Velocity and Temperature Characterization of the First Vacuum Stage Expansion in an Inductively Coupled Plasma - Mass Spectrometer

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ABSTRACT

VELOCITY AND TEMPERATURE CHARACTERIZATION OF THE FIRST VACUUM STAGE EXPANSION IN AN INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETER

William Neil Radicic
Department of Chemistry and Biochemistry
Master of Science

The inductively coupled plasma – mass spectrometer (ICP-MS) is the analytical instrument of choice for trace element detection and quantification. Despite the popularity of ICP-MS, significant degradation in sensitivity and precision occurs as the result of matrix and instrument–induced effects. The sources of these effects are not well understood, characterized, or correlated to particular plasma operating condition settings or matrix compositions and involve both neutral and charged species. The purpose of this study is to characterize the behavior of metastable Ar (I) atom and Ca (II) ion through the measurement of Doppler velocities and fluorescence line width “temperatures.”
For the characterization of Ar (I), axial and radial velocity and temperature profiles were collected as a function of nebulizer rate, incident ICP power and matrix composition to establish a behavioral baseline for neutral species in the first vacuum stage expansion of an ICP-MS. Velocities were determined from the Doppler shift of laser-induced Ar (I) fluorescence compared to stationary population wavelength reference. Unambiguous evidence of a thick Mach disk forming 10-12 mm downstream and persisting through 17-18 mm downstream, under standard ICP conditions, conflicts with the widely held view of a thin Mach disk located between 15-17 mm downstream.

Characterization of Ca (II) ion focused on the effect of changing ICP conditions and matrix composition on calcium ion Doppler velocity and temperature profiles in the first vacuum stage expansion. Evidence of the plasma potential acceleration of ions through the interface was found as a higher Ca (II) terminal velocity than that of Ar (I) under standard ICP conditions. Additionally, the effect of a lithium matrix on Ca (II) velocity and temperature profiles was generally opposite than on Ar (I) velocity and temperature profiles.
ACKNOWLEDGEMENTS

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I thank my research advisor, Paul B. Farnsworth, for his mentorship, patience, faith, and support in accomplishing this master degree in exactly 24 months. Jeffrey H. Macedone is a true professional and friend who made daily life in the Farnsworth group interesting, productive, and fun … thank-you Jeff. I would also like to thank Uchenna Paul, Andrew Mills, and the other members of the Farnsworth group for their insights, friendship, and research assistance.

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Chapter 1. Introduction

The design goal of an ideal inductively coupled plasma – mass spectrometer (ICP-MS) is simple: convert an analytically important sample directly into the gas phase, ionize 100% of the analyte in a perfectly stable radio-frequency inductively coupled plasma and selectively sample and detect ions at any concentration. In practice, modern ICP-MS instrument performance depends on the complex balance of scientific and engineering constraints to achieve much more modest performance objectives. Although the first direct current plasma jets were first described in the 1920’s, it wasn’t until the 1970’s when the first analytically useful ICP sources were developed and characterized[1].

While inductively coupled plasma – mass spectrometers (ICP-MS) have been in commercial use since 1983[2], and most aspects of their operation have been studied and/or modeled, exactly how and why analyte ions fail to reach the detector is not well understood. Houk and Niu have stated “certain weaknesses of ICP-MS, such as matrix effects and the low overall ion transmission of quadrupole instruments could be overcome to some extent if the ion extraction process were understood thoroughly”[3].

Given the ICP-MS’s relatively short history and rapid development as the leading trace elemental analytical tool, the method and its complexities warrant significant exploration.

Because of these poorly understood complexities and, in some areas, their significant contributions to ICP-MS’s decreased analytical performance, it is the current goal of our research group to better understand how ions behave through the interface of an ICP-MS. This work comprises a small part of the overall effort of my current colleagues and those colleagues who have gone before to ask the questions “what is happening to the ions?”
and “what is happening to the atoms?” We believe that by better understanding what specific chemistry and physics is occurring in the interface region of an ICP-MS, we may be able to better identify and correct for matrix effects and ion transmission losses. This work focuses on a spatial characterization of neutral and charged species using velocity and temperature measurements to quantify the effects of certain instrument operating conditions and sample composition variations on ion and atom behavior in the first vacuum stage of an ICP-MS as shown in Figure 1-1.

1.1 Overview of ICP-MS Interface Function and Design

The interface region of an ICP-MS is a mechanical, thermal, and electrical bridge between two vastly different environments. An ICP-MS consists of two parts: inductively coupled plasma (ICP) and a mass spectrometer (MS). The inductively coupled plasma serves as the ion source and the mass spectrometer serves as the ion detector. The inductively coupled plasma operates at atmospheric pressure while the mass spectrometer is maintained at high vacuum. Regions of the inductively coupled
plasma can reach temperatures of 7,000 to 10,000K[3,4] while the ions slightly exceed room temperature (~400K: calculated from electron energy) at the ion trap of a quadrupole mass spectrometer[5]. The challenges faced in interface design are effectively stated by Niu and Houk: “One of the principal tricks in the whole experiment is to reduce the pressure and density without losing too many ions”[3]. In fact, current ICP-MS designs do lose too many ions, despite part per trillion sensitivities.

Currently, the most common sampling interface for commercial ICP-MS instruments is a water-cooled nickel cone with a 1mm orifice. Nickel has been historically used as a sampling cone material due to its excellent blend of physical durability, chemical stability, and high thermal conductivity compared to some other important commercial metals and alloys as shown in Table 1-1.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Thermal Conductivity (W/cm K)</th>
<th>Density (g/cm³)</th>
<th>Coef. of Linear Exp. (µin/ in. °F)</th>
<th>Electrical Resistivity (µΩ*cm)</th>
<th>Modulus of Elasticity (Mpsi)</th>
<th>Melting Point (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>1.1</td>
<td>8.89</td>
<td>6.6</td>
<td>10</td>
<td>30</td>
<td>2625</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>0.3</td>
<td>8.02</td>
<td>9.6</td>
<td>72</td>
<td>28</td>
<td>2600</td>
</tr>
<tr>
<td>Carbon Steel</td>
<td>1.0</td>
<td>7.86</td>
<td>6.7</td>
<td>10</td>
<td>30</td>
<td>2760</td>
</tr>
<tr>
<td>Copper</td>
<td>4.0</td>
<td>8.91</td>
<td>9.3</td>
<td>1.7</td>
<td>17</td>
<td>1980</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.3</td>
<td>5.0</td>
<td>4.9</td>
<td>80</td>
<td>16.5</td>
<td>3300</td>
</tr>
<tr>
<td>Aluminum</td>
<td>3.0</td>
<td>2.8</td>
<td>12.7</td>
<td>4</td>
<td>10.5</td>
<td>1185</td>
</tr>
</tbody>
</table>

Although there are other possible cone materials, as shown in Table 1-1, nickel has a unique combination of physical and chemical characteristics that have made it the material of choice for cone construction. It is important for cone life that the material has a high thermal conductivity and relatively high melting point to withstand the high
plasma temperatures and quickly transfer absorbed heat to the cooling medium. Physical dimensional stability of the cone is important as well. Vaughn and Horlick[7] have found that changing orifice size alone in either the sampling or skimmer interfaces changes the sensitivity of an ICP-MS instrument and therefore low coefficients of thermal expansion are desirable. Additionally, pressure differentials at the interface orifices work cooperatively with high temperatures and material bombardment to degrade the dimensional stability of the interface orifice. Modulus of elasticity is one indicator of material “toughness” in the face of continual mechanical and thermal stresses. Electrical characteristics of cone material not only determine how well the floating potential generated by the plasma can go to ground, thus reducing the potential’s effect on ion transport, but also influence the rate at which sample components accumulate at the sampling orifice. Macedone et al.[8] found that ion transport efficiency is negatively affected by and correlates well with the measured plasma potential just upstream of the sampling cone, and Niu and Houk found that reducing the plasma potential is important to “practical operation of an ICP-MS device” [3]

Despite nickel’s favorable physical, chemical, and electrical characteristics and history of widespread use, recent research published by Colas and co-workers indicates that nickel alone may not be the best material for sampling cones, and that alternative cone designs involving Cu-Ni laminates provide better long-term precision and are more robust[9]. This example of improving the design and performance of perhaps the most mechanically simple, extensively modeled, and well-understood component in an ICP-MS system suggests there is significant improvement possible through the careful characterization
and analysis of less-well-understood and more behaviorally complex regions of an ICP-MS such as the supersonic expansion of atoms and ions in the first vacuum stage of an ICP-MS.

