective at blocking the heat because it must cool a larger volume. A recirculation region can also form behind the cone and lead to a higher heat flux.

- **Separated cone regime:** The injectant gas leaves the sample with so much velocity and momentum that it penetrates far upstream into the plasma. The cone has now become detached from the sample surface. Heat from the plasma
can now come in direct contact with the surface; cooling via injectant gas in this regime is negligible.

Uhl designed an injection probe and graphite plug for his work [27]. A few preliminary tests were run and some emission data was collected, but there are questions about how the data was collected and its validity [28]. His gas injection holder was later destroyed in order to make modifications to his probe. The probe Uhl designed is used as the basis for the design of the final holder for this study. The main section of the probe is also used in this study to cool the new holder and deliver gas to the graphite plug. This study uses Uhl’s work as a starting point to reintroduce gas injection capabilities to the UVM ICP torch facility.

The information gathered by the four studies mentioned has been used to help guide the work done for the study presented in this thesis. The temporal PICA emission data gathered in Tillson’s work [25] as well as the methodology developed by both Tillson and Uhl is used in this study. Tillson’s data is used as a baseline to determine the accuracy and validity of the gas injection results. The methodology is used to gather comparable emission data from each test. The flow regime information was used to help choose injection flow rates for the new injection probe to make sure that the injection stayed within the film regime in order to provide the best cooling.

Information found by Bessire [18] was used to determine that the early injection gases should be Carbon Dioxide, Hydrogen, and then a mixture thereof, as these were the most common gases found pyrolysis mixture from PICA. The first gas injected was CO$_2$ in order to test the injection system as well as the survivability of the probe. Next H$_2$ was injected followed by a mixture of the two was injected. The results of these tests are presented in Chapters 6 and 7.
Chapter 2

ICP Facility and Experimental Arrangement

2.1 UVM 30kW Inductively Coupled Plasma Torch

The 30 kW Inductively Coupled Plasma (ICP) Torch facility at UVM is used to produce high enthalpy plasma flows in order to replicate the environment a spacecraft experiences during planetary entry [21]. The facility is designed to replicate stagnation point heat transfer at these flight conditions. The current configuration produces a stable, subsonic plasma flow that simulates post shock non-equilibrium boundary conditions. Previous work has shown that the facility can replicate the flight trajectory boundary layer by matching post shock total pressure, total enthalpy, and the velocity gradient of the hypersonic flight condition [9]. Figure 2.1 shows a comparison between in-flight and ICP facility conditions.
The use of ICP-type facilities for atmospheric entry and hypersonic testing applications is not new, but arc-heated facilities are more commonly used for these investigations in the United States. However, in arc-heaters, the direct arc attachment to electrodes produces molten copper as a stream contaminant. Copper atom lines are strongly evident in emission measurements and raise questions about flow chemistry. In an ICP torch, heating is done through electron excitation via magnetic field coupling, thus providing a contaminant-free flow. Extensive information on induction heating can be found in reference [13].

The UVM ICP torch facility is capable of providing chemically pure air, $N_2$, $O_2$, $CO_2$, $Ar$ plasmas, including mixtures thereof. The plasma jet is currently defined by the 36 mm inner diameter of the quartz tube. The normal operating pressure of the facility is 160 Torr. During normal facility operating conditions the plasma ball in the induction zone has a temperature on the order of 10,000 Kelvin. The plasma flows vertically upward and exits the quartz tube as a free jet that cools as it evolves.
towards a local thermodynamic equilibrium (LTE) state. By the time the plasma reaches the test sample it is between 5,000 and 6,000 Kelvin. A schematic of the UVM facility can be seen in Figure 2.2 and operating parameters are given in Table 2.1.

Figure 2.2: Schematic of the UVM 30 kW ICP torch facility. The power supply, gas injection system, test chamber, and water cooling system can be seen [21].

<table>
<thead>
<tr>
<th>Test Gas</th>
<th>Ar, N₂, O₂, Air, CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Power</td>
<td>30 [kW]</td>
</tr>
<tr>
<td>Normal Operating Pressure</td>
<td>100 to 200 [torr] (13 to 26 [kPa])</td>
</tr>
<tr>
<td>Stagnation Heat Flux</td>
<td>10 to 150 [W/cm²]</td>
</tr>
<tr>
<td>Mach Range</td>
<td>0.3 to 1.4 [-]</td>
</tr>
<tr>
<td>Plasma Jet Diameter</td>
<td>36 [mm]</td>
</tr>
<tr>
<td>Operating Frequency</td>
<td>2 to 3 [MHz]</td>
</tr>
</tbody>
</table>

Table 2.1: UVM 30 kW ICP torch parameters.

Figure 2.2 shows several of the main components of the UVM 30 kW ICP Torch facility. These components are the 30 kW radio frequency (RF) power supply, gas injection block, quartz tube, test chamber, cooling system, and vacuum pump. All
of these systems must work simultaneously for the facility to produce a safe and sustainable plasma jet. Room temperature test gas is first routed through the injector block where it is directed through an annulus into the 36 mm inner diameter quartz tube. The annulus produces a recirculating flow within the quartz tube which helps promote coupling as well as cool the tube and prevent it from melting. A water-cooled copper induction coil surrounds the quartz tube and is used to conduct the alternating RF current from the power supply. This setup can be seen in Figure 2.3. The alternating current in the coil produces an alternating magnetic field that couples with the test gas, heating and ionizing it. This produces the plasma ball inside the quartz tube. The plasma then flows up the quartz tube and out into the pressure controlled stainless steel test chamber. Finally the gas flows through a heat exchanger before passing through the main vacuum pump and out of the lab. Further information concerning the design and operation of the facility can be found in references [14,20,25,27]
2.2 Injection Probe Design

The probe that is used to provide the cooling and the gas flow to the gas injection sample holder was initially designed by Uhl and is know as the 'insertion' probe [27]. This probe uses the facility’s chilled water loop as its cooling source. The original sample holder connection points for the probe were very complicated. To remedy this, the probe has undergone heavy modifications since it was originally built. Unfortunately, these modifications also eliminated the gas injection capabilities. The existing gas injection plumbing was turned into a cooling water inlet and all connection points inside the probe were removed. Because of this, a new gas injection holder had to be designed and new gas line plumbing had to be installed. The new
holder will be discussed in the next section.

The probe is held to the test chamber by a hinged door. This door enables the probe to be moved vertically as well horizontally within the chamber, even under full vacuum conditions. The horizontal motion of the probe is of great importance as it allows the facility to reach a steady state operating condition before the sample is inserted into the plasma flow. It also allows the flow of the injectant gas to stabilize before coming in contact with the plasma. All contact points between the door and the probe are electrically insulated with sheets of teflon. This is to prevent any electrical conduction between the plasma and probe/sample.

Figure 2.4 shows the probe installed in the chamber as well as the translating door.

![Figure 2.4: Outer portion of gas injection probe and the translating door. [27].](image-url)
The injection gas flow is controlled by a MKS M100B series mass flow controller. The gas flows through the controller at volume flow rates that are programmed into the LabView program that controls the facility. It then flows through a nylon tube into a softer silicone tube that is inside of the injection probe itself. This tube is attached to the sample holder via a barbed fitting. The injectant gas flows through the silicon tube into a settling chamber inside the sample holder. From there, it travels through the graphite plug and into the plasma stream.

2.2.1 Gas Injection Holder

A new gas injection holder was designed for this study. At the onset of the design process, several design goals were laid out for the holder. These goals were: inclusion of gas injection and pressure tap ports, easy access for instrumentation, ease of use, ability to use the graphite plug, and ability to survive long duration tests in the facility. Unfortunately, these goals proved to be to difficult to achieve all at once. A probe and holder were designed and built that met most of these goals but, due to its size, was not cooled properly and could not survive more than a few minutes in the facility. Figure 2.5 shows an image of the original holder after overheating caused failure in the torch.
After the failure of the original holder and a few attempts to make small changes to the design, it was scrapped and the decision to design a holder that would work with the original gas injection probe mentioned above was made. This probe could provide cooling water access to the back face of the holder and it was determined that this would greatly increase the survivability of the holder.

The first holder designed to be used with this probe had two pieces that screwed together. This was done in order to facilitate access to the graphite plug while still separating the water from the settling chamber. This holder held up much better than the initial holder that was designed but still suffered from inadequate cooling at harsher torch conditions. It is believed that the small air gap between the two pieces of the holder caused enough of a thermal barrier that the bottom piece overheated at higher heat flux conditions. Figure 2.6 shows an image of this two-piece after some early testing.
After the failure of the two-piece holder it was decided that the next design would be machined out of a single piece of copper stock. In order to seal the settling chamber from the cooling water, a copper disc was soldered into place. This holder, which is also the final holder designed and the holder used to acquire all the data presented in this thesis, consists of four parts. These parts are: the holder, a copper spacer, a copper disk, and a brass barbed fitting.

The holder was designed to have the same outer geometry as the PICA pucks that were tested by Tillson [25]. The outer diameter is 25 mm and the height is 27 mm. The holder is designed to work with the collar attachment system currently in place on the insertion probe. Inside the holder is a channel that supports the graphite plug and also serves a setting chamber for the injectant gas before it enters the plasma flow. This channel is slightly wider than the outer diameter of the plug in order to insulate the plug from the colder copper holder. This was done in an attempt to increase the surface temperature of the plug and more closely replicate the material temperatures.
of PICA. Figure E.1 shows a CAD drawing of the holder - further drawings can be found in Appendix E.

![Figure E.1: CAD drawing of the holder.](image)

**Figure 2.7:** CAD drawing of final gas injection holder (dimensions in mm).

The remaining components of the holder mentioned above are then stacked in place in the inner channel of the holder. First the graphite plug is inserted in an orientation so that its tapered end mates with the tapered end of the holder. Then the 5 mm copper spacer is inserted. This spacer provides the volume for the settling chamber while also holding the plug in place. Finally the brass barbed fitting is screwed into the copper disk and the assembly is inserted on top of the spacer. The disc and fitting are then soldered into place. Soldering was chosen as the attachment method because trials using Permatex® RTV red developed leaks as soon as the copper began to heat up in the torch. The solder provides a reliable seal while also firmly holding the entire assembly in place. It also has the smallest impact on the overall cooling of the holder. Care was taken when soldering the components together so that large amounts of flux did not flow down into the graphite plug. After soldering the holder was exposed to the plasma with gas flowing through it for about 5 minutes.
to try and remove any flux that had flowed down into the settling chamber and the graphite plug.

This final holder has been tested extensively in the facility and been proven to survive in even the harshest conditions. The holder was exposed, with gas injection, to a full Nitrogen condition for over 5 minutes with no signs of wear on the holder or glow upon shutdown. No test has been run to date where the holder showed signs of wear or failure after the test. Figure B.2a shows the holder in place on the insertion probe inside of the test chamber.

![Figure 2.8: Holder installed inside the test chamber.](image)

### 2.2.2 Graphite Plug

The graphite plug is the most important component of the injection holder and probe. It is the final component that the injectant gas flows through before entering the plasma flow. The plug was designed by Uhl in order to approximately match the
permeability of PICA [27]. It is made out of poco graphite in order to reduce the amount impurities introduced into the experiment. The plug is 13 mm in diameter and 8 mm tall. It tapers down to 11 mm over the last 3 mm, which is the taper that the holder was designed to match. In order to facilitate the gas flow, the plug has 69 0.3 mm holes drilled into it. These holes are spaced at 1 mm apart. Figure 2.9 shows a CAD drawing of the plug as well as an actual image.

![CAD drawing of face of graphite plug.](image1.png)  
(b) Image of virgin graphite plug.

**Figure 2.9:** Graphite plug [27].

Care was taken when using the plug, as the graphite will ablate away with time in the facility. This process can be slowed using buffered conditions, but any condition that introduces oxygen into the flow will cause the plug to ablate.