A study of how atoms and ions flow from an ICP through the interface and on to the mass spectrometer must meet several criteria: the probing method must not 1) interfere with the subject of study, 2) be simple, and 3) be highly selective. The first requirement of non-interference reduces the list of possible methods to visual observation and energy transition excitation or relaxation methods. In our group we use both methods to study various aspects of ion and atom transmission, but in this research we use laser-induced fluorescence as our primary method of probing the environment in the first vacuum stage of an ICP-MS, which occurs immediately downstream of the sampling interface cone. Laser-induced fluorescence fulfills the criteria of simplicity and selectivity well. Using the well-established and proven techniques of signal modulation and lock-in detection to excite and detect specific elemental electronic transitions, we are able to spatially map important thermal and kinetic behavior of specific ions and atoms simply by changing the wavelength of our excitation laser.

1.2 Analytical Strengths and Weaknesses of ICP-MS

Every analytical instrument has strengths and weaknesses. Challenges facing ICP-MS are significant. According to Olesik and Stewart [10], just getting the analyte from the sample beaker to the interface involves damaging matrix effects generated in each ICP-MS component from sample introduction and aerosol production to ion transport through
the sampling interface. Once through the sampling interface, analyte ions face unpredictable influences from ionized matrix components that interfere with analyte trajectory and therefore selection and inclusion by the second-stage skimmer interface. Perhaps the most significant weakness of ICP-MS is the continuing lack of concrete understanding about the mechanisms that lead to observed analytical problems. In one effort, Chen and Farnsworth[11] performed analyte ion distribution studies in the second stage vacuum in an attempt to characterize the ion beam and issued the following statement:

“The experiment suggests that the distribution of material in the deposit depends on factors other than the spatial distributions of analyte ions in the ion beam. Neutral atoms can affect the formation of the deposit, as can either charged or neutral micro-particulates. Caution is urged in the use of deposition experiments of this type to study ion beam behavior.”

Their findings indicate that the mechanisms leading to matrix effects are neither simple nor dependent on a single variable. The identification of significant matrix effects not only in the plasma, but also upstream from the second stage skimmer interface points to an urgent need to characterize and understand not only analyte ion distributions in the first vacuum stage, but non-analyte ion and neutral atom distributions as well. These matrix components have a visibly significant but poorly understood negative effect on analyte detection sensitivity. In the following sections, applicable theory concerning the
analytical performance criteria affecting an ICP-MS sampling interface will be reviewed and the impact of velocity and temperature characterization will be discussed.

1.2.1 Ionization Efficiency

Ionization efficiency is defined as the degree of formation of M(II) and M(III) from various atoms \([M(1)]\) at a given temperature and number density as defined in equations (1-1) and (1-2),

\[
\left( \frac{M(II)}{M(II) + M(I)} \right) \cdot 100\% \tag{1-1}
\]

\[
\left( \frac{M(III)}{M(III) + M(II) + M(I)} \right) \cdot 100\% \tag{1-2}
\]

where \(M(I)\) is the neutral atom, \(M(II)\) is the singly charged ion, and \(M(III)\) is the doubly charged ion. Currently, other members of our research group are performing laser-induced fluorescence probes of the first vacuum stage in an attempt to account for all atomic and ionic species for a particular element. This process occurs in the cooler (~6,000-8,000K) \([1]\) central region of the plasma, surrounded by a much hotter cylindrical region that can reach 10,000K \([3]\). Due to the flow and density characteristics of high frequency radio frequency (RF) inductively coupled plasmas, samples are introduced into the central channel of the plasma, allowing the sample to continue axially toward the first sampling interface as it is ionized. This central region is where most, if not all, of the analyte ionization occurs. The properties of this region are of great interest in answering questions about matrix effects.
The most important property of this central channel of the inductively coupled plasma is its temperature. According to Hieftje and co-workers [12] the gas kinetic temperature is one of the most important pieces of information, along with number densities, required to determine how ions are formed in an ICP source. The gas kinetic temperature of the ionizing region of the plasma is also often called the stagnation temperature when the plasma is coupled to a vacuum interface. While gas kinetic temperature is often calculated from pressure differences between the source and in the first vacuum chamber [3], stagnation temperature is calculated from the terminal velocity measured in the first vacuum stage as shown in Equation (1-3), where \( m \) is the mass of the analyte, \( v_{\text{inf}} \) is the terminal Doppler velocity of the analyte, measured at the center of the fluorescence peak, and \( k \) represents the Boltzmann constant.

\[
T_{\text{stagnation}} = \frac{mv_{\text{inf}}^2}{5k}
\]  

(1-3)

The central role of the plasma gas kinetic temperature or stagnation temperature on the ionization efficiency of the analyte in an ICP-MS instrument is a primary motivation for using velocity and temperature to characterize atomic and ionic behavior in the first vacuum stage of an ICP-MS. An additional source of reduced analytical sensitivity of certain ICP-MS instruments is an artificially high detector background due to the detection of stray photons from the source [13]. It is clear, at least in this respect, that reduction of plasma incident power to the minimum level required would reduce the plasma temperature and thus reduce the prevalence of stray photons reaching the ion
detector in addition to reducing cooling loads and thermal wear to the interface. Through a careful measurement of ion and atom velocities, clear relationships between plasma operating conditions, matrix composition, and the source ionization environment can be outlined.

1.2.2 Transport Efficiency

Transport efficiency is defined in Equation (1-4) and is an important indicator of the effect of instrument operating conditions and matrix composition choices on ICP-MS sensitivity. In addition to being difficult to calculate, mechanisms influencing ion transport efficiency are not well understood.

\[
\text{efficiency} = \frac{\text{analyte\_ion\_flux through the skimmer cone}}{\text{analyte\_ion\_flux through the sampling cone}}
\] (1-4)

As discussed before, many different aspects not only of ICP-MS interface design, but also sample preparation and introduction affect how the sample is ionized and how the non-analyte components affect the analyte transport through the first vacuum stage. Literature suggests that the most significant upstream ICP-MS function affecting analyte transport efficiency is sample vaporization [14,15,16,17,18,19]. In these sample introduction studies, it is common to evaluate analyte transport efficiency without considering the ionization source’s influence on the sample’s degree of ionization and matrix chemistry. As is frequently stated in the literature, increased solvent loading and incomplete desolvation cools the plasma and reduces the degree of ionization, and changes the collisional dynamics in the plasma due to increased hydrogen and oxygen
atom loading from residual sample water [3]. To adequately compare the efficacy of the various wet and dry sample introduction methods, the ionization source’s gas kinetic temperature must be characterized as a function of plasma operating conditions and matrix composition.

1.2.3 Sensitivity

Sensitivity, as defined by IUPAC, is calibration sensitivity (S), which is the slope of the calibration curve (m) in Equation (1-5)[1].

\[ S = mc + S_{bl} \] (1-5)

Based on this definition, where c is the analyte concentration and \( S_{bl} \) is the instrumental blank, sensitivity determinations are only valid as long as the instrument sample composition conditions are consistent with the instrument calibration conditions. An additional limitation of this definition of sensitivity is that the calibration curve must be linear. Mandel and Stiehler[4] proposed a slightly different definition of sensitivity, Equation (1-6) and called it *analytical sensitivity* (\( \gamma \)), where m is the slope of the calibration curve and \( s_a \) is the standard deviation of the measurement.

\[ \gamma = \frac{m}{s_a} \] (1-6)

This definition, although not directly dependent on concentration as in Equation (1-5), still is dependent on concentration-related effects on the magnitude of \( s_a \). Based on the definition of both types of sensitivity discussed, the common requirement for comparable sensitivity values is a linear calibration curve.
As stated earlier, the challenge in using analytical sensitivity as a characteristic for ICP-MS performance comes from the non-linear relationship between analyte concentration and signal standard deviation ($s$). Borisov and co-workers [20] found direct evidence of Cu and Zn concentration control and consistency problems in their laser-ablation sample introduction method that produced non-linear calibration curves. While they state that the calibration curve could be made linear by normalizing to Cu signal or to crater volume, this method does not account or correct for variations in absolute Cu or Zn content that is introduced into the plasma, mass selected and eventually mass detected. The high degree of random error induced by the variable mass loading of the ionizing plasma must affect the reproducibility of $s$ throughout the experiment’s linear (calibration) dynamic range and thus reduce the validity of any reported analytical sensitivity using this method. Ingle and Crouch[4] make the following statement that includes an indirect reference to the significance of the type of error that an uncharacterized plasma source response to matrix composition variability will have on analytical sensitivity.