Figure 2.10 shows a section view CAD model of the complete holder assembly and a picture of the finished holder post testing. All components except for the spacer are present in the CAD model.
2.3 Emission Spectroscopy

Emission spectroscopy is the relatively simple, non-intrusive, diagnostics technique that was used during this study. It was used to observe, identify, and track the key pyrolysis gas species during gas injection tests. Emission spectroscopy works by collecting the light that is emitted by atomic and molecular transitions. This light is then separated into its wavelengths and the data is converted into absolute intensity.

Atomic and molecular transitions occur when an atom or molecule is in one of its thermally excited upper states and returns to a lower, sometimes ground, energy state [13]. This process releases a photon of a certain wavelength that can be identified by a spectrometer. These transitions can take place between levels associated with either electrical, rotational, or vibrational states. For atoms, only electronic transitions are possible, but molecules can exhibit all three transitions.
In previous work, key pyrolysis species were identified [25]. These species were: CN Violet, NH, OH, H\textsubscript{\alpha}, and H\textsubscript{\beta}. These same species were also investigated in this work. Table 2.2 lists the wavelength, transitions, oscillator strengths, and Einstein A coefficients for these species.

**Table 2.2:** Pyrolysis gas species of interest with spectroscopic constants [25].

<table>
<thead>
<tr>
<th>Specie</th>
<th>Transition</th>
<th>( \lambda ) (nm)</th>
<th>( f )</th>
<th>( A_{ul} ) (sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN Violet ( \Delta v=0 )</td>
<td>( B^2\Sigma^+ \rightarrow X^2\Sigma^+ )</td>
<td>365 - 390</td>
<td>( 3.36 \times 10^2 )</td>
<td>( 1.49 \times 10^7 )</td>
</tr>
<tr>
<td>CN Violet ( \Delta v=-1 )</td>
<td>( B^2\Sigma^+ \rightarrow X^2\Sigma^+ )</td>
<td>400 - 425</td>
<td>( 2.95 \times 10^3 )</td>
<td>( 1.54 \times 10^6 )</td>
</tr>
<tr>
<td>CN Violet ( \Delta v=+1 )</td>
<td>( B^2\Sigma^+ \rightarrow X^2\Sigma^+ )</td>
<td>330 - 360</td>
<td>( 6.57 \times 10^3 )</td>
<td>( 2.53 \times 10^6 )</td>
</tr>
<tr>
<td>OH</td>
<td>( A^2\Sigma^+ \rightarrow X^2\Pi )</td>
<td>305 - 330</td>
<td>( 8.00 \times 10^4 )</td>
<td>( 1.21 \times 10^5 )</td>
</tr>
<tr>
<td>NH</td>
<td>( A^3\Pi \rightarrow X^3\Pi^- )</td>
<td>325 - 350</td>
<td>( 8.00 \times 10^3 )</td>
<td>N/A</td>
</tr>
<tr>
<td>H\textsubscript{\alpha}</td>
<td>( 3p^2P^0 \rightarrow 2s^2S )</td>
<td>656</td>
<td>( 6.41 \times 10^1 )</td>
<td>( 4.41 \times 10^7 )</td>
</tr>
<tr>
<td>H\textsubscript{\beta}</td>
<td>( 4d^2D \rightarrow 2p^2P^0 )</td>
<td>486</td>
<td>( 1.19 \times 10^1 )</td>
<td>( 8.42 \times 10^6 )</td>
</tr>
</tbody>
</table>

### 2.3.1 OceanOptics Spectrometer

An OceanOptics HR4000CG-UV-NIR USB powered line-of-sight emission spectrometer was used to collect the data for this study. The collection range of this spectrometer is 200 - 1100 nanometers. The large wavelength range is ideally suited to collect emission spectra from the key species that are the focus of this study. Table 2.3 shows the specifications for this spectrometer. A quartz tungsten halogen lamp was used to calibrate the spectrometer and convert the relative intensity values into absolute values in \( W cm^{-2} \mu m^{-1} sr^{-1} \). The calibration procedure for the spectrometer...
can be found in Chapter 3.

<table>
<thead>
<tr>
<th>Table 2.3: Spectrometer specifications [25].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HR4000CG-UV-NIR</strong></td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
</tr>
<tr>
<td><strong>Slit Width</strong></td>
</tr>
<tr>
<td><strong>Grating</strong></td>
</tr>
<tr>
<td><strong>FWHM</strong></td>
</tr>
<tr>
<td><strong>Resolution</strong></td>
</tr>
</tbody>
</table>

The emission collection setup can be found in Figure 2.11a. The light (dashed line) is collected through a z-fold arrangement by bouncing it off a 50mm diameter 250mm focal length concave mirror, then off a 25mm flat mirror and through a 4.76mm aperture. Finally the light travels through a 400µm diameter, 2m in length optical fiber to the spectrometer. The z-fold geometry is used in order to save space from the mirror to the fiber entrance while maintaining a one to one imaging length. The collection can be translated vertically from the face of the sample down to any desired distance below the face. The standard location for emission collection is 2 mm below the sample surface. During this study the location ranged from the surface (0 mm) to 10 mm below the surface. Example collection locations are shown in Figure 2.11b as red dots.
Figure 2.11: *Left:* A top view of the emission spectrometer setup showing the location of the test chamber (1), 25-mm diameter flat mirror (2), aperture (3), lens tube (4), 50-mm diameter, 250-mm focal length concave mirror (5) and fiber optic cable, spectrometer assembly (6). *Right:* Emission locations (red dots) shown under cut-away view of holder.

The initial collection location is determined prior to the test using a Helium-Neon continuous wave laser centered at 633 nm. The laser light travels through the optical setup in reverse and the laser dot is centered at the desired collection location. The location can then be accurately translated vertically during a test using the ThorLabs translation stage.
CHAPTER 3

SPECTROMETER CALIBRATION

3.1 PREVIOUS WORK

There have been two previous attempts to calibrate the OceanOptics spectrometers by members of the lab. These attempts have all had a few shortcomings. Both of the attempts and their shortcomings will be explored in this section.

The first attempt involved collecting the emission from the Newport 63355 lamp and initially dividing it by the integration time over which it was gathered. This converted the emission measurement file of \textit{counts} into \textit{counts s}^{-1}. Next the spectral irradiance data for the lamp provided by Newport (units $mW \, m^{-2} \, nm^{-1}$) was divided by the \textit{counts s}^{-1} file. This produced the final calibration file of units $mW \, s \, m^{-2} \, nm^{-1} \, \textit{counts}^{-1}$. In order to use this file the ICP acquired emission data was divided by its integration time and then multiplied by the calibration file. This produced a final file with units of $mW \, m^{-2} \, nm^{-1}$. In order to convert the emission file from spectral irradiance to spectral radiance, a division by the UVM solid angle was undertaken. This solid angle was calculated to be $8.727 \times 10^{-4} \, sr$ for the
3/16 aperture size. This yielded a final file with the units of $mW \ m^{-2} \ nm^{-1} \ sr^{-1}$.

Although at first glance, many aspects of the first technique seem to be correct. The main problems with this technique are that the solid angle of the UVM collection system has recently been calculated to be $6.97 \times 10^{-4}$ and that the use of Irradiance data in this form is not necessarily correct. It is believed that the conversion from Irradiance to Radiance data is a bit more complex; this will be explained in the next section.

The second attempt at calibration was largely the same as the first. The main difference is that the integration time was not used to create the calibration file. A second difference was that the unit conversion was done in order to convert the Newport provided data of $mW \ m^{-2} \ nm^{-1}$ into $W \ cm^{-2} \ \mu m^{-1}$. This was done by dividing the Newport data by a factor of $10^4$. In order to convert to spectral radiance and its per $sr$ unit, the final result was again divided by the UVM solid angle. The solid angle used by this second approach was $1.576 \times 10^{-4}$. This is different from the first but still not correct according to the most recent calculations. Both the unit conversion and the solid angle division took place at once in these calculations, resulting in a division by $1.576$ as the two powers of $10^4$ cancel out.

This second method again suffers from the same shortcomings as the first, namely the incorrect solid angle and irradiance to radiance conversion. In the following section a new calibration method is described which aims to correct both of these shortcomings.
3.2 New Method

3.2.1 Irradiance to Radiance

First the conversion of irradiance to radiance will be addressed. Radiance is formally defined as the radiant flux emitted by a surface, per unit projected area, per unit solid angle. Spectral radiance is the radiance of a surface per unit wavelength. The conventional units for spectral radiance are $W \ cm^{-2} \ \mu m^{-1} \ sr^{-1}$. Irradiance is defined as the radiant flux received by a surface per unit area, while spectral irradiance is the irradiance received per unit wavelength. A common unit for spectral irradiance is $W \ m^{-2} \ nm^{-1}$. Care was taken when converting between the two as not only must the solid angle be taken into account but the size of the emitter as well. Equation 3.1 describes how the radiance ($R$) is related to the irradiance ($I$) by the emitter area ($dA_e$), the receiver area ($dA_r$), and the solid angle ($\Theta$)(equation 12.10 in Fundamentals of Heat and Mass Transfer [4]).

$$R = \frac{IdA_r}{dA_ecos(\theta)\Theta} \quad (3.1)$$

In order to use this equation it must be assumed that the lamp is a diffuse emitter. As the coil is fairly tightly wound, this assumption was considered valid for the purpose of this study. The values for $dA_e$ and $dA_r$ are 0.21 cm$^2$ and 1 cm$^2$, respectively, according to Newport. The solid angle ($\Theta$) was calculated using Equation 3.2 below, where $A$ is the area of the receiver and $r$ is the distance from the receiver to the lamp. For the Newport 63355 lamp the value of $r$ is 50 cm.
\[ \Theta = \frac{A}{R^2} \]  

Using the above equation and its values for the Newport lamp the solid angle was calculated to be \(4 \times 10^{-4}\) steradians. Both the emitter and receiver may be approximated as differential areas due to the solid angle being much smaller than one. Finally, in order to convert the Newport provided units of \(mW \ m^{-2} \ nm^{-1}\) into units of \(W \ cm^{-2} \ \mu m^{-1}\), the irradiance values were divided by \(10^4\). Combining this factor of \(10^4\) with Equations 3.1 and 3.2, as well as the other variables mentioned above, leads to the following equation for the spectral radiance of the Newport 63355 lamp.

\[ R = \frac{I \times 1}{0.21 \times 4} \]  

### 3.2.2 Calibration Procedure

The calibration of the OceanOptics spectrometer requires the following components: the spectrometer and its optical setup (250 mm focal length concave mirror z-fold), the Newport model 63355 calibration lamp with its power supply, the lab computer with SpectraSuite, and the ICP facility window through which the emission is normally gathered. The calibration setup is modeled after the emission collection setup of the facility with the lamp taking the place of the plasma. When setting up the optical system care was taken to place the lamp 50 cm from the concave mirror in order to ensure the accuracy of the calibration. The 250 mm focal length mirror will focus correctly at this distance. Using the He-Ne laser focus the setup on the filament of the lamp. The lamp was turned on and set to the power to the levels specified in the
lamp manual. It was then allowed to warm up for a period of 30 minutes. An image of the setup can be seen in Figure 3.1.