“If the word sensitivity is used to convey the ability to detect a concentration difference, only the analytical sensitivity should be employed. The ability to detect a concentration difference depends on the ability to detect a readout signal difference, which is limited by readout resolution, noise, or other random errors involved in determining the analytical signal.”
What we can learn from their warning is that known errors caused by matrix effects and variations in plasma conditions should be characterized, and corrections made for them. Eventually, it should be possible to devise a scheme where corrections for random mass-loading variations could be made by monitoring the changes in gas kinetic temperature of the ionizing source if the relationship between analyte mass loading, analyte and matrix concentrations and gas kinetic temperature were characterized. Reduced sensitivity reliability due to inherent ICP-MS design factors further underlines the need for a careful characterization of the effect of matrix composition on plasma gas kinetic temperature by studying ion and atom behavior in the first vacuum stage of an ICP-MS.

### 1.2.4 Detection Limit

One of the most highly advertised performance characteristics of ICP hyphenated methods is its limit of detection. Detection limit is defined as the analyte concentration producing a signal equal to a confidence factor (k) times the standard deviation of the blank (s\(_{bl}\)) eq. (1-7).

\[
DL = ks_{bl}/m \\
\text{(1-7)}
\]

As in other performance definitions depending on the linearity of the calibration curve slope (m), detection limit (DL) is highly dependent not just on the overall linearity of the calibration curve, but most importantly on linearity near the zero concentration intercept. It is often assumed that the calibration curve is linear, but Doner and co-workers [21] found that non-linearity in their Au calibration curve at low concentrations in blood
serum raised their reported limit of detection. In clinical cases, the ICP method limit of detection is often much lower than levels determined to be clinically significant in patients, but this practical distinction matters little to the analytical chemist whose goal is to maximize analytical performance of an ICP instrument. As is true for sensitivity improvement, reducing the standard deviation of the instrument response to a blank depends on careful control of plasma operating conditions and awareness of the quantified impacts of variations in gas kinetic temperature caused by instrumental design factors and operator decisions.

1.2.5 Precision and Accuracy

Precision is reproducibility, and accuracy defines how close to the true value the experimental value falls. A purported expert [22] in instrument design and standardization, the author of the Inorganic Ventures website suggests that “precision of an ICP measurement is a function of many factors that are beyond our control” and then offers several work-around techniques that appear to be designed to compensate for our lack of fundamental understanding of causes of degraded precision in an ICP instrument. When commenting on challenges facing ICP methods regarding accuracy, this expert states: “slight differences in the matrix can cause a considerable systematic error having a definite bias. Internal standardization has been the most common approach toward correcting this problem and this approach does work well in many cases”[22]. It is important to note that internal standardization assumes that all conditions in an ICP instrument remain constant. The previously mentioned ICP “standardology” [sic]
expert[22]. qualifies his lengthy advice regarding matrix effect compensation by internal standardization (IS) and poses the rhetorical question:

“If your plasma temperature were to go up or down is the IS likely to follow the same pattern of intensity change as the analyte? This is where many IS problems occur (i.e. - an IS with the same plasma / temperature behavior as the analyte is difficult [at best] to find for each analyte while avoiding other issues listed...)

It has been well established by Niu and Houk [3] in their comprehensive review paper that critical plasma characteristics such as the initial radiation zone (IRZ), normal analytical zone (NAZ), plasma tail positions and dimensions, as well as the gas kinetic temperature are sensitive to changes in aerosol gas flow rate, power, and water loading. The NAZ contains a majority of the atomic analyte ions; therefore its physical proximity to the first vacuum stage sampling interface is critical to efficient and precise ion transmission to the ion detector. Not surprisingly, differences between the wide ranges of sample introduction methods can greatly influence, often unpredictably, sample composition and these critical ICP operating parameters. Since it is accurate to say that plasma / temperature behavior has not been well characterized and is poorly understood as it depends on plasma operating conditions and matrix composition, it is fair to claim that ICP instrumental precision and accuracy can be improved through a rigorous characterization of the relationship between ion/atom behavior in the first vacuum stage and source conditions such as gas kinetic temperature (or stagnation temperature).
1.3 Matrix Effects

Matrix effects or errors are a type of systematic error and are broadly defined as interferences from non-analyte sample components that affect the analytical signal. According to Ingle and Crouch [4] “matrix errors arise because of differences between the matrix of the analytical sample and the matrix of the external standards or blanks used for calibration.” Matrix effects can be classified into two general categories: blank interferences (or additive interferences), and analyte interferences (or multiplicative interferences). These two types of analytical signal interferences are discussed in detail in the following sections. Currently the most successful methods of compensating for matrix effects involve either duplicating the analytical sample matrix to the calibration, and/or blank matrix (matrix matching), or spiking the analytical sample with known concentrations of analyte to isolate analyte signal response from concomitant signal influences. Both methods avoid dealing with the underlying causes of the interferences and are only useful in simple or known matrices to simultaneously determine a small number of analytes. Seldom does real world sample analysis involve such simple sample composition. Consequently, a more thorough understanding of ICP response to these various types of interferences could make more sophisticated, automated, and preemptive compensation for matrix effects possible. Figure 1-2 shows the effects of blank (b) and analyte (c) type of matrix effects on total signal $E_t$. 
1.3.1 Blank, or Additive Interferences

As shown in Figure 1-2, graph a) indicates the ideal situation where the blank signal, $E_{bk}$ is added to the analytical signal, $E_s$, and yields an accurate (absence of systematic error or bias) total signal, $E_t$. Blank or additive interferences create the situation shown in graph Figure 1-2 b). A matrix component in the sample produced an elevated blank signal, $E'_{bk}$, that was not present (or active) in the standards blank producing $E_{bk}$. This can be caused by improper standards preparation, but most commonly is due to inaccurate matrix matching. If the matrix element contributing to $E'_{bk}$ is present in both the sample and the standards in the same concentration, this condition will be evident by a non-zero calibration curve intercept [4].

![Figure 1-2](image_url)

Figure 1-2. a) no interferences, b) blank interference, c) analyte interference. $E_{bk}$: true blank signal; $E'_{bk}$: apparent blank signal; $E_t$: total signal; $E'_t$: apparent total signal

Blank or additive interference consist of two types: spectral and non-spectral. Spectral interferences (in ICP instruments) are usually directly due to the presence of a
concomitant whose emission or mass overlaps with that of the analyte. Matrix induced spectral interferences can be corrected for or eliminated by reducing the bandpass of the detector. However, this may have the undesirable effect of proportionally reducing the analyte signal. Spectral interferences may especially contribute to the overall matrix effect when analyte and non-analyte components are structurally or chemically similar. Recently, Shen and co-workers have found that although magnetic sector ICP methods require smaller sample sizes and have higher sample throughput, they have “spectral interferences and instrumental blanks [that] are significant and must be addressed [23].” Kotseva and Piperov [24] recognize that, in the LA-ICP-MS (Laser Ablation) analysis of electrolytes in mineral fluid inclusions, “the blank is of great importance, for empirical reading of the many sided uncontrollable interference.” It would be an understatement to claim that effective matrix matching or standard addition methods of compensating for unforeseen blank interferences in characterization of mineral fluid electrolytes is extremely difficult and subject to frequent human error.

Non-spectral blank interferences, like spectral blank interferences, are caused by non-analyte influence of analyte spectral signals. From the literature, it appears that geochemists suffer most significantly from spectral and non-spectral blank interferences due to the inherently unknown composition of their analytical samples from nature. Analytical pre-characterization of samples to determine precise blank matrix composition often is impractical due to the highly variable nature of natural geological specimens. Geochemists such as Mihaljevic and co-workers [25] have reviewed the growing application of ICP methods in geochemistry, but recognize the potentially significant
challenges presented by spectral and non-spectral interferences as they pertain to geologically common elements. Although non-spectral interferences are not as commonly encountered as spectral interferences, isolating the offending concomitant and properly identifying its contribution to matrix errors can prove daunting.

1.3.2 Analyte, or Multiplicative Interferences

Figure 1-2 graph (c) shows an effect of analyte interferences on the true total analyte signal ($E_t$) by suppressing $E'_s$, the apparent analyte signal and expressing interference-biased signal ($E'_t$). Whereas blank interferences have proven the greatest challenge for analytical fields like geochemistry, Zoriy and co-workers have found analyte interferences frequently degrade both accuracy and precision in ultra-trace isotope ratio determinations. Examples include isobaric interference and isotope peak tail overlap [26]. Analyte interferences can be subdivided into two categories, spectral and non-spectral. The much more common non-spectral interferences can be further divided into two types: specific and non-specific. In ICP emission methods, spectral analyte interferences are marked by decreased analyte emission caused by concomitant absorption of emitted photons [4].

Reduction or understanding of non-specific analyte interferences is the most significant potential outcome possible as a result of a full understanding of ionic and atomic behavior in the first vacuum stage interface of an ICP-MS as a function of matrix composition. Analyte/matrix sample chemistry is easily studied in the aqueous phase prior to sample introduction, but is not useful in correcting for non-spectral analyte
interferences because sample analyte/matrix chemistry in the first vacuum stage is subject to dramatically different phase, temperature, charge, and number density conditions. Because the mechanisms leading to physical and chemical (non-specific and specific) interferences are unknown in any environment, save the original pre-sample introduction form, these interferences are the most difficult to predict and correct. Conventional methods such as matrix matching and standard addition often prove ineffective due to the unknown composition of real world samples or the unknown, often non-linear, impact of analyte concentration spiking. Water quality analysts from Phoenix, AZ [27] have resorted to mathematical correction methods to overcome the matrix-enhanced detection of potassium after matrix matching, standard addition, and gradual dilution methods proved cumbersome or ineffective.

1.3.3 Relationship between Velocity, Temperature, and Matrix Effects

Currently, the chemistry which occurs beyond the sampling interface in the first vacuum stage is not well understood due to the unknown influences of supersonic fluid flow, 6,000 K+ temperature extremes, and unknown atomic and ionic densities. Despite the challenges of accurately characterizing such a region, certain “remotely collected” measurements can open the window to a region previously described only by theory and calculations. Laser-induced fluorescence has long existed as a superior analytical method to selectively determine both qualitative and quantitative characteristics of analyte atoms and ions. By collecting and measuring the fluorescence from carefully planned atomic and ionic excitation schemes, we have been able to determine the velocity and temperature of specific spatial regions of the first vacuum stage of an ICP-MS. From this
robust and reproducible data, we can determine the gas kinetic, or stagnation temperature that led to the observed atomic and ionic velocity and temperature profiles. Additionally, the velocity and temperature data, combined with other interface region data from related projects in our research group, give insight into the physical and chemical environment of the instrumental region responsible for delivering analyte to the mass selector and detector. Recent research suggests that the dominant matrix effect on the ion beam in the first vacuum stage expansion is space charge [28], while mass bias and other interference mechanisms appear to dominate elsewhere in an ICP-MS system.

1.4 Summary

While an ever growing list of research publications highlight the expanding application of ICP methods in new fields, an ever-present theme in the literature is the uncertainty in how to best correct for matrix errors. In the past, when ICP method application was limited to the fundamental research corner of analytical chemistry or “black box” commercial applications, perhaps the traditional methods of matrix matching, standard addition, or gradual dilution were sufficient to adequately correct for some of the most common causes of degraded ICP analytical performance. In the last decade however, the explosion in the number of new sample introduction, mass selection, and ion detection methods have increased the potential number of interferences due to blank, analyte, spectral, non-spectral, physical, chemical, and unknown interference combinations as the complexity of sample chemistry increases. In the mean time, understanding about the relationship between the consequences of applying these methods in conjunction with ICP and the fundamental nature of ICP behavior itself has progressed much more slowly.
It is safe to say that innovation has outstripped understanding when it comes to compensating for increasingly complex matrix effects created by increasingly complex hyphenated ICP instruments. Closing the gap between innovation and understanding requires characterization and behavioral understanding of the common denominator in all ICP methods, the interface region between the plasma and the mass spectrometer.
References


   


Chapter 2. Velocity and Temperature Characterization of Metastable Argon (I) in the First Vacuum Stage of an ICP-MS

2.1 Introduction

ICP-MS instruments use an inductively coupled argon plasma as an ionization source. Because it is the most prevalent element entering the interface to the first vacuum stage, we decided to characterize the behavior of argon metastable atoms by measuring the laser-induced fluorescence spectra of the Ar (I) $4s^{3/2} \rightarrow 4p^{5/2}$ transition. Characterization of neutral argon atom provides a good measure of bulk plasma behavior, since according to calculations by Niu and Houk [1], approximately 99.6% of argon remains un-ionized as it passes through the 8,000 K plasma.

![Ar I energy levels diagram](image)

Figure 2-1. Excitation and fluorescence wavelengths of Ar I

A thorough understanding of how the bulk of mass, in the first vacuum stage, behaves is important to understanding the behavior of analyte ions and atoms in the same region and
as a baseline against which we can examine ion behavior. As discussed in the introduction, laser-induced fluorescence is the technique of choice in measuring Doppler velocities and random component line-width “temperatures” The laser-induced fluorescence scheme to detect metastable argon (I) atom is shown in Figure 2-1. This particular species transition can be considered representative of the bulk plasma due to the low degree of carrier gas ionization as discussed earlier. In the following sections, the experimental procedures, parameters, and instruments used to determine spatially resolved argon atom velocity and temperature profiles are outlined and explained.

2.2 Experimental Setup

Figure 2-2 shows the general setup used to collect and measure argon atom fluorescence. It is important to point out that the excitation and collection occurs inside the first vacuum stage in order to duplicate the physical environment found in a generic first vacuum stage region.

![Figure 2-2. Schematic of LIF excitation & collection geometry](image)

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There is a 45° orientation of the excitation and collection optics to the supersonic flow axis. This is done to prevent the optics from disrupting the supersonic expansion behavior. This 45-degree orientation is taken into account in the calculation of Doppler velocities and has also allowed us to determine both radial and axial velocity components of the expansion, and to use those vectors to calculate the location and shape of the expansion from the sampling orifice.

2.2.1 Calibration of Spectroscopic Ruler

In order to measure laser-induced fluorescence and determine velocity and line-width in a meaningful way, a fixed scale of reference must be established. In this series of experiments, a Fabry-Perot confocal etalon is used and must be calibrated to known frequency spacing. While there are many ways to determine this value, this research used the Doppler-free absorption spectra of rubidium to determine the frequency spacing of our confocal etalon shown in Figure 2-3. In order to calibrate the etalon, the interference

Figure 2-3. Photograph of confocal Fabry-Perot etalon
fringes from the etalon are correlated with the known frequency spacing of the rubidium atom using a least-squares-fit.

A Doppler-free saturation spectrum was collected using the setup shown in Figure 2-4. The quality of the rubidium atom Doppler-free spectrum depends on the degree of pump and probe beam overlap inside the rubidium gas cell shown in Figure 2-4. The procedures and equipment used to calibrate the interferometer using the rubidium saturated absorption spectrum are described in detail in Patterson’s M.S. thesis [2].

![Figure 2-4. Doppler-free saturation spectroscopy experimental setup](image_url)

The spectra collected are shown in Figure 2-5. The Doppler-broadened absorption line is shown by Figure 2-5(b) and is produced by the reference beam interaction with rubidium atoms in the gas cell. Figure 2-5(a) is the result of the overlap between the counter-propagating pump and probe beams. The lamb dips occur as a result of rubidium atoms with zero velocity in relation to the direction of the counter-propagating beams reaching
an absorbance transition. The Doppler-free spectrum is determined by subtracting the background (b) from the lamb dip-containing absorption signal (a) to produce a baseline-resolved rubidium Doppler-free saturation spectrum indicated Figure 2-5(c).

Figure 2-5. Rubidium atom Doppler-free saturation spectroscopy experimental results. a) saturated absorption spectrum; b) Doppler-broadened spectrum; c) Doppler-free spectrum

The rubidium Doppler-free spectrum is shown in Figure 2-6 and correlates well with literature values (Table 2-1) as well as with previous experimental results from our group [2]. Figure 2-7 shows the overlay of a Doppler-free rubidium spectrum with interferometer fringes produced by the Fabry-Perot etalon. By performing a least squares fit between the known rubidium fringe spacing and measured etalon interferometer
spacing, we calculated the free spectral range of the etalon to be 751.7 MHz by performing a least squares fit of the rubidium fringe spacing to the etalon fringe spacing (Figure 2-8). Knowing the calibration of the etalon allows for the creation of a spectral ruler to measure fluorescence line widths as well as Doppler shifts.