![Image of the setup](image.png)

**Figure 3.1:** Emission spectroscopy calibration setup [27].

Using SpectraSuite, the integration time was adjusted until the light input into the sensor was just below the saturation limit of 16,000 counts. This ensured the use of the full capabilities of the spectrometer during calibration. The integration time as well as the aperture setting were recorded. For this work, an integration time of 0.01 seconds was used during the calibration of the HR4000CG-UV-NIR spectrometer. Finally emission measurements of the lamp were taken. An example of the spectrometer output for a 0.01 second integration time can be seen in Figure 3.2.
The output from the spectrometer is given in units of counts. This must be converted to units of \([W \, cm^{-2} \, \mu m^{-1} \, sr^{-1}]\) to give absolute intensity (spectral radiance). The conversion is done using the known output from the tungsten lamp given by Newport. Figure 3.3 shows this data at the given distance of 50 cm in units of \(W \, cm^{-2} \, \mu m^{-1} \, sr^{-1}\). The original Newport data provides the lamp emission in units of spectral irradiance \(mW \, m^{-2} \, nm^{-1}\). This has been converted to spectral radiance and the proper units using the method described in the previous section.
Using both of the above data sets the calibration file was created by dividing the
Newport lamp data by the spectrometer data acquired during the calibration. This
produced a calibration file with units of $W \, cm^{-2} \, \mu m^{-1} \, sr^{-1} \, count^{-1}$. An example of
this file can be seen in Figure 3.4.

Figure 3.3: Tungsten lamp emission data provided by Oriel at a distance of 50 cm.

Figure 3.4: Final calibration file for HR4000CG-UV-NIR spectrometer.
Because of the lack of light provided by the tungsten lamp in the UV region and the spectrometers poor performance in the IR region, the usable range of the spectrometer is limited to the 200 - 1000 nm range. The MatLab code used to generate the calibration code can be found in Appendix A.

3.3 USING THE CALIBRATION FILE

The equation used to produce calibrated emission results can be found below.

\[
Emission = (\text{Raw Emission Data}) (\text{Cal File}) \left( \frac{t_{\text{cal}}}{t_{\text{test}}} \right) \left( \frac{a_{\text{cal}}}{a_{\text{test}}} \right)
\]  

(3.4)

Where \( t_{\text{cal}} \) and \( T_{\text{test}} \) and the calibration and test emission integration times respectively. \( a_{\text{cal}} \) and \( a_{\text{test}} \) are the calibration and test aperture areas, respectively, and are used to ensure any aperture differences are taken into account.

The calibration procedure has been verified against the Planck function for the blackbody radiation of a surface. This equation predicts the radiance of a blackbody at a given temperature \( (T) \) and wavelength \( (\lambda) \). Initially it has units of \( W \text{ m}^{-2} \text{ m}^{-1} \text{ sr}^{-1} \), but when divided by \( 10^{10} \) is converted to units of \( W \text{ cm}^{-2} \mu \text{m}^{-1} \text{ sr}^{-1} \). The equation has the form [4]:

\[
B = \epsilon \frac{2hc^2}{\lambda^5} \frac{1 \times 10^{-10}}{\exp \left( \frac{hc}{k_B T \lambda} \right) - 1}
\]  

(3.5)

Where \( hc \) is Planck’s constant multiplied by the speed of light and is equal to \( 1.986 \times 10^{-25} \text{ J m} \), \( c \) is the speed of light at \( 3 \times 10^8 \text{ m/s} \), \( k_B \) is the Boltzmann constant at \( 1.38 \times 10^{-23} \text{ J K}^{-1} \), and \( \epsilon \) is the emissivity of the material. The furnace in
the UVM Plasma lab was used to heat a piece of poco graphite up to various temperatures between 1270 and 1470 Kelvin. Emission measurements were taken with the HR4000C-UV-NIR spectrometer and the temperature was recorded by a 2-color pyrometer. The calibrated emission results as well as the Planck function prediction are shown in Figure 3.5. An emissivity of 0.83 was applied to the Planck function as this is a good gray body representation of poco graphite.

Figure 3.5: Shows calibrated emission data and grey body Planck data for poco graphite ($\epsilon=0.83$).
Local thermodynamic equilibrium (LTE) is a condition in which the excitation and de-excitation of atomic and molecular particles is caused primarily by collisions between the particles instead of through radiative emission or absorption [24]. LTE is not a complete equilibrium condition, it is what’s known as a quasi-equilibrium state. A quasi-equilibrium state is one in which the conditions of the system are not in complete equilibrium. In the case of the UVM ICP facility, the plasma flow is in equilibrium with itself but not with its surroundings. If the plasma flow is assumed to be in equilibrium with itself, and therefore in an LTE state, then the conditions of the plasma are based solely on collisions between particles, and the atomic and molecular state populations can be assumed to be at their equilibrium levels [25].

At equilibrium levels, a particle’s characteristics are governed by the Boltzmann distribution. The equation for the electronic state Boltzmann distribution at LTE temperature is shown in Equation 4.1. In this equation $n_i$, $g_i$, and $\varepsilon_i$ are the number density, degeneracy, and energy level of electronic state level $i$. $n_o$ and $g_o$ represent the ground state level. $k_B$ and $T_{LTE}$ are the Boltzmann constant and LTE temperature.
respectively [13].

\[
\frac{n_i}{g_i} = \frac{n_o}{g_o} \exp\left(\frac{-\varepsilon_i}{k_B T_{LTE}}\right) \tag{4.1}
\]

Equation 4.2 relates the ground state number density \(n_o\) to the total number density \(n_s\) of the species, where \(Q_{el}\) is the electronic partition function.

\[
\frac{n_o}{g_o} = \frac{n_s(T_{LTE})}{Q_{el}(T_{LTE})} \tag{4.2}
\]

Combining Equations 4.1 and 4.2 produces an equation for the upper state number density \(n_i\) has been replaced with \(n_u\).

\[
n_u = \frac{g_u \exp\left(\frac{-\varepsilon_u}{k_B T_{LTE}}\right)}{Q_{el}(T_{LTE})} n_s \tag{4.3}
\]

Where \(g_u\) is the upper state degeneracy, \(\varepsilon_u\) the upper state energy. Defined at LTE as:

\[
Q_{el}(T_{LTE}) = \sum_i g_i \exp\left(\frac{-\varepsilon_i}{k_B T_{LTE}}\right) \tag{4.4}
\]

A simplification can be made to equation 4.4 in which one realizes that the higher energy level exponential terms go to 0 (due to them being large negative numbers) and the ground state term goes to 1 [23].

\[
Q_{el}(T_{LTE}) = g_o \exp\left(\frac{-\varepsilon_0}{k_B T_{LTE}}\right) + g_1 \exp\left(\frac{-\varepsilon_1}{k_B T_{LTE}}\right) + g_2 \exp\left(\frac{-\varepsilon_2}{k_B T_{LTE}}\right)
\]

\[
= g_o + 0g_1 + 0g_2 = g_o \tag{4.5}
\]
Combining Equations 4.3 and 4.5 gives the following equation for the upper state number density:

\[ n_u = \frac{g_u e^x p \left( \frac{-\varepsilon_u}{k_B T_{LTE}} \right)}{g_o} n_s \]  

(4.6)

The assumption of a LTE condition is a key assumption used for the ICP torch. It allows for the further assumption that the plasma is close to an equilibrium state before coming in contact with the test article. This simplifies the mathematical and spectroscopic analysis of the interactions that occur between the pyrolysis gases and the plasma flow. It also leads to less complex and time consuming computer simulations of the phenomena seen in the facility.

Previous work has been done in the UVM ICP facility with full Nitrogen plasmas and it was found that these are not in a LTE state [15]. Work has also been recently completed by Tillson which suggests that pure Argon plasmas, as well as other plasmas diluted with Argon, are in a LTE state. The data gathered for this study also included free stream measurements of Argon plasmas. This data was analyzed using the emission spectroscopy LTE analysis developed by Tillson [25]. This technique is described in the next section below.

## 4.1 Emission Spectroscopy

A tool that can be used to analyze and determine if the plasma is in an LTE state is emission spectroscopy. The collection of the emission data used the same methodology as described in Section 2.3. Emission data, after calibration, is presented in terms of intensity with units \( W \ cm^{-2} \ \mu m^{-1} \ sr^{-1} \), also known as spectral radiance. The
integrated intensity of a spectral feature can be used to find the number density of
the upper state of the transition via the following equation [13].

\[
E\left[\frac{W}{cm^3 sr}\right] = \frac{n_u A_{ul} \Delta \varepsilon_{ul}}{4\pi}
\] (4.7)

In this equation \(A_{ul}\) is the Einstein coefficient and \(\Delta \varepsilon_{ul}\) is the difference between
the upper and lower transition energy levels. The transition energy level (\(\varepsilon\)) is given
by the equation:

\[
\varepsilon_i = h c \nu_i
\] (4.8)

where \(h\) is Planck’s constant and \(c\) is the speed of light. The integrated intensity
can be found using the following equation where \(l\) is the emission pathlength (2.54
cm for underneath a sample and 3.8 cm for the free stream in the UVM ICP facility).

\[
E = \int_{\lambda_1}^{\lambda_2} \frac{I}{l} d\lambda
\] (4.9)

Combining Equations 4.8 and 4.9 with Equation 4.7 and solving for the upper
number density leads to the following equation:

\[
n_u = \frac{4\pi}{A_{ul}} \frac{\int_{\lambda_1}^{\lambda_2} \frac{I}{l} d\lambda}{hc(\nu_u - \nu_l)}
\] (4.10)

The final piece of the puzzle is the total number density \(n_s\). Under the LTE
assumption, the total number density of a species can be found using the ideal gas
law.
Where $\chi_s$ is the mole fraction of the species in question and $P$ is the pressure. Substituting this equation into Equation 4.6 gives a second equation for the upper state number density dependent only on the LTE temperature.

$$n_u = \frac{g_u e^{\frac{-h c \nu_u}{k_B T_{LTE}}}}{g_o} \frac{\chi_s P}{k_B T_{LTE}}$$ (4.12)

Setting the two equations for upper state number density equal to each other and rearranging so the temperature terms are on the same side leads to the following equation:

$$T_{LTE} e^{\frac{h c \nu_u}{k_B T_{LTE}}} = \chi_s \frac{g_u}{g_o} \frac{P}{k_B} \frac{10^6 A_n h c (\nu_u - \nu_l)}{4 \pi \int_{\lambda_1}^{\lambda_2} I_1 d\lambda}$$ (4.13)

This equation cannot be solved algebraically but can be solved numerically using a software suite such as MATLAB. As the LTE temperature is the only unknown, solving the equation is fairly straightforward. The $10^6$ is introduced in order to convert m$^3$ into a cm$^3$ and align the units. This method will produce a path averaged LTE temperature across the entirety of the plasma jet based on the emission signal gathered. It is best used for free stream measurements as there are no outside reactions occurring, nor are external contaminates being introduced into the flow which could effect the emission signal. The method and final equation presented above are used in the next chapter to further analyze the test conditions and verify the LTE temperature and assumption.
Chapter 5

LTE Temperature Analysis of Test Conditions

The understanding and characterization of the flow conditions with the UVM ICP facility is important for multiple reasons. It helps validate results produced by the laboratory, enables better comparisons with other facilities, and allows future models of the facility to obtain a higher level of accuracy. In this section, the same LTE temperature analysis approach that was used by Tillson is applied to free stream data collected during gas injection tests. The temperatures and their associated uncertainties are presented as well as the emission data associated with the measurements.
5.1 Emission Based Temperature Analysis and Sensitivity

As stated above, the emission data gathered during gas injection tests can also be used to further validate results of the free stream flow temperature of the Argon and Argon diluted plasma conditions used for the tests. These temperatures are based on the LTE temperature analysis described in the previous chapter. The flow conditions that the LTE analysis was applied to were a pure Argon flow, dilute Nitrogen flow, dilute Oxygen flow, and a dilute air flow. Equation 4.13 was solved for the LTE temperature using a MATLAB solver with the constants presented in Table 5.1.

Table 5.1: Argon Spectroscopic Constants and Energy Levels [19,25].