Figure 2-6. Rubidium Doppler-free spectrum with peak assignments (ascending scan)
Figure 2-7. Rubidium spectrum and etalon interference fringes (ascending scan)

Figure 2-8. Least squares fit of interferometer fringe spacing to Rb spectrum spacing
2.2.2 Argon Doppler Velocity

Perhaps the most important characteristic of atoms and ions in the first vacuum stage is velocity. From an accurate terminal velocity measurement in the first vacuum stage, the unambiguous gas kinetic temperature of the source of can be determined. According to Hieftje and co-workers [3], electron-energy distributions, gas-kinetic temperatures, ground-state analyte atom and ion number densities, electron concentrations, and densities of excited-state Ar species are critical identifying features of source conditions. Despite the importance of gas kinetic temperature information in any study of ICP-MS behavior, there remains a high degree of reliance on theoretical and indirectly determined gas kinetic temperatures [4,5,6,7] to characterize the plasma source.

In order to quantify the laser-induced fluorescence Doppler shift of argon atoms in the first vacuum stage (Figure 2-9), the argon atom fluorescence from an iron-argon hollow cathode lamp (WL-22611, Imaging and Sensing Technology, Horseheads, NY) operated
at 5 mA and 250 VDC served as a representative stationary population marker. The excitation source is an external cavity tunable diode laser (2010, EOSI, Boulder, CO) piezo-scanned through the fluorescence resonance frequency by a function generator (Hewlett Packard 33120A Arbitrary Waveform Generator) triangle wave function. Because the argon atoms are contained in the hollow cathode lamp, the center position of the fluorescence represents the zero mean velocity argon population. The observed frequency shift, $\Delta \nu$, (accounting for observation angle, $\theta$) of the argon fluorescence, $\lambda_{\text{max}}$, in the expansion region in relation to the fluorescence in the hollow cathode lamp stationary reference can be converted to a velocity (Equation 2-1 and Figure 2-9). A thorough background discussion of laser-induced fluorescence Doppler velocity ($V_D$) determination is covered in Patterson’s thesis [2].

$$V_D = \lambda_{\text{max}} \Delta \nu / \cos (\theta)$$  \hspace{1cm} (2-1)

2.2.3 Argon “Temperature”

The line width of fluorescence represents the random motion component of argon atoms in the supersonic expansion. Despite the absence of local thermal equilibrium in the supersonic expansion, Equation (2-2) shows how a temperature may be calculated from the FWHM of the Doppler broadened line ($\Delta v_D$) where $M$ is the molar mass and $R$ is the gas constant.

$$T = [(\Delta v_D/2)^2][M/(2 \ln (2R))]$$  \hspace{1cm} (2-2)
While spatial temperature profiles are not as useful as spatial velocity profiles in studying the effects of plasma operating conditions and matrix composition, temperature profiles provide valuable corroborating evidence of shock structure and thermal heterogeneity in analytically important regions of the first vacuum stage of an ICP-MS.

Figure 2-10. Stationary reference and expansion fluorescence collection setup

2.2.4 Laser-induced Fluorescence – Emission Discrimination

One of the more significant challenges in characterizing the plasma in an ICP-MS is a low signal-to-noise ratio due to high background caused by analyte and matrix emission. Coincident with the desired laser-induced fluorescence at 842.546 nm are competing argon emission lines at 842.465 nm and 840.821 nm. Detecting the comparatively weak fluorescence signal at 842.465 nm with strong competing emission lines required the use
of a narrow bandpass filter (CVI Laser, LLC, Albuquerque, NM), a 99% opaque neutral density filter (Corion Filters, Spectra-Physics, Durham, UK), and signal modulation and lock-in detection using a lock-in amplifier (Stanford Research Systems SR830 DSP Lock-in Amplifier). The excitation laser was modulated at approximately 1kHz using an optical chopper (SCITECH Instruments). The stationary reference signal was similarly modulated and detected using an analog lock-in amplifier (Stanford Research Systems SR510 Lock-in Amplifier). An overview of the experimental setup is shown in Figure 2-10 and has been described previously [8].

2.2.5 Fluorescence Collection and Measurement

The determination of velocity and “temperature” from raw experimental data requires several processing steps. Data were collected with a National Instruments BNC-2110 analog-to-digital converter on a Pentium® class personal computer. Four data channels were collected simultaneously: the interferometer signal from the Fabry-Perot confocal etalon shown in Figure 2-3 and amplified by a current amplifier (Stanford Research Systems SR510 Low-Noise Pre-Amplifier); the function generator signal output; the lock-in detected optogalvanic effect signal from the Fe/Ar hollow cathode lamp; and the laser-induced fluorescence from the first vacuum stage collected by a Hamamatsu photomultiplier tube and lock-in detected and amplified by the SR830 lock-in amplifier. The function generator was set for a triangle wave function at 10 mHz (10^-3 Hz) frequency, 2.5 VPP amplitude, and a variable offset as required. All time constants were set to 300 ms or less to avoid over-filtering effects. All lock-in amplifier phase settings were optimized and verified by -90° offset tests. Examples of the raw data and the pre-fit
formatted Microsoft™ Excel data files are shown in Appendix A. All data sets consist of five complete scan cycles at 10 mHz/cycle with data collected once every 0.05 seconds. Creation of the frequency ruler with the function generator output for each scan was accomplished by first associating the piezoelectric voltage reported by the function generator with the interferometer fringe maxima shown in Table 2-1. The Function, Function Gen^2, and Freq Ruler data columns are fit using the LINEST function from Microsoft™ Excel to produce second order equation coefficients (Table 2-2), which when related to the function generator output, produce a correlated frequency axis (υ) to measure Doppler shifts and line widths as shown in Equation 2-3.

Table 2-1. Creation of frequency ruler using interferometer fringes and etalon spacing

<table>
<thead>
<tr>
<th>Fringe #</th>
<th>Function Gen</th>
<th>Function Gen^2</th>
<th>Freq. Ruler (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-1.66</td>
<td>2.7556</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>-1.462</td>
<td>2.137444</td>
<td>751.7</td>
</tr>
<tr>
<td>2</td>
<td>-1.257</td>
<td>1.580049</td>
<td>1503.4</td>
</tr>
<tr>
<td>3</td>
<td>-1.252</td>
<td>1.567504</td>
<td>2255.1</td>
</tr>
<tr>
<td>4</td>
<td>-1.045</td>
<td>1.092025</td>
<td>3006.8</td>
</tr>
<tr>
<td>5</td>
<td>-0.835</td>
<td>0.697225</td>
<td>3758.5</td>
</tr>
<tr>
<td>6</td>
<td>-0.645</td>
<td>0.416025</td>
<td>4510.2</td>
</tr>
<tr>
<td>7</td>
<td>-0.459</td>
<td>0.210681</td>
<td>5261.9</td>
</tr>
<tr>
<td>8</td>
<td>-0.271</td>
<td>0.073441</td>
<td>6013.6</td>
</tr>
<tr>
<td>9</td>
<td>-0.088</td>
<td>0.007744</td>
<td>6765.3</td>
</tr>
<tr>
<td>10</td>
<td>0.105</td>
<td>0.011025</td>
<td>7517</td>
</tr>
<tr>
<td>11</td>
<td>0.286</td>
<td>0.081796</td>
<td>8268.7</td>
</tr>
</tbody>
</table>

Once the fluorescence data are calibrated to a frequency axis, the stationary reference and the expansion fluorescence can be compared and Doppler shifts calculated by fitting Gaussian functions to the stationary and Doppler shifted fluorescence signals. An
example of the Mathcad® fitting worksheets authored by P. B. Farnsworth is included in Appendix B.

Table 2-2. Example coefficients from LINEST fit

<table>
<thead>
<tr>
<th></th>
<th>3824.59</th>
<th>7132.804</th>
</tr>
</thead>
<tbody>
<tr>
<td>-296.7847</td>
<td>174.97045</td>
<td>88.08376</td>
</tr>
<tr>
<td>3824.59</td>
<td>255.8883</td>
<td>88.08376</td>
</tr>
<tr>
<td>7132.804</td>
<td>88.08376</td>
<td>88.08376</td>
</tr>
<tr>
<td>0.9957587</td>
<td>#N/A</td>
<td>#N/A</td>
</tr>
<tr>
<td>195.1372</td>
<td>#N/A</td>
<td>#N/A</td>
</tr>
<tr>
<td>1056.4986</td>
<td>9</td>
<td>#N/A</td>
</tr>
<tr>
<td>80459856</td>
<td>342706.9</td>
<td>#N/A</td>
</tr>
</tbody>
</table>

\[ \nu = \text{FunctGen} \times 3824.59 + \text{FunctGen}^2 \times -296.79 + 7132.80 \quad (2-3) \]

The Gaussian fitting worksheet returns the average velocity (V), velocity standard deviation (\(\sigma_v\)), average temperature (T), and temperature standard deviation (\(\sigma_T\)) based on five measurements. For expansion regions with bimodal behavior, P. B. Farnsworth wrote a Gaussian fitting Mathcad® worksheet that fit the bimodal peak to two Gaussians. Accordingly, it returned two average temperatures, two average velocities, and standard deviations for each velocity and temperature average. Additionally, the dual Gaussian fit worksheets have been modified to return relative area-under-the-curve values for the two component Gaussian fits. An example of this worksheet can also be found in Appendix B. Sample calculations, formatted Excel data, and fitted single, dual, and area worksheets are included in Appendix A.
2.3 Results and Discussion

The following data are the result of an initial set of exploratory experiments designed to determine regions of analytical significance and the degree of influence that common ICP plasma operating condition choices have on atomic behavior beyond the sampling interface. These data represent a starting point for further exploration and characterization by those researchers who will continue this work. In these first experiments, the effects of ICP incident power, nebulizer rate, and matrix composition choices on argon (I) velocity and temperature distributions are studied. Table 2-3 outlines the standard experimental conditions for these experiments. The effect of varying parameters from the standard conditions is explored and reported. The ICP torch is oriented horizontally. For orientation purposes, the Z-axis corresponds to the axial flow direction of supersonic expansion; the Y-axis corresponds to up and down; and the X-axis is perpendicular to the Y-axis and parallel to the ground.

<table>
<thead>
<tr>
<th>Table 2-3. Standard ICP operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP Incident Power</td>
</tr>
<tr>
<td>Nebulizer Rate</td>
</tr>
<tr>
<td>Sample Composition</td>
</tr>
<tr>
<td>Torch Outer Gas rate</td>
</tr>
<tr>
<td>Torch Central Gas rate</td>
</tr>
<tr>
<td>Torch – Cone Distance</td>
</tr>
<tr>
<td>First Vacuum Stage Pressure</td>
</tr>
</tbody>
</table>

2.3.1 Velocity Profiles for Metastable Argon (I) Atom

Comprising over 99% of the mass entering the first vacuum stage in an ICP-MS, argon (I) atoms make a natural choice for first characterization efforts.
2.3.1.1 Axial Velocity Profiles

The first experiments were designed to profile velocity distributions axially downstream from the sampling cone inside the first vacuum stage. Using stepper motor controlled excitation-collection optics, we scanned from $z = 2$ mm to $z = 20$ mm in 1 mm increments. This scan was performed under standard operating conditions with ultra-pure Millipore® filtered water as the sample (>18 MΩ Resistivity). The objective of this experiment was to determine 1) a baseline argon (I) velocity profile under standard plasma operating conditions with no matrix concomitants; 2) the gas kinetic temperature of the plasma source from the terminal velocity in the supersonic expansion; and 3) the location and thickness of the Mach disk. The results of this scan are shown in Figure 2-11. The maximum velocity occurs around $z = 8$ mm downstream at approximately 2300 m/s. This experimental value corresponds well to theoretical predictions [9]. The expansion remains clearly single-mode until $z = 10$ mm downstream, where emergence of the slower, “hot” atom population becomes visible as an asymmetric shoulder in the expansion fluorescence signal (Figure 2-12). From the maximum (terminal) velocity measured in the single-mode region of the supersonic expansion, $v_{\text{inf}} = 2295 \pm 20$ m/s, and applying Equation (1-3), we calculate the stagnation temperature in the source to be $5061 \pm 45$ K. This is consistent with theoretical predictions and experimental findings of others [2,9,10,11,12].

Although clearly visible, the slow-hot distribution’s fluorescence could not be fit until $z = 11$ mm downstream, when its amplitude was at least 15% that of the fast-cold (narrower
distribution than slow-hot) population’s fluorescence signal. The relatively large error bars at the boundaries of the bimodal behavior are consistent with the correspondingly

![Graph of velocity distribution](image)

Figure 2-11. Argon (I) axial velocity profile, standard conditions, H₂O sample 35% = 1.4 L/min, 15% = 0.6 L/min. V1: fast-cold population; V2: slow-hot population.

high uncertainty in Gaussian curve-fitting two population’s fluorescence signals -- when one is a small size fraction of the other. We have determined that this is an artifact of the curve-fitting algorithm and is consistent with results we present elsewhere. The position and size of the Mach disk became immediately evident as we plotted the Ar (I) axial velocity distribution profile.
Figure 2-12. Ar (I) bimodal distribution (~4000 MHz) at z = 10mm, OGE: stationary ref.

Figure 2-13. Ar (I) bimodal distribution (~3000 MHz) at z = 18mm, OGE: stationary ref.
As discussed earlier, the bimodal region is approximately 8 mm thick from visual
detection of emergence of the slow-hot population to the disappearance of the fast-cold
population. For proof of the Mach disk dimensions, it is apparent by visual inspection of
the argon (I) fluorescence in Figure 2-13, the much diminished, but still present cold
distribution is visible around 3000 MHz as a small, sharp protrusion from the otherwise
broad hot population signal. Despite evidence of a laser mode hop, which shifted the
stationary optogalvanic effect (OGE) reference center position from around 5000 MHz to
5500 MHz, the Doppler shift of the fast-cold population remains approximately 2500
MHz and the slow-hot population shift remains approximately 500 MHz. This provides
assurance of the reliability of this experimental setup and its results despite occasional
diode laser mode instabilities.

The downstream position of a Mach disk ($x_m$) in a free supersonic jet expansion can be
estimated with Equation (2-4) where $d$ is the diameter of the sampling orifice, $P_b$ is
background pressure, and $P_o$ is atmospheric pressure. Substituting values for our
experimental setup and physical location 4500 feet above sea level: $d = 1$ mm, $P_o = 650$
torr, $P_b = \sim 1$ torr; the predicted position for the Mach disk is 17 mm downstream.

$$x_m = 0.67 \ d \ (P_o/P_b)^{1/2} \quad (2-4)$$

Based on the Ar (I) axial velocity distribution profile shown in Figure 2-11, the predicted
$x_m$ corresponds well with the downstream Mach disk boundary, but fails to account for
almost 7 mm of bimodal shock structure upstream of its predicted position. Even a 50%
increase in background pressure (1.5 torr) only moves the predicted Mach disk position up to 14 mm, a full 3-4 mm too far downstream compared to its observed location. There is a noticeable void in the literature discussing thickness of the Mach disk. This lack of understanding about the location and dimension of a shock structure could create significant analytical errors and loss of instrumental sensitivity if the skimmer cone is placed too far downstream in this region of bimodal gas behavior. Through the use of a Gaussian area integration Mathcad® worksheet provided by P.B. Farnsworth, the Mach disk’s changing population composition was determined and is shown in Figure 2-14.

Figure 2-14. Composition of Mach disk, z = 12 mm to 17 mm (standard conditions)
Low minority signal amplitudes at the boundaries (z = 11 mm and z = 18 mm) preclude accurate integration of the population component fitted Gaussians. However, this Mach disk structure indicates that an atom experiences a gradual 5 to 8 mm long transition between the zone of silence conditions (>2300 m/s) and background gas conditions (<1000 m/s).