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>(g_o)</th>
<th>(g_i)</th>
<th>(A_{ul} \ (sec^{-1}))</th>
<th>(v_u \ (cm^{-1}))</th>
<th>(v_l \ (cm^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>738 nm</td>
<td>3</td>
<td>5</td>
<td>(8.47 \times 10^6)</td>
<td>107299</td>
<td>93751</td>
</tr>
<tr>
<td>763 nm</td>
<td>5</td>
<td>5</td>
<td>(2.45 \times 10^7)</td>
<td>106238</td>
<td>93144</td>
</tr>
<tr>
<td>772 nm</td>
<td>1</td>
<td>3</td>
<td>(1.17 \times 10^7)</td>
<td>107496</td>
<td>94554</td>
</tr>
<tr>
<td>794 nm</td>
<td>1</td>
<td>3</td>
<td>(1.86 \times 10^7)</td>
<td>107132</td>
<td>94554</td>
</tr>
<tr>
<td>912 nm</td>
<td>5</td>
<td>3</td>
<td>(1.89 \times 10^7)</td>
<td>104102</td>
<td>93144</td>
</tr>
</tbody>
</table>

The spectrum and resultant temperatures for each test case are shown in Figures 5.1, 5.2, 5.3, and 5.4. A total of 3 different emission data sets were run through the analysis for each flow condition. The figures below show one of those data sets for each case.
Figure 5.1: Emission spectrum with calculated Argon temperatures for a pure Argon plasma.

Figure 5.2: Emission spectrum with calculated Argon temperatures for a dilute Oxygen plasma.
Figure 5.3: Emission spectrum with calculated Argon temperatures for a dilute Nitrogen plasma.

Figure 5.4: Emission spectrum with calculated Argon temperatures for a dilute air plasma.

Averaging the temperatures of the five probed features for each individual case, and then averaging the three cases for each flow condition gives an estimate of the
flow temperature for each condition. The average temperatures calculated across the cases were: 7900 K for pure Argon, 7800 K for dilute Oxygen, 6780 K for the dilute Nitrogen flow, and 6950 K for the dilute air flow. These temperatures make sense in a physical sense, as energy is absorbed in the mixture conditions by the dissociation of molecules. This energy absorption drives down the temperature. The dilute air plasma temperature also makes sense relative to the dilute Nitrogen and Oxygen conditions as air is 78% Nitrogen and 20% Oxygen. Therefore the air plasma temperature should be closer to the dilute Nitrogen plasma temperature.

5.1.1 Uncertainty Analysis

An uncertainty analysis was performed on Equation 4.13 and the results for each test condition. The analysis was conducted using the second uncertainty procedure described in Appendix C. In this procedure uncertainty is determined as a decimal percentage. Equation 4.13 contains four terms with uncertainties. Those are the mole fraction \((\chi_{Ar})\), the pressure \((P)\), the Einstein coefficient \((A_{ul})\), and the integrated intensity \((I)\).

The first three terms have uncertainties based on their measurement apparatuses. The mole fractions are found via the mass flow meters that have an uncertainty of \((\Delta \chi/\chi) = 0.01\). The pressure is measured by the pressure transducer which has an uncertainty of \((\Delta P/P) = 0.01\). The uncertainty of the Einstein A coefficients has been reported by Wiese [31]; each term has an uncertainty of \((\Delta A_{ul}/A_{ul}) = 0.25\).

The uncertainty of the integrated intensities is found by taking the root mean square of the calibration uncertainty \((\Delta Cal/Cal = 0.028)\) and the calculation uncertainty (standard deviation) of each feature of interest. Table 5.2 shows the uncer-
tainties of each feature for each condition. It can be seen in the table that all of the
uncertainties are the same. This is due to the fact that the calibration uncertainty is
so much higher than the integrated area standard deviation. Therefore the calibration
uncertainty dominates the total uncertainty.

Table 5.2: Integrated intensity uncertainty ($\Delta I/I$) for each argon line in each condition

<table>
<thead>
<tr>
<th>Argon Line (nm)</th>
<th>Argon</th>
<th>Argon/N$_2$</th>
<th>Argon/O$_2$</th>
<th>Argon/air</th>
</tr>
</thead>
<tbody>
<tr>
<td>738</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
</tr>
<tr>
<td>763</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
</tr>
<tr>
<td>772</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
</tr>
<tr>
<td>794</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
</tr>
<tr>
<td>912</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
</tr>
</tbody>
</table>

To determine the effect of each term’s uncertainty on the calculated temperature,
the term was changed by its uncertainty while all other terms were kept constant. The
new temperature was then determined for each feature. This new temperature was
compared to the average temperature presented in the previous section to determine
the temperature uncertainty with respect to that term, ($\Delta T/T)_x$. This was repeated
for each term for each condition. With the temperature uncertainty for each term
known for each feature, the total feature temperature uncertainty, ($\Delta T/T)_{feature}$, was
calculated using a root mean square average. The results are shown in Tables 5.3,
5.5, 5.4, and 5.6.
### Table 5.3: Temperature uncertainty in 40 SLPM Argon.

<table>
<thead>
<tr>
<th>Argon Line (nm)</th>
<th>$(\Delta T/T)<em>{\chi</em>{Ar}}$</th>
<th>$(\Delta T/T)_P$</th>
<th>$(\Delta T/T)_{Aul}$</th>
<th>$(\Delta T/T)_I$</th>
<th>$(\Delta T/T)_{feature}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>738</td>
<td>0.00062</td>
<td>0.00062</td>
<td>0.0121</td>
<td>0.00149</td>
<td>0.0123</td>
</tr>
<tr>
<td>763</td>
<td>0.00061</td>
<td>0.00061</td>
<td>0.0126</td>
<td>0.00157</td>
<td>0.0127</td>
</tr>
<tr>
<td>772</td>
<td>0.00064</td>
<td>0.00064</td>
<td>0.0119</td>
<td>0.00140</td>
<td>0.0120</td>
</tr>
<tr>
<td>794</td>
<td>0.00053</td>
<td>0.00053</td>
<td>0.0114</td>
<td>0.00144</td>
<td>0.0115</td>
</tr>
<tr>
<td>912</td>
<td>0.00059</td>
<td>0.00059</td>
<td>0.0132</td>
<td>0.00165</td>
<td>0.0133</td>
</tr>
</tbody>
</table>

### Table 5.4: Temperature uncertainty in 40 SLPM Argon and 2 SLPM Oxygen.

<table>
<thead>
<tr>
<th>Argon Line (nm)</th>
<th>$(\Delta T/T)<em>{\chi</em>{Ar}}$</th>
<th>$(\Delta T/T)_P$</th>
<th>$(\Delta T/T)_{Aul}$</th>
<th>$(\Delta T/T)_I$</th>
<th>$(\Delta T/T)_{feature}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>738</td>
<td>0.00050</td>
<td>0.00050</td>
<td>0.0119</td>
<td>0.00151</td>
<td>0.0120</td>
</tr>
<tr>
<td>763</td>
<td>0.00062</td>
<td>0.00062</td>
<td>0.0124</td>
<td>0.00148</td>
<td>0.0125</td>
</tr>
<tr>
<td>772</td>
<td>0.00052</td>
<td>0.00052</td>
<td>0.0115</td>
<td>0.00144</td>
<td>0.0116</td>
</tr>
<tr>
<td>794</td>
<td>0.00054</td>
<td>0.00054</td>
<td>0.0112</td>
<td>0.00148</td>
<td>0.0113</td>
</tr>
<tr>
<td>912</td>
<td>0.00050</td>
<td>0.00050</td>
<td>0.0123</td>
<td>0.00162</td>
<td>0.0125</td>
</tr>
</tbody>
</table>
Table 5.5: Temperature uncertainty in 40 SLPM Argon and 2 SLPM Nitrogen.

<table>
<thead>
<tr>
<th>Argon Line (nm)</th>
<th>$(\Delta T/T)_{\chi Ar}$</th>
<th>$(\Delta T/T)_P$</th>
<th>$(\Delta T/T)_{Aul}$</th>
<th>$(\Delta T/T)_I$</th>
<th>$(\Delta T/T)_{feature}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>738</td>
<td>0.00058</td>
<td>0.00058</td>
<td>0.0104</td>
<td>0.00130</td>
<td>0.0105</td>
</tr>
<tr>
<td>763</td>
<td>0.00042</td>
<td>0.00042</td>
<td>0.0106</td>
<td>0.00142</td>
<td>0.0107</td>
</tr>
<tr>
<td>772</td>
<td>0.00044</td>
<td>0.00044</td>
<td>0.0102</td>
<td>0.00118</td>
<td>0.0103</td>
</tr>
<tr>
<td>794</td>
<td>0.00046</td>
<td>0.00046</td>
<td>0.0099</td>
<td>0.00122</td>
<td>0.0100</td>
</tr>
<tr>
<td>912</td>
<td>0.00043</td>
<td>0.00043</td>
<td>0.0107</td>
<td>0.00143</td>
<td>0.0108</td>
</tr>
</tbody>
</table>

Table 5.6: Temperature uncertainty in 40 SLPM Argon and 2 SLPM air.

<table>
<thead>
<tr>
<th>Argon Line (nm)</th>
<th>$(\Delta T/T)_{\chi Ar}$</th>
<th>$(\Delta T/T)_P$</th>
<th>$(\Delta T/T)_{Aul}$</th>
<th>$(\Delta T/T)_I$</th>
<th>$(\Delta T/T)_{feature}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>738</td>
<td>0.00057</td>
<td>0.00057</td>
<td>0.0106</td>
<td>0.00128</td>
<td>0.0107</td>
</tr>
<tr>
<td>763</td>
<td>0.00042</td>
<td>0.00042</td>
<td>0.0108</td>
<td>0.00149</td>
<td>0.0109</td>
</tr>
<tr>
<td>772</td>
<td>0.00044</td>
<td>0.00044</td>
<td>0.0101</td>
<td>0.00132</td>
<td>0.0102</td>
</tr>
<tr>
<td>794</td>
<td>0.00045</td>
<td>0.00045</td>
<td>0.0100</td>
<td>0.00120</td>
<td>0.0101</td>
</tr>
<tr>
<td>912</td>
<td>0.00056</td>
<td>0.00056</td>
<td>0.0112</td>
<td>0.00126</td>
<td>0.0113</td>
</tr>
</tbody>
</table>

Once the individual features are known, the overall temperature uncertainty can then be calculated using a root mean square average. The overall temperature uncertainties are shown in Table 5.7.
Table 5.7: Overall temperature uncertainties.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Uncertainty</th>
<th>T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.028</td>
<td>±220</td>
</tr>
<tr>
<td>Ar/O2</td>
<td>0.027</td>
<td>±210</td>
</tr>
<tr>
<td>Ar/N2</td>
<td>0.023</td>
<td>±155</td>
</tr>
<tr>
<td>Ar/air</td>
<td>0.024</td>
<td>±165</td>
</tr>
</tbody>
</table>

The overall uncertainties are low, this indicates one of two things. Either the methods more calculating the LTE temperature are highly accurate, or somewhere in the calculations a source of error was not taken into account. This error would most likely comes from the calibration of the spectrometer. The individual uncertainties also indicate that that primary source of uncertainty are the Einstein coefficients. If the uncertainties hold true, and the flows are indeed in local thermodynamic equilibrium, then the free steam temperatures measured are reasonably accurate.
Chapter 6

Injection Testing Results

An important aspect of this work was the replication of pyrolysis gases at a steady state condition using the aforementioned gas injection probe and holder. Emission data was taken at the sample surface and then point-wise along the stagnation line using the HR4000CG-UV-NIR spectrometer and optical setup mentioned in Section 2.3.1. Table 6.1 shows the four test conditions, the test gas composition, and the power supply amperage.