2.3.1.1.1 Effect of Nebulizer Rate

Changes in nebulizer rate, as previously discussed, have well-established effects on ICP-MS sensitivity. While the magnitude of the effect of changing nebulizer (and solvent loading) on observed sensitivity has been well documented in an attempt to find one set

![Figure 2-15. Effect of reducing nebulizer rate 28% from standard conditions 35% = 1.4 L/min, 15% = 0.6 L/min, V1: fast-cold population; V2 slow-hot population.](image_url)
of “robust” plasma operating conditions [13], the effect of changing nebulizer rates on the plasma stagnation, or gas kinetic temperature has not been well characterized. Figure 2-15 shows the velocity distribution profile effect of reducing the nebulizer rate from 35% (1.4 L/min) to 15% (0.6 L/min). The effect of reducing the nebulizer rate approximately from 1.4 L/min to 0.6 L/min increases the terminal velocity, \( v_{\text{inf}} \), at \( z = 8 \) mm downstream in the zone of silence from \( 2295 \pm 20 \) m/s \((5061 \pm 45) \) K to \( 2648 \pm 17 \) m/s and corresponds to a source gas kinetic temperature of \( 6922 \pm 45 \) K, a 37% increase in source temperature.

Figure 2-16. Composition of Mach disk, \( z = 10 \) mm to 18 mm (0.6 L/min nebulizer)
Figure 2-17. Ar (I) bimodalality (~4000 MHz) at z =10 mm (0.6 L/min nebulizer)

Figure 2-18. Ar (I) bimodalality (~3500 MHz) at z=18 mm (0.6 L/min nebulizer)
Corresponding with significantly higher source temperatures, the size and composition of the Mach disk undergoes significant changes as well. Because equations predicting the position of the Mach disk are gas and temperature independent, the predicted position does not change.

The thickness of the Mach disk increases slightly and structure changes significantly as is shown in Figure 2-16. As shown in Figures 2-17 and 2-18, the bimodal character is detectable as far upstream as $z = 10$ mm and as far downstream as $z = 18$ mm. An interesting result of reducing the nebulizer rate to 0.6 L/min is the compositional change of the bimodal velocity distribution. At 1.4 L/min nebulizer, the bimodal Ar atom population at the detectable onset of the Mach disk 12 mm downstream had approximately 55% fast-cold atoms, and approximately 45% slow-hot atoms. At 0.6 L/min nebulizer, the bimodal Ar atom population 12 mm downstream was approximately 67% fast-cold atoms, and approximately 33% slow-hot atoms – an apparent 22% increase of fast-cold atoms surviving 12 mm downstream as the result of reducing nebulizer rate 28%. While we predicted that reducing nebulizer rate increases plasma gas kinetic temperature, we did not anticipate this magnitude of change in bimodal atom population distribution.

2.3.1.1.2 Effect of Incident Power

As it was found that changes in nebulizer rate have predictable effects on the plasma gas kinetic temperature and significantly affect neutral species behavior in the first vacuum stage expansion, we expect changes in ICP incident power to likewise affect plasma gas
kinetic temperature and neutral species behavior. In this series of experiments, we varied ICP incident power, holding all other plasma operating conditions and matrix composition constant and measured Ar (I) velocities 8 mm downstream, well within the single mode population zone of silence. The first power experiment involved increasing ICP incident power from 850 W to 1250 W in 50 W increments. Figure 2-19 shows that increasing power 47% results in an 11% increase in velocity. Having established that power fluctuations less than 50 W do not significantly affect observed Ar (I) velocities, we explored the effect of ICP incident power on the Ar (I) velocity profile. Axial velocity profiles were collected from 2 mm to 20 mm
downstream at 850 W and 1250 W. The results are shown in Figure 2-20. At 850 W and z = 8 mm downstream the terminal velocity ($v_{\text{inf}}$) was $2091 \pm 51$ m/s compared to $2295 \pm 20$ m/s at 1250 W and the same downstream position. The lower $v_{\text{inf}}$ under 850 W conditions corresponds to a gas kinetic temperature of $4091 \pm 102$ K compared to $5061 \pm 45$ K at 1250 W measured in the same axial position.

![Axial Ar velocity profile](image)

**Figure 2-20.** Axial Ar velocity profile, V1: fast-cold population; V2: slow-hot population; 35% = 1.4 L/min, 15% = 0.6 L/min

In addition to the lower velocities and lower calculated source temperature, Ar (I) signal intensities dropped dramatically beyond 12 mm downstream with no evidence of the emergence of bimodal velocity distributions. In fact, Ar (I) signal between 14-16 mm
downstream was indistinguishable from background noise. The observed ~250 m/s velocity difference at \( z = 8 \) mm between the 1250 W and 850 W power settings is consistent with the incident ICP power experiment results shown in Figure 2-19. The Mach disk was not detectible due to low Ar (I) fluorescence. We attributed low Ar (I) fluorescence to the incident ICP power. Because there was no detectible Mach structure, shock structure compositional information at 850 W was not obtained. Research by Stepan and co-workers [14] found that increasing ICP incident power to 1500 W resulted in ICP emission that was less sensitive to changes in nebulizer rate and matrix composition. However, arbitrary changes in ICP incident power may result in undesired changes in first vacuum stage expansion behavior and structure.

Figure 2-21. Effect of adding 50 ppm lithium matrix, 35% = 1.4L/min, V1: fast-cold population; V2: slow-hot population
2.3.1.3 Effect of Matrix Composition

We sought to quantify the effect of adding 50 ppm lithium matrix concomitant to our pure H₂O analyte. This series of experiments aspirated a 50 ppm lithium solution into the plasma under otherwise standard operating conditions (1250 W incident ICP power, 1.4 L/min nebulizer rate). The effect of the lithium matrix on the axial velocity profile of Ar (I) is shown in Figure 2-21. The terminal velocity \( v_{\text{term}} \) at \( z = 8 \) mm downstream for Ar (I) with 50 ppm Li is \( 2350 \pm 15 \) m/s. This velocity corresponds to a plasma gas kinetic temperature of \( 5307 \pm 34 \) K, a slight increase from \( 5061 \pm 45 \) K under
standard conditions (1250 W, 1.4 L/min, H₂O). The change in Mach disk composition due to the addition of a low concentration of lithium can be seen in Figure 2-22.

Addition of low concentrations of lithium matrix resulted in a slight increase in terminal velocity and a corresponding ~250 K increase in source gas kinetic temperature. Additionally, the compositional structure at the onset of the Mach disk is approximately 62% fast-cold atoms and 38% slow-hot atoms. This represents a net increase of the fast cold atom population 12 mm downstream compared to the population under standard conditions, but not as large of a population increase as is seen when reducing nebulizer rates. This slight, yet significant matrix-induced source temperature increase spawns more questions than answers about the influence of non-analyte species. Matrix element influences on analyte behavior in the first vacuum stage expansion and source gas kinetic temperature can be more fully characterized and potentially explained by answering two questions: 1) what is the effect of increasing matrix element mass on analyte behavior and observed gas kinetic temperature; and 2) what is the effect of matrix element concentration on analyte behavior and source temperature? The mechanisms leading to matrix effects remain poorly understood.

2.3.1.2 Radial Velocity Profiles

The following results represent a third dimension to the first vacuum stage expansion characterization effort. Radial velocity profiles, while not as analytically important as axial measurements, provide valuable evidence regarding the lateral dimensions of the supersonic expansion. As the supersonic expansion slows and begins to collide with
background gases in the first vacuum stage, in addition to the previously discussed axially oriented Mach disk, a lateral shock structure called the “barrel shock” forms as the lateral expansion slows and collides with background gasses. Similar in structure to the Mach disk, the barrel shock can be located, measured, and its population composition determined through measurement of Ar (I) Doppler velocities. The effect of changing plasma operating conditions and matrix composition on the width of the zone of silence as well as the thickness and population composition of the barrel shock should assist in resolving the debate about the role of space-charge or mass-bias, as the more significant matrix effect in the first vacuum interface expansion [15, 16]

2.3.1.2.1 Characterization of the Barrel shock

Radial velocity profile experiments were collected at z = 10 mm downstream along the y-axis. Because of the 45º orientation of our excitation optics in relation to the axial direction, as shown in Figure 2-23, it is necessary to scan in the vertical, or y-axis direction to collect radial velocity data that is free from excitation Doppler shifts. In later discussion it is shown how purposely collecting excitation Doppler shifts in the x-axis direction provides important information about the shape of the expansion at the sampling orifice. The first radial experiment was under standard conditions with pure water. Figure 2-24 shows the radial velocity profile of Ar (I) at z = 10 mm.
Figure 2-23. Excitation (horizontal) and collection (vertical) optics

Figure 2-24. Radial velocity profile of Ar (I) under standard conditions (@ z = 10 mm)

35% = 1.4L/min, V1: fast-cold population; V2: slow-hot population.
The lateral shock structure, the barrel shock, began to form and was detectable 2 mm radially from the z-axis. As with the emergence (and disappearance) of the Mach disk, the uncertainty associated with fitting minority boundary populations with two Gaussians leads to the large error bars near the inner and outer boundaries of the barrel shock. Additionally, background noise in the negative radial direction is higher than in the positive radial direction due to the vertically oriented (Figure 2-23) collection optics imaging the sampling orifice when located in the – y-axis region. Data in the + y-axis region was collected every 0.25 mm to provide high-resolution barrel shock structure information.