Table 6.1: Gas injection test conditions.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Plasma Composition</th>
<th>Amperage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Argon</td>
<td>40 SLPM (71.4 g/min) Ar</td>
<td>2.5</td>
</tr>
<tr>
<td>Dilute Nitrogen</td>
<td>40 SLPM (71.4 g/min) Ar - 2 SLPM (2.5 g/min) N₂</td>
<td>2.5</td>
</tr>
<tr>
<td>Dilute Oxygen</td>
<td>40 SLPM (71.4 g/min) Ar - 2 SLPM (2.9 g/min) O₂</td>
<td>2.5</td>
</tr>
<tr>
<td>Dilute Air</td>
<td>40 SLPM (71.4 g/min) Ar - 2 SLPM (2.6 g/min) Air</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Three gas mixtures were injected into the plasma through the gas-injection probe. The first was pure Carbon Dioxide. CO₂ and its constituent CO are emitted by PICA during the pyrolysis process, therefore is an injectant gas of interest for this study [18]. The next gas injected was Hydrogen. Lastly a 50-50 mixture by volume, totaling 282
sccm, of the two gases was injected.

The injection rates used were chosen to be low enough so that the gas flow would be in the thin film regime mentioned earlier. Table 6.2 shows the flow rates as well as their conversions into grams per minute.

**Table 6.2:** Injection volumetric flow rates in standard cubic centimeters per minute (sccm) and grams per minute.

<table>
<thead>
<tr>
<th>sccm</th>
<th>g/min CO₂</th>
<th>g/min H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>141</td>
<td>0.28</td>
<td>0.013</td>
</tr>
<tr>
<td>148</td>
<td>0.29</td>
<td>0.013</td>
</tr>
<tr>
<td>218</td>
<td>0.43</td>
<td>0.019</td>
</tr>
<tr>
<td>282</td>
<td>0.56</td>
<td>0.025</td>
</tr>
<tr>
<td>351</td>
<td>0.70</td>
<td>0.031</td>
</tr>
<tr>
<td>493</td>
<td>0.97</td>
<td>0.044</td>
</tr>
</tbody>
</table>

Upon reducing the data it was found that there was not much difference in the results from different flow rates. Therefore the following sections present data from the 282 sccm total volumetric injection rate for the three different injection gas mixtures. In the following subsections, results are presented for a 282 sccm (0.56 g/min) CO₂ gas injection flow rate.

### 6.1 Carbon Dioxide Injection Results

As stated above the first gas to be injected into the flow was Carbon Dioxide. Below are the results for CO₂ injection into pure Argon, dilute Nitrogen, dilute Oxygen, and dilute air plasmas.
6.1.1 CO₂ IN ARGON

Figure 6.1 shows the emission results at 2 mm for 282 sccm CO₂ injected into a pure Argon (71.4 g/min) plasma. The CN Violet band structure can be seen at 386 nm, the $\Delta v = \pm 1$ are also present at 359 and 416 nm although in much lower intensities. A sodium line is also visible at 281 nm and is most likely from some contaminates present on the copper holder.

The line on the far right of the figure at 697 nm is an Argon line. The small cluster of emission lines around 310 nm is most likely the OH band. Items of note in this figure are the presence of the CN and OH bands. They have relatively low intensities when compared to later results their presence is interesting because there is no Hydrogen or Nitrogen being introduced into the flow. The presence of these gases is most likely due to small levels of contamination in the flow from minute leaks in the gas lines.
The dashed line in the figure shows the integrated total emission value along the wavelength axis. The figure shows that at 2 mm below the sample face, the most radiative power comes from the small CN band. It also shows that the CO$_2$ injection into pure Argon does not produce much overall radiative power, totaling to about 0.007 Watt/cm$^2$ sr between 200 and 700 nm.

6.1.2 CO$_2$ in Dilute Nitrogen

In Figure 6.2 the emission results for 282 sccm CO$_2$ injection into a dilute Nitrogen (71.4 g/m Ar, 2.5 g/min N$_2$) plasma at 2 mm can be seen. The main CN bandhead at 386 nm can clearly been seen as the defining emission feature. The CN $\Delta v = \pm 1$ are also both strongly present with the +1 at 359 nm and the −1 at 416 nm. The bump at 450 nm is the CN Violet $\Delta v = −2$.

![Figure 6.2: 282 sccm CO$_2$ injected into a dilute Nitrogen plasma at 2 mm below the sample face.](image)

The integrated power also shows that this condition produces over ten times the
radiative power when compared to the pure Argon condition. The total radiative power is about 0.1 Watt/cm² sr from 100 to 700 nm. Again, almost all of the radiative power is coming from the CN bands. This higher integrated power shows that this plasma condition is much harsher for a material emitting CO₂ gas.

For the dilute Nitrogen test condition a spatial emission data set was also collected. This data can be seen in Figure 6.3 showing a spatial trace of the main CN bandhead at 385.8 nm along the stagnation point.

**Figure 6.3:** 282 sccm CO₂ injected into a dilute Nitrogen plasma spatially tracking CN at 385.8 nm from 0 mm to 5 mm.

From the figure it can be seen that the peak CN intensity for this flow rate lies at 2 mm below the sample face. This reaffirms that the standard emission gathering location of 2 mm below the sample face is a good location to continue collecting emission.
6.1.3 CO₂ IN DILUTE OXYGEN

Figure 6.4 shows the 282 sccm CO₂ injection condition in a dilute Oxygen (71.4 g/min Ar, 2.9 g/min O₂) flow. Again the main CN bandhead at 386 nm is present and OH is also present at 310 nm. An Oxygen line at 616 nm can also be seen. Once again the Argon line at 697 nm is visible in the data.

![Graph showing spectral radiance vs. wavelength for CO₂ injection into dilute Oxygen plasma.]

**Figure 6.4:** 282 sccm CO₂ injected into a dilute Oxygen plasma at 2 mm below the sample face.

Again the presence of both OH and CN allude to contamination in the flow, although at a very small level. The integrated power value of just above 0.005 Watt/cm² sr shows that this is not a harsh condition in terms of radiative power for CO₂ injection. The expectation is that once Hydrogen is introduced into the flow this will change due to the formation of OH.
6.1.4 CO$_2$ IN DILUTE AIR

The final condition for CO$_2$ gas injection was a combination of the previous three, the dilute air (71.4 g/min Argon, 2.6 g/min air) condition. Figure 6.5 shows the 2 mm emission scan for this condition. It must be noted that the raised level of the emission from 250 nm to 350 nm is most likely due to a bad background subtraction that was taken at the time of the test.

![Figure 6.5: 282 sccm CO$_2$ injected into a dilute air plasma at 2 mm below the sample face.](image)

The CN Violet main bandhead at 386 nm as well as the $\Delta v = \pm 1$ at 357 and 416 nm are clearly visible. The $\Delta v = -2$ is visible as well at 450 nm. The OH lines are barely visible at this scale. The Sodium line at 281 nm is also visible.

The integrated power line shows a major increase in the radiative power from the CN Violet lines. This indicates that the main force behind the radiative power is the CN molecule. The total radiative power between 200 and 700 nm is about 0.07 Watt/cm$^2$ sr.
6.2 **Hydrogen Injection Results**

The second gas to be injected through the injection probe into the plasma flow was Hydrogen. This gas was chosen because it is also a major component of the gases produced by PICA according to the literature [18]. The expected emission bands from Hydrogen injection include: NH around 337 nm, OH around 307 nm, H\(_\alpha\) at 657 nm, and H\(_\beta\) at 487 nm. For all Hydrogen tests data was taken at the standard 2 mm location and spatially from 0 to 5 mm at 0.5 mm intervals. The 282 sccm volumetric flow rate data for the four test cases is presented below.

6.2.1 **H\(_2\) in Argon**

The first torch condition for the Hydrogen injection tests was the pure Argon condition (71.4 g/min Argon). Figure 6.6 shows the 2 mm emission scan for 282 sccm Hydrogen injection. The most prevalent feature in this scan is the NH line at 337 nm. The H\(_\alpha\) line at 657 nm is also strong. The lines at 603 and 697 nm are both Argon. A small amount of OH was also detected, appearing around 310 nm.
Figure 6.6: 282 sccm H\textsubscript{2} injected into a pure Argon plasma at 2 mm below the sample face.

Again the presence of NH in this scan indicates that there is contaminate Nitrogen in the flow, although not much of it. The offset of the data from 0 indicates shows that the background subtraction applied to the data before collection was not quite exact. The integrated power line shows that the overall radiative power of the Hydrogen injection into a pure Argon plasma is not very strong, totaling to 0.01 Watt/cm\textsuperscript{2} sr. Note that due to the bad background subtraction the power is likely an overestimate. The line also shows that the NH molecule has the greatest effect on the power.

Figure 6.7 shows the spatial distribution of the five traced species up to 5 mm below the sample face along the stagnation line. The figure shows the CN is completely absent from the interrogated areas, which makes sense as there should be no Carbon in the flow and also very little Nitrogen. The OH line is also almost completely absent.
Figure 6.7: Spatial tracing of the five key species in a 282 sccm H\textsubscript{2} injected into a pure Argon plasma.

After 1.5 mm the population of NH rises slightly before declining after 3.5 mm. The H\textsubscript{α} trace increases steadily after 1.5 mm and looks to almost plateau after 4.5 mm. H\textsubscript{β} increases steadily from 2.5 to 4.5 mm below the sample face and then sharply increases after 4.5 mm. A re-run of the experiment where the emission data was collected up to 10 mm would reveal more about the two Hydrogen species.

6.2.2 H\textsubscript{2} in Dilute Nitrogen

Figure 6.8 shows the 2 mm emission scan from the 282 sccm Hydrogen gas injection into a dilute (71.4 g/m Ar, 2.5 g/min N\textsubscript{2}) Nitrogen condition. The figure shows that the NH spectra at 337 nm easily dominates all other spectra. The H\textsubscript{α} line at 657 nm is also fairly strong and a small amount of H\textsubscript{β} can also be seen at 486 nm.
Figure 6.8: 282 sccm H$_2$ injected into a dilute Nitrogen plasma at 2 mm below the sample face.

The integrated power line shows a much higher radiative power output for this condition than the pure Argon condition. The total power output is just above 0.05 Watt/cm$^2$ sr from 200 to 700 nm. It can also be seen that most of the power comes from the intense NH emission.

Figure 6.9 shows the spatially resolved traces of the key species. From the figure it is easy to see that the NH signature dominates emission until about the 3.5 mm mark where H$_\alpha$ then rises above it. H$_\beta$ also appears around the 2 mm mark but is not nearly as intense as the two species mentioned before. The emission is also fading quickly at the 5 mm distance, so about a mm or so of further scans would be required to fully visualize the spatial profile of the emission.
6.2.3 \( \text{H}_2 \) in Dilute Oxygen

In Figure 6.10 the 2 mm emission scan for 282 sccm Hydrogen injected into a dilute (71.4 g/min Ar, 2.9 g/min \( \text{O}_2 \)) Oxygen condition is shown. The main OH band is clearly visible around 310 nm as well as the \( \Delta v = +1 \) around 282 nm. The 282 nm band could also be contaminate Sodium appearing. The main NH band can also be seen at 337 nm. \( \text{H}_\alpha \) is the strongest feature in the emission spectra at 657 nm with \( \text{H}_\beta \) appearing at 486 nm.
Figure 6.10: 282 sccm H₂ injected into a dilute Oxygen plasma at 2 mm below the sample face.

The integrated power line shows that a majority of the spectral power comes from the OH band, but the Hα band also adds a significant amount. The total power from 200 to 700 nm is just shy of 0.05 Watt/cm² sr.

Figure 6.11 shows the spatial trace of the key species. It is interesting to note that the Hα line increases sharply after 1 mm, plateaus at 2 mm and then stays relatively steady for the next 3mm. The Hβ band steadily increases from 1.5 mm until 3.5 mm where it peaks and then declines. The OH band increases steadily until 2 mm and then decreases at about the same rate until approaching 0 at 4 mm. NH is only slightly present, peaking around the 2 to 2.5 mm mark. This shows that there is again a limited Nitrogen contamination in the flow. Further spatial data would help to fully characterize the spatial curve of the two Hydrogen bands.
6.2.4 \textbf{H}_2 \text{ IN DILUTE AIR}

The 2 mm emission for the final Hydrogen injection condition in dilute air (71.4 g/min Argon, 2.6 g/min air) can be seen in Figure 6.12. It was thought that the air condition emission scans would be a combination of the three previous scans. This proved to be true and makes sense because air is mainly made up of Oxygen and Nitrogen. The spectra is again dominated by the NH band at 337 nm, but the OH band is also present around 310 nm. OH $\Delta v = +1$ can be seen at 282 nm. $\text{H}_\alpha$ and $\text{H}_\beta$ are also present at 657 and 486 nm respectively.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6.11.png}
\caption{Spatial tracing of the five key species in a 282 sccm H\textsubscript{2} injected into a dilute Oxygen plasma.}
\end{figure}
Figure 6.12: 282 sccm H$_2$ injected into a dilute air plasma at 2 mm below the sample face.

The integrated line shows that the OH and NH spectra are responsible for most of the power generation. The air condition does not produce as much power as the dilute Nitrogen or Oxygen, producing just above 0.03 Watt/cm$^2$ sr from 200 to 700 nm.

Figure 6.13 shows the final spatial emission trace of the Hydrogen suite of injection testing. The figure shows the presence of all the key species with the exception of CN. As in the 2 mm emission scan, NH is the strongest emitter until it is overtaken by H$_\alpha$ at 4 mm from the sample face. OH is also steadily present from the face until about 4 mm. H$_\beta$ emission becomes detectable around the 3 mm mark but has the lowest maximum magnitude of the four emitting species. A few more spatial data points further out from the sample surface would be useful to obtain in a future test in order to obtain a more complete picture of the spatial data.
6.3 Mixture Injection Results

The final gas injected into the plasma through the gas injection holder was a 50-50 mixture of Carbon Dioxide and Hydrogen totaling to 282 sccm. On a mass flow basis this is 0.279 g/min of CO\textsubscript{2} and 0.013 g/min of H\textsubscript{2}. The goal of these results was to produce an emission spectra that was as close as possible to those of PICA. Only the injection results are presented in this section; the comparison results are presented in Chapter 7. Presented below are the mixture results for the pure Argon, dilute Nitrogen, dilute Oxygen, and dilute air cases.
6.3.1 Mixture in Argon

The first condition presented for mixture results is the pure Argon (71.4 g/min Argon) condition. The emission results at 2 mm are presented in 6.14. When comparing this figure to the previous two pure Argon emission scans (Figures 6.1 for CO$_2$ and 6.6 for H$_2$) it can be seen that the CN line is nearly nonexistent at 385 nm when compared to the CO$_2$ injection emission. The NH line at 337 nm is still present in both the H$_2$ injection and mixture cases although it is weaker in the mixture emission scan. A new feature is also present in the mixture case that was not seen in either the CO$_2$ or the H$_2$ case and that is the presence of OH at 310 nm. This makes sense as the CO$_2$ dissociation produces O which would then bond with the dissociated H to produce OH. The H$_\alpha$ line is strongly present at 657 nm and the H$_\beta$ is also visible at 487 nm. The Argon line at 697 is visible as well.

Figure 6.14: CO$_2$ and H$_2$ mixture injected into a pure Argon plasma at 2 mm below the sample face.
The integrated power line shows that most of the radiative power is produced by the OH band and that overall only just above 0.005 Watt/cm$^2$ sr is produced in total between 200 and 700 nm.

Figure 6.15 shows the spatial distribution of the key species from 0 to 10 mm. Closer to the face both H$_\alpha$ and OH are present in nearly equal amounts, but as the OH begins to decline around 1.5 mm the H$_\alpha$ line increases sharply. The H$_\alpha$ increase is followed about a millimeter later by the H$_\beta$ line. H$_\alpha$ then proceeds to decrease after 5.5 mm but did not fade out completely before the collection was ended at 10 mm. H$_\beta$ peaks at 4 mm and then steadily decreases until about 9.5 mm. The NH line also increases slightly after 1 mm but then decreases again after 3 mm. Given that the H$_\alpha$ line does not completely disappear by the end of the collection range, a few more data points would be beneficial to understand how far upstream the hydrogen penetrates into the plasma flow.

**Figure 6.15:** Spatial tracing of the five key species in a 282 sccm CO$_2$ and H$_2$ mix, injected into a pure Argon plasma.
6.3.2 Mixture in Dilute Nitrogen

As before, the second plasma condition tested with the mixture condition was the dilute Nitrogen (71.4 g/min Ar, 2.5 g/min N\textsubscript{2}) condition. The 2 mm emission scan for this condition is shown in Figure 6.16. In this figure all five key species are visible, indicating that they are all present at the 2 mm collection location. NH (337 nm) is the tallest peak of the emission but the CN Violet main band (385 nm) as well as the \( \Delta v = \pm 1 \) (359 and 416 nm) are very clear as well. The CN Violet \( \Delta v = -2 \) can also be seen at 450 nm. OH also appears around 310 nm, although at a much lower intensity than NH or CN Violet. Both H\textsubscript{\alpha} (657 nm) and H\textsubscript{\beta} (487 nm) are also visible.

![Figure 6.16: CO\textsubscript{2} and H\textsubscript{2} mixture injected into a dilute Nitrogen plasma at 2 mm below the sample face.](image)

The integrated line shows that although the NH band has the highest peak, it produces only about half the radiative power of the main CN Violet band. The total Radiative power between 200 and 700 nm is just shy of 0.075 Watt/cm\textsuperscript{2} sr. This is slightly less than then radiative power for the CO\textsubscript{2} condition, which was just under
2 Watt/cm² sr. The reason for this is most likely that the Nitrogen is not only being used to for CN Violet but also NH, therefore less CN Violet is produced and the overall radiative power is reduced.

Figure 6.17 shows the spatially resolved measurements of the key species. This figure is dominated by the CN and NH lines up until about 2.75 mm where they are passed in radiance by Hα. The CN band peaks at exactly 2 mm while the NH line peaks just before at 1.5 mm. This again helps to confirm that the 2 mm emission collection location is an appropriate location. The OH spectra peaks at 1 mm and then begins to steadily decline until it vanishes at 3.5 mm. The Hα line increases until 3 mm and then sharply declines before plateauing around 5.5 mm and then disappearing around 9 mm. From this figure it can be concluded that most of the reactions taking place for the mixture injection into a dilute nitrogen condition take place within the first 4 mm upstream of the sample face. This is different from the pure Argon case where the Hα trace lasted beyond 10 mm.
Figure 6.17: Spatial tracing of the five key species in a 282 sccm CO$_2$ and H$_2$ mix, injected into a dilute Nitrogen plasma.

6.3.3 MIXTURE IN DILUTE OXYGEN

Figure 6.18 shows the 2 mm emission scan for the dilute Oxygen (71.4 g/min Ar, 2.9 g/min O$_2$) test condition with the mixture being injected. At this condition the strongest peak radiator is H$_\alpha$ at 657 nm. The OH band system is also prevalent around 310 nm and the $\Delta v = +1$ system can be seen slightly around 282 nm. NH is slightly visible at 337 nm and can be attributed to minor Nitrogen contamination in the flow. The H$_\beta$ and Ar lines can also be seen at 486 and 697 nm respectively.
Figure 6.18: CO$_2$ and H$_2$ mixture injected into a dilute Oxygen plasma at 2 mm below the sample face.

The integrated power line shows that the total radiative power between 200 and 700 nm is about 0.022 Watt/cm$^2$ sr. The majority of the power is radiated by the OH and H$\alpha$ lines at roughly the same amount per species. The mixture for this condition produces less overall radiative power than the pure H$_2$ injection but does produce significantly more power than the pure CO$_2$ condition.

The spatially resolved traces of the five key species are shown in Figure 6.19. From the figure it can be seen that the emission spectra is dominated spatially by H$\alpha$, which begins to increase in intensity at 0.5 mm, peaks at 2.5 mm, and then falls steadily through the 10 mm distance. The OH trace also increases steadily from 0 mm until it peaks at 1.5 mm. It then decreases steadily until finally disappearing at 4.5 mm. The NH trace shows some intensity between 1 and 3 mm but is much weaker than the other lines with the exception of CN which is negligibly present in the scans. The H$\beta$ trace increases as the OH trace begins to decline. It peaks at 3 mm and then declines.
slowly before plateauing at around 9 mm. The figure also shows that the intensities of H\(_{\alpha}\) and H\(_{\beta}\) had not yet gone to zero before the scanning ended. This indicates that the next experiment at these conditions should take a longer spatial scan.

Figure 6.19: Spatial tracing of the five key species in a 282 sccm CO\(_2\) and H\(_2\) mix, injected into a dilute Oxygen plasma.

6.3.4 Mixture in Dilute Air

The final mixture injection test involved injecting into a dilute air (71.4 g/min Argon, 2.6 g/min air) plasma. The 2 mm scan for this can be seen in Figure 6.20. The scan looks very similar to the scan taken in the dilute Nitrogen condition (Figure 6.16) with the exception that the OH band is stronger in intensity and the overall CN Violet and NH bands are weaker in intensity. All five key species are visible in the emission snapshot. NH at 337 nm is the strongest followed by the CN Violet main band at 386 nm and the \(\Delta v = \pm 1\) at 359 and 416 nm. The CN violet \(\Delta v = -2\) can also be seen at 450 nm. OH is visible again at 310 nm and the \(\Delta v = +1\) is visible at
282 nm. H_α is strongly present at 557 nm and the H_β emission was also detected at 487 nm.

Figure 6.20: CO_2 and H_2 mixture injected into a dilute air plasma at 2 mm below the sample face.

The dilute air plasma with mixture injection does not emit quite as much radiative power as the dilute Nitrogen condition. This is most likely due to the fact that the CN band is less intense in the dilute air condition than in the dilute Nitrogen condition. The total radiative power from 200 to 700 nm for the dilute air condition is just above 0.05 Watt/cm^2 sr. Again most of the power comes from the main CN Violet band and the NH band. The OH band also provides a significant amount of power.

Figure 6.21 shows the spatially resolved traces of the five key species along the stagnation line. The figure shows that both the CN Violet and NH bands rise sharply for the first millimeter and peak between 1.5 and 2 mm. They then decline steadily, with both returning close to 0 at the 5 mm mark. The OH trace increases steadily to 1 mm and then decreases until it reaches 0 at about 3.5 mm. The OH
peak is about half that of the CN Violet and a quarter of the NH peak. H\(_{\alpha}\) increases slowly to 1 mm then rapidly increases in intensity before peaking at 2.5 mm. The intensity of the trace then rapidly decreases before leveling off at 4.5 mm. After 6 mm the H\(_{\alpha}\) trace slowly decreases through the 10 mm mark. The final trace is H\(_{\beta}\), this trace increases slowly and peaks at a low intensity at 2.5 mm. The trace then decreases slowly again and becomes negligible around 5 mm. An interesting note is the increase of H\(_{\alpha}\) that corresponds with the decrease in NH. This indicates that as the NH decomposes into N and H that the H then begins to radiate as H\(_{\alpha}\) and H\(_{\beta}\).

![Intensity of Spectra vs Distance from Face, Ar+Air Flow, H\(_2\)141 + CO\(_2\)141 [sccm]](image)

**Figure 6.21:** Spatial tracing of the five key species in a 282 sccm CO\(_2\) and H\(_2\) mix, injected into a dilute air plasma.

### 6.4 Injection Testing Summary

The injection tests were very successful in providing good results and proving the viability of the probe. The Carbon Dioxide injection suite was the first set of tests
run and provided a baseline for the operation of the probe. The tests also showed that some contaminate Nitrogen is present in most plasma conditions due to the fact that CN was present to some extent in each scan. The dilute Nitrogen spatial scan confirmed that the peak CN is at the 2 mm location. The data gathered from the test suite provided a solid baseline as to what CO$_2$ injection into the facility looks like.

The Hydrogen injection suite showed the presence of both NH and OH, indicating that a very small amount of contaminate Oxygen is present along with the Nitrogen in the plasma at all conditions. The spatial Hydrogen data showed that H$_\alpha$ and H$_\beta$ penetrate much further upstream than any of the molecules do. Due to this, further testing is require in order to obtain the full spatial characteristics of the Hydrogen injection. The data also shows that as NH dissociates the H atoms released can be traced in the increase of H$_\alpha$ and H$_\beta$. The Hydrogen injection emission results yield a second baseline, this time for Hydrogen, to which the mixture data can be compared.

Finally, the mixture injection suite showed that the mixture emission results are a combination of the CO$_2$ and H$_2$ results. The data gives some insight into how the two gases dissociate in the boundary layer and form OH. This is easily seen in the pure Argon case. The spatial mixture data shows that CN Violet, and NH follow the same general trends in terms of peaks and penetration depth. OH also follows these same trends but to a much lesser extent with the molecule dissociating much sooner.
CHAPTER 7

PICA AND INJECTION COMPARISON

This chapter contains the results comparison between the PICA data gathered by Tillson [25] and the mixture injection data presented in Section 6.3. The data prove the viability of using the injection probe to simulate the pyrolysis of PICA in a steady state condition. The four sections below present the comparison results for each different standard condition. Due to the fact that the PICA data is temporally resolved and not steady state, PICA emission snapshots were chosen based on how they matched with the steady state injection data. All data presented in this section was taken at the 2 mm collection location using the same emission setup described in Section 2.3.

7.1 COMPARISON IN ARGON

The first comparison is between data taken in the pure Argon (71.4 g/min Ar) flow condition. For this condition the PICA and injection emission data were very different. This is due to the fact that the pyrolysis gases contain more species than just
Carbon Dioxide and Hydrogen. The presence of these other species is detected in the emission measurements through the presence of spectra in the PICA data that are not present in the injection data. Figure 7.1 shows the comparison between the PICA data taken at 10 seconds versus the steady state injection mixture data.

![Figure 7.1: 2 mm PICA emission data (red) and 2 mm mixture injection data (blue) and residual in pure Argon.](image)

From the figure it can be seen that the two emission scans vary greatly both in terms of intensity as well as spectra present. For the injection data (blue) the two pyrolysis spectra detected are a small amount of OH (310 nm) and NH (337 nm). The OH is present due to the the Oxygen from the Carbon Dioxide and the Hydrogen combining. The NH is present due to the Hydrogen combining with the contaminate Nitrogen. In the 650 to 700 nm H$_\alpha$ can be seen at 657 nm and an Argon line at 697 nm.

The PICA data (red) contains many more spectra than the mixture data. The main feature is the CN Violet $\Delta v = 0$ at 385 nm as well as the $\Delta v = \pm 1$ to either
side at 359 and 416 nm. The NH feature at 337 nm is much larger than the one from the injection scan. OH is also present at nearly the same level as in the injection. C$_2$ Swan, which was not detected in any injection tests is also present in the PICA data from this condition. The $\Delta \nu = 0$ band is located at 520 nm with the +1 at 475 nm and the -1 at 545 nm. The strong line around 590 nm is Sodium. H$_{\alpha}$ is also present in the PICA data although not as strong as in the injection data.

An overall comparison of these two spectra does not show much similarity. The only possible match is between the OH bands. The injection OH spectra is slightly more intense than the PICA spectra, but it is comparable. As for the rest of the spectra in the PICA emission, the molecules that are present for these spectra are most likely coming from the PICA material itself. This further proves that the pyrolysis gases contain more than just Carbon Dioxide and Hydrogen. There is much more Nitrogen present in the PICA data than in the mixture data, indicating that it must be coming from the PICA itself. The C$_2$ Swan feature is also of interest and does not appear in the injection. This molecule is most likely coming from the fiber substrate of the PICA and is not necessarily a product of pyrolysis.

### 7.2 Comparison in Dilute Nitrogen

For the dilute Nitrogen test case (71.4 g/min Ar, 2.5 g/min N$_2$) two separate PICA time stamps are looked at. These time stamps are 14 seconds and 27 seconds. The emission comparison data for these times are presented in Figures 7.2 and 7.3 respectively. The two different times of PICA data were chosen because the injection spectral data could be matched to different spectra in the PICA data at those times.
The first figure (Figure 7.2) shows the PICA emission scan that matched in NH intensity with the injection scan. The second figure (Figure 7.3) shows the PICA emission scan that matched with the CN emission of the injection scan.

**Figure 7.2:** 2 mm PICA emission data (red) at 14 seconds and 2 mm mixture injection data (blue) and residual in dilute Nitrogen.

In the above figure it can be seen both from the emission scans and the residual plot that the NH feature at 337 nm match up very well in intensity. The reason for the spike in the residual at the NH line is due to the slight shift in the line location from the spectrometer. The figure also shows that the tiny amount of OH present around 310 nm also matches well. The CN bands centered at 385 nm do not match in intensity but all three vibrational levels can clearly be identified in both data sets. Once again Sodium appears in the PICA spectrum around 590 nm. Additionally the H\(\alpha\) band is strong in the injection emission at 657 nm and also slightly visible in the PICA emission.

The second figure shows the comparison of PICA at 27 seconds vs the steady state...
Figure 7.3: 2 mm PICA emission data (red) at 27 seconds and 2 mm mixture injection data (blue) and residual in dilute Nitrogen.

Injection. In the figure it can be seen that the overall CN band and the vibration levels closely match, but this is the only spectra that matches. For the injection results the NH band is much more intense than the PICA NH band and the OH is also present to a much greater level. Again a Sodium line is present in the PICA data and H$\alpha$ is much stronger in the injection case.

Overall, the two figures show that the injection probe can be successful at modeling the emission of PICA, at steady state, in a dilute Nitrogen plasma. Tweaking of the injection flow rates of Carbon Dioxide and Hydrogen is needed in order to provide a closer match of the spectra, but the current trend is promising. The data also shows that to more closely match the CN spectra in the 14 second figure (Figure 7.2) more CO$_2$ is needed, while removing some of the H$_2$ may help to reduce the H$\alpha$ signature. In order to more closely match the 27 second PICA data (Figure 7.3) less H$_2$ is needed. Reducing the Hydrogen injection would reduce both the OH and NH
as well as the Hα spectra, bringing the two emission snapshots into closer agreement.

### 7.3 Comparison in Dilute Oxygen

The next condition for the comparison between the PICA and steady state injection emission data is the dilute Oxygen (71.4 g/min Ar, 2.9 g/min O₂) condition. The OH band was focused on when choosing the proper temporal PICA emission for the comparison. Figure 7.4 shows the 7 second PICA data versus the steady state injection data.

**Figure 7.4:** 2 mm PICA emission data (red) at 7 seconds and 2 mm mixture injection data (blue) and residual in dilute Oxygen.

The figure shows that the OH spectra around 310 nm dominate the overall spectrum but are not the most intense. The Δν = +1 is also visible at 282 nm. Both bands are very similar between the two data sets. The NH band at 337 nm can also be seen, but is much stronger in the PICA data than in the injection data. The main
CN band at 385 nm is easily identified in the PICA data but is barely visible in the injection data. This indicates that there is some Nitrogen contamination in the flow and that there is most likely some Nitrogen within the PICA sample tested.

The Hydrogen alpha and beta lines are visible in the injection data set at 657 and 487 nm, respectively. The H$_\alpha$ is the most intense band with a max intensity of about $33 \text{ } Wcm^2\mu m^{-1}sr^{-1}$. A small amount of Hydrogen alpha is also visible in the PICA data set. The Argon line at 657 nm is also visible in both data sets. The intense line at 580 nm in the PICA data is Sodium and the two visible lines after 600 nm in the injection data are Oxygen lines.

Overall, the two data sets closely match for the OH bands. The NH band also is present in both sets as is the CN band to a lesser extent. As in the previous two compared conditions, the Hydrogen lines do not match up at all and the Sodium line that is present in the PICA data is not present in the injection data.

### 7.4 Comparison in Dilute Air

The final comparison, and the most important for Earth entry, is the dilute air condition (71.4 g/min Argon, 2.6 g/min air). The PICA to injection data comparison for this condition is shown in Figure 7.5. The PICA emission snapshot that most closely matched the injection emission data spectrum for this condition was the 10 second data.
Figure 7.5: 2 mm PICA emission data (red) at 10 seconds and 2 mm mixture injection data (blue) and residual in dilute air.

As seen in the figure the overall match between the two data sets for the dilute air condition is quite good. Discrepancies exist again for both H\(_\alpha\) at 657 nm and H\(_\beta\) at 487 nm, as well as Sodium at 580 nm. The Argon line at 697 nm is also visible in the injection data set but not in the PICA set. The OH around 310 nm spectra matches quite closely but the injection data is slightly higher than the PICA data. The NH spectra matches almost exactly with the biggest difference coming from a shift in the detection wavelength. The main CN band at 386 nm, as well as the \(\Delta v = \pm 1\) at 359 and 416 nm, are close in intensity as well, with the PICA data being slightly more intense than the injection data. The residual plot shows a much more qualitative image of the difference between the two data sets.

The comparison between the two data sets yields the conclusion that the injection probe is capable of closely modeling the PICA pyrolysis gas emission signatures in a dilute air condition. With further refinement of the injection gas mixture even
closer results should be achievable. The refinement would most likely consist of a slight increase to the Carbon Dioxide injection rate and a decrease to the Hydrogen injection rate. This should increase the amount of CN seen while simultaneously decreasing the OH and Hydrogen signatures.

7.5 Comparison Results Summary

In summary, the comparison between the injection emission data and the PICA emission data in the previous sections proves that the injection probe can replicate PICA emission spectra at certain test times in dilute Nitrogen, Oxygen, and air conditions. For the 50-50 by volume mixture of Carbon Dioxide and Hydrogen, totaling 282 standard cubic centimeters per minute in dilute Nitrogen, the PICA data was matched for NH at 14 seconds and CN at 27 seconds. For the same injection condition in dilute Oxygen the OH spectra was closely matched at 7 seconds for the PICA data. The dilute air condition with the same injection condition the full spectrum between 250 and 450 nm was closely matched at 10 seconds for the PICA data. When it came to the Argon test condition the data did not closely match. This is most likely due to the other molecules that are present in the PICA pyrolysis gas besides carbon Dioxide and Hydrogen.

A constant across all four test cases was the greater intensity of Hydrogen alpha and beta in the injection emission data versus the PICA data. This indicates that the volume flow rate, and therefore mass flow rate, of Hydrogen was higher than the actual rate during PICA pyrolysis. Reducing the flow rate of Hydrogen should lead to a closer match between the PICA and the injection data. A reduction in the
overall flow rate of injectant would reduce the emission seen, thereby more closely simulating PICA pyrolysis after the initial blowing of gases. The probe would then be simulating, to a greater degree, the rate of pyrolysis efflux that coincides with the majority of flight conditions a spacecraft using a PICA heat shield would encounter during atmospheric entry.
Chapter 8

Conclusion

8.1 Summary

The goal behind the research for this thesis was to design and build a gas-injection probe in order to simulate and study the steady state PICA pyrolysis gas interactions with a plasma similar to that found during atmospheric entry. Studying the interactions in the boundary layer between the simulated pyrolysis gases and the plasma increases the understanding of the reactions occurring at this location and can be used to help validate numerical models.

First, the current and past research on the subject was discussed, including work done at UVM. Attempts at gas-injection as well as the emission results of PICA from previous studies were detailed. Shortcomings of current numerical models were addressed as well. Next the operating conditions and components of the UVM 30 kW Inductively Coupled Plasma Torch Facility were described. Then, the design of the gas-injection probe was presented. The new holder and graphite plug were also discussed. Fourth, the experimental arrangement and emission spectroscopy were
explained. Finally, the results of the study were presented.

The study itself consisted of three different gas mixtures each being injected into four different plasma conditions. The three gas mixtures were: pure Carbon Dioxide, pure Hydrogen, and a 50-50 mixture of the two by volume. The four plasma conditions were: pure Argon, dilute Nitrogen, dilute Oxygen, and dilute air. The plasma conditions were chosen to match previous PICA work so as to produce data at the same test conditions. Single point emission scans as well as spatially resolved traces of the key species (CN Violet, NH, OH, H\(_\alpha\), and H\(_\beta\)) were presented.

In the pure Carbon Dioxide injection tests, CN was the main molecule seen in the scans. Because of this, the integrated radiative power also depended heavily on the presence of CN Violet. The dilute Nitrogen test had the highest level of CN Violet and the spatial data from that test showed that it is still detectable even at 4 mm upstream of the sample face.

The pure Hydrogen injection tests showed NH and H\(_\alpha\) as the dominant species. OH was also present to a lesser extent with the exception of the dilute Oxygen test where it and H\(_\alpha\) were the dominate species. The integrated radiative power showed that NH and H\(_\alpha\) were the primary sources of emissive power. The spatially resolved traces of the key species showed that the two Hydrogen states remain detectable much further upstream of the face than either OH or NH. The data shows the OH dissociates much earlier than NH as well.

The mixture injection data showed that the two gases mix in the boundary layer to form other molecules. This can best be seen in the pure Argon case where there is a relatively high intensity of OH compared to the two pure gas tests at the same condition. The mixture data also showed that when both CN and NH are present the
NH is much more intense than the CN, but the two follow the same general spatial trends. From the data, the longer upstream penetration of Hydrogen can again be seen. The integrated radiative power showed that all three of the major radiators (CN, NH, and Hα) from the pure gas tests contribute to the overall emissive power of the mixture tests. The data also showed that CN and NH generally contribute the majority of this power.

8.2 Future Work

Much more work can still be done in order to more closely model the pyrolysis gases of PICA. First, a more accurate mixture could be created between the Carbon Dioxide and the Hydrogen in order to increase the match between the injection and PICA emission data. The rate of injection could then be reduced, from current levels, to more closely simulate the later stages of pyrolysis. Once a full suitable mixture has been found it can then be tested in the entire range of torch conditions in order gather emission data for those conditions. Two important conditions to test would be a full air condition that simulates Earth’s atmosphere as well as a CO₂ condition simulating Mars entry. These tests would simulate two entry conditions that PICA has been, and could again, be used for in the near future.

Once the correct injection rates have been established, investigative methods that require longer times at steady state can be used. One such method is laser induced florescence or LIF. Two-photon LIF could be used with the steady state operation of the probe to study CO and O, and single-photon LIF could be used to further probe CN. OH, NH, and H could also be probed with LIF.
Once the techniques and calibration for the IsoPlane spectrometer have been developed this spectrometer can then be used to obtain higher resolution, spatially resolved measurements of the boundary layer. In this study measurements were only taken, pointwise, every half millimeter. The data collected by the IsoPlane would have much greater spatial resolution.

8.3 Conclusion

In conclusion, the results provided by this study have shown that the new gas-injection probe designed and built for the UVM 30 kW Inductively Coupled Plasma Torch Facility is capable of simulating the pyrolysis mechanics of PICA in a steady state condition. The data that has been collected from the probe for this study has been proven to be similar to that of PICA. A few tweaks of the injection mixture are still needed before complete similarity has been achieved, but the results are very close. The probe can then be used to study the steady state interaction of those gases with many different plasma conditions, using an array of methods. The data can also be used to begin to validate numerical models which may eventually help design the next PICA heat shields for exploration missions to Mars and beyond.
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% Calibration Conversion File
%C. T.illson
%7–31–2015
%Edited by NCM Aug 2017
%After Reading Heat Transfer Book Edit

clear all
close all
c;lc

% [Oriel Tungsten–Halogen Emission Curve/Collected Emission] * [Solid Angle Conversion]
% [mW/m2 nm] /[au counts] * [au conversion]

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D = 241.887467247558; %
E = -173363.0298415; %
F = 53266485.7148184; %
G = -6814364357.74668; %
H = 0; %

wavelength = calibrationFILE(:,1);
test_emission = calibrationFILE(:,2);

Irradiance = (wavelength.^-5).*exp(A*B./wavelength).*((C*D./wavelength.^2)+(E.*wavelength.^3)+(F.*wavelength.^4)+(G.*wavelength.^5))

Irradiance = Irradiance./1e4; % Convert to [W/cm^2 um]
Emit_Intensity = (Irradiance.*1)./(21+4e-4); % [W/cm^2 um sr]
% Plotting Individual Calibration Curves

% Experimental calibration curve
figure(1)
hold on
plot(W, test_emission, 'b', 'LineWidth', 2)
xlabel('$\lambda$ [nm]', 'Interpreter', 'latex')
title('Experimentally measured calibration spectra', 'Interpreter', 'latex')
axis([min(wavelength) max(wavelength) 0 16000])
set(gca, 'FontSize', 22)
hold off

% Oriel supplied curve
figure(2)
hold on
plot(W, Emit_Intensity, 'r', 'LineWidth', 2)
xlabel('$\lambda$ [nm]', 'Interpreter', 'latex')
ylabel('I [W cm$^{-2}$ $\mu$m$^{-1}$ sr$^{-1}$]', 'Interpreter', 'latex')
title('Oriel Lamp Data', 'Interpreter', 'latex')
set(gca, 'FontSize', 22)
hold off

% Creating Calibration File
% Lamp Emission Divided by solid angle to get counts/sr
calibrated_data = Emit_Intensity ./ (test_emission);
save(['10millisec_3_16ap_calfile.txt'], 'calibrated_data', '-ascii')
figure(3)
hold on
plot(W, calibrated_data, 'LineWidth', 2)
xlabel('$\lambda$ [nm]', 'Interpreter', 'latex')
ylabel('Counts/sr', 'Interpreter', 'latex')
title('Calibration File', 'Interpreter', 'latex')
set(gca, 'FontSize', 22)
axis([min(wavelength) max(wavelength) 0 0.000015])
hold off
APPENDIX B

INJECTION PROBE ASSEMBLY

PROCEDURE

The conversion of the insertion probe from sample holder to injection holder is described in the following section. The total time required is on average less than one hour.

Components needed:

• Insertion probe.

• Assembled Gas injection holder.

• High-Temperature Silicon Rubber Tubing, Durometer 70A, 1/8' ID, 1/4' OD.

• Bored-Thru 3/8' x 1/4' Swagelok reducing union(Figure B.2b).

• 1/4' x 1/4' Swagelok union.
Steps:

1. Remove the insertion probe from the facility and remove any sample holders from it.

2. Remove the top plug from the front of the probe (Figure B.1a).

3. Attach the bored-thru Swagelok fitting to the gas-inlet fitting on the back of the probe (Figure B.1b).

4. Feed the 1/4" flexible tubing through the back bored-thru fitting and out the bottom of the front of the probe. Use a hex driver or other tool to push the tubing down and out of the probe via the hole where the top plug was.

5. Check to make sure the high temperature o-ring is still in its place on the bottom of the probe. If it is damaged or missing replace it.

6. Screw the collar onto the probe leaving room to attach the gas-injection holder to it.

7. Push the 1/4" tubing on the barbed fitting as far as it will go.

8. Put the holder in its place in the collar.

9. Holding the holder steady, screw the collar up into place until it is tightly securing the holder to the probe. Try not to let the holder rotate.

10. Spray some water into the top plug hole in order to check the o-ring and tubing seals.

11. Screw the top plug back into place using new Teflon.
12. Push some of the 1/4" tubing back into the probe and then swage the tubing to the bored-thru fitting.

13. Cut the tubing leaving about 3-4 inches after the swage.


15. Place the probe back into its spot on the test chamber.

16. Attach the water inlet and outlet hoses to the other two swages. The inlet is the fitting closer to the gas-inlet.

17. Attach the gas-injection hose.

18. Turn on the water and watch for leaks around the holder.

19. If no leaks are detected, screw down the probe mount and slowly vacuum out the chamber while watching for leaks at the holder.

20. If no leaks are detected the probe and holder are ready for testing.
(a) Front section of insertion probe.  

(b) Back section of insertion probe.

Figure B.1: Front and back section of the insertion probe. Important components are labeled.

Figure B.2: Left: Holder fully installed. Right: Bored-thru fitting.
To uninstall the holder follow the following steps:

1. Shut off the water and remove the water lines.

2. Remove the gas-injection hose from the back of the probe.

3. Put a bin underneath the holder and slowly unscrew the collar until the holder comes loose.

4. Cut the rubber tube above the barb and remove the holder. DO NOT PULL HARD ON THE TUBE OR YOU MAY BREAK THE SOLDER SEAL.

5. Remove the remainder of the internal tube through the back of the probe.

6. Replace the bored-thru fitting with the standard fitting.

7. Reattach the the two water inlet hoses to the gas injection fitting and the closer side fitting.

8. Reattach the water outlet to the rear fitting.

9. The probe is now ready for standard samples.

10. Remove the remainder of the tubing from the barb on the gas injection holder and clean/inspect the holder.
Appendix C

Uncertainty Analysis Procedure

All measurements taken have a certain amount of uncertainty. This is because no matter how accurate or precise an instrument is it still has some uncertainty associated with it. In other words no instrument is perfect. Any manipulation of the data gathered from this instrument therefore contains this uncertainty as well. The general equation for deriving uncertainty is shown in Equation C.1.

\[
\sigma_A = \sqrt{\sigma_{x_1}^2 \left( \frac{\partial A}{\partial x_1} \right)^2 + \sigma_{x_2}^2 \left( \frac{\partial A}{\partial x_2} \right)^2 + \sigma_{x_3}^2 \left( \frac{\partial A}{\partial x_3} \right)^2 + \ldots + \sigma_{x_n}^2 \left( \frac{\partial A}{\partial x_n} \right)^2} \quad (C.1)
\]

The equation is based on a variation of the least squares mean reduction technique. Each sigma (\(\sigma\)) represents the uncertainty of a measurement technique and the derivative (\(\partial A/\partial x\)) terms represent the uncertainty of each variable as it is passed through the equation in question.

An alternative method to finding the uncertainty is to vary the variables in the equation of focus by their respective uncertainty percentages. For example, if a variable has an uncertainty of \(\pm 5\%\), then it is varied by that much in the equation and the effect on the final product is recorded in terms of a percentage ((\(\Delta A/A\))x).
In using this technique the uncertainty of the final measurement with respect to each individual variable is found. The total uncertainty is then found by applying the root mean square technique shown in Equation C.2. This gives the final uncertainty as a decimal percentage.

\[
\left( \frac{\Delta A}{A} \right)_{\text{total}} = \sqrt{\left( \frac{\Delta A}{A_{x_1}} \right)^2 + \left( \frac{\Delta A}{A_{x_2}} \right)^2 + \left( \frac{\Delta A}{A_{x_3}} \right)^2 + \ldots + \left( \frac{\Delta A}{A_{x_n}} \right)^2} \quad \text{(C.2)}
\]
Appendix D

Sample Test Matrix
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<th>Date</th>
<th>Folder ID</th>
<th>Flow Rates</th>
<th>Amperage</th>
<th>Base Pressure (torr)</th>
<th>Sample Location</th>
<th>Collection Location</th>
<th>Aperture (in)</th>
<th>Integration Time (s)</th>
<th>Plug</th>
<th>Injection Gas</th>
<th>Injection Rate (sccm)</th>
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**Figure D.1:** Gas-injection test matrix.
Appendix E

CAD Drawings
Figure E.1: Drawing of gas-injection holder.
Figure E.2: Drawing of sealing disc.
Figure E.3: Drawing of graphite plug [27].
**Figure E.4:** Assembly of complete gas-injection holder.