Figure 2-25. Composition of barrel shock, y = 2 mm to 6 mm (standard conditions)
Under standard conditions at $z = 10$ mm downstream, the maximum velocity occurs near the $z$-axis and is $2346 \pm 25$ m/s. The barrel shock forms with an initial composition of approximately 78% fast-cold atoms and 22% slow-hot atoms and persists radially through $y = 6$ mm (Figure 2-25). $Z = 10$ mm was chosen for the downstream location radial profiles because of the common placement of the second stage skimmer interface 10 mm downstream.

2.3.1.2.2 Effect of Nebulizer Rate

It is reasonable to expect that the radial velocity distribution would behave similarly to the axial velocity distribution with a change in nebulizer rate. Figure 2-26 shows that

![Figure 2-26. Effect of changing nebulizer rate, 35% = 1.4L/min, 15% = 0.6 L/min; V1: fast-cold population; V2: slow-hot population](image-url)
decreasing the nebulizer rate from 1.4 L/min to 0.6 L/min results in an increase in maximum velocity from $2346 \pm 25$ m/s under standard conditions to $2692 \pm 17$ m/s under reduced nebulizer rate conditions. Unlike the observed nebulizer rate induced composition change in the Mach disk, the barrel shock composition appears virtually unchanged (Figure 2-27) despite a reduction in nebulizer rate and approximately 15% increase in maximum atom velocities. Changing nebulizer rates appears to have less of an effect on off-axis atomic behavior than axial flow atomic behavior.
2.3.1.2.3 Effect of Incident Power

At 850 W ICP incident power, the Ar (I) population in our observation volume fluoresced below our detection limits and made detection and measurement of the barrel shock impossible. Additionally, because the axial velocity profiles at 850 W indicated a lack of shock structure and significant regions (12 to 18 mm downstream) with no detectible Ar (I) fluorescence, the effect of incident power on the radial velocity profile of Ar (I) was not determined.

Figure 2-28. Effect of adding 50 ppm lithium matrix, 35% = 1.4L/min, V1: fast-cold population; V2: slow-hot population
2.3.1.2.4 Effect of Matrix Composition

Adding 50 ppm lithium resulted in unexpected effects on Ar (I)’s axial velocity profile and Mach disk composition. Combined with Ar (I)’s observed relative barrel shock insensitivity to the effects of changing nebulizer rates, we collected the radial velocity profile with the addition of 50 ppm lithium. (Figure 2-28) What is apparent in both axial and radial velocity distributions, upon adding 50 ppm lithium, is that maximum velocities increase slightly while shock structure remains relatively unchanged. Additionally, the presence of lithium seems to increase the noise on the fluorescence signal that manifests itself in this data as the result of poor Gaussian fits. The observed decrease in signal intensity, resulting in lower fluorescence signal to noise, is consistent with lithium matrix effect studies performed by Lehn and co-workers [17].

Based on results in the literature and in our research, future characterization of atomic (and ionic) behavior in the first vacuum stage should include two and three-variable factorial experiments designed to quantify the effect and significance of changes in plasma operating conditions and matrix composition on zone of silence width, as well as analyte and non-analyte ion beam widths in the first vacuum stage expansion. The collection of high-resolution (~0.25 mm increment) radial velocity profiles at common second stage skimmer interface distances for species of interest will definitively show the effect of incident power, nebulizer rate, and matrix composition on atomic, ionic beam, and bath gas behavior and structure.
2.3.1.2.5 Hemispherical Expansion Validation

The first vacuum stage expansion is often approximated and modeled as a free supersonic jet expansion. The free supersonic jet expansion has been extensively modeled and is well characterized [18,19]. Because conditions in the first vacuum stage interface do not exactly match the conditions of an ideal free supersonic jet expansion (i.e. presence of ion-induced coulombic forces), it is important to characterize the expansion for the neutral bath gas, using Ar (I) as a marker, in order to validate the assumption that the bulk expansion behaves in accordance with theoretical models. Due to the 45° orientation of our excitation optics in the x-z plane, scanning in the x-axis direction results in a radial profile that is Doppler shifted with respect to the 45° orientation of the collection optics in the y-z plane. Figure 2-29 shows the geometry for the radial Doppler velocity experiment.

Flow Centerline (Z-axis)

![Diagram showing flow centerline and velocity vectors](image)

Figure 2-29. Calculation of velocity vectors in first vacuum stage
$V_1$ equals $V_2$ and these represent the true expansion vectors of the expansion at two points with $z_1 = z_2$ and $x_1 = -x_2$. $\Theta_D$ is the Doppler-shifted observation angle, $\Theta_v$ is the angle between expansion vectors with velocities $V_1$ and $V_2$ and the axial centerline ($z$-axis). In order to ensure a clean set of Doppler-shifted velocities, the $y$ and $x$-axis radial scans were performed under standard conditions within the zone of silence at $z = 8$ mm downstream, prior to any shock structure, and radially within the inner boundaries of the barrel shock from $x = +2.5$ mm to $x = -2.5$ mm. The results of these scans are shown in Figure 2-30.

**Figure 2-30.** Radial ($x$, $y$) Ar (I) Doppler velocities $z = 8$ mm downstream
The results of applying equations (Appendix C) used to resolve $V_{\text{obs1}}$ and $V_{\text{obs2}}$ into velocity vector components $V_x$ and $V_z$ are shown in Figure 2-31.

![Graph showing velocity vectors](image)

Figure 2-31. First vacuum stage Ar I expansion velocity vectors, the sampling orifice is at $z = 0$ mm.

The expansion vectors in Figure 2-31 demonstrate the supersonic expansion is spherical and originates from a point approximately 1 mm downstream from the calibration point of our excitation/collection optics (0.5 mm upstream of the orifice exit). Since our sampling orifice is 1 mm in diameter, this data validates the assumption that the neutral Ar (I) supersonic expansion is spherical and thus agrees fairly well with free supersonic jet expansion theory.
2.3.2 Temperature Profiles for Metastable Argon (I) Atom

The following data represent the random component of motion, or “temperature” profiles of argon (I) atom resulting from changes in nebulizer rate, ICP incident power, and matrix composition. Literature suggests there is competition between coulombic and gas kinetic forces as the primary interference mechanism in the first vacuum stage expansion depending on downstream distance, sample composition, and upstream ionizing source conditions [17]. It is important to note that the temperatures reported are the result of the approximate 50% / 50% convolution of perpendicular temperatures and parallel temperatures due to the 45º excitation and collection angle in relation to the axial flow direction.

2.3.2.1 Axial Temperature Profiles

Figure 2-32 shows the axial temperature profile of argon (I) atom under standard plasma operating conditions and pure water sample. The bimodal character of the Mach disk region between z = 11 mm and z = 17 mm downstream is evident, and the poor Gaussian fit of Mach disk boundary minority populations, resulting in high error bars at 11 mm and 17 mm, is consistent with previous discussions. The fast-cold population temperature corresponding with the expansion terminal velocity ($v_{\text{int}}$) at z = 8 mm downstream is 223 ± 21 K, the lowest temperature found in the first vacuum stage expansion under standard conditions. This value is higher than the theoretical free supersonic jet expansion value (~150 K) calculated by Niu and Houk [1] using Equation (2-5) and is consistent with the difference between our experimentally measured source gas kinetic temperature (5061 ± 45 K) and their calculated (~5000 K) source gas kinetic temperature. $T_o$ is the
temperature outside the sampler, $T$ is the temperature inside the jet at position $x$, corresponding to Mach number ($M$) calculated by Equation (2-6), $\gamma$ is the ratio between $C_p$ and $C_v$, (for argon 1.667), and $D_o$ is the sampling orifice diameter.

$$T_o / T = 1 + M^2 (\gamma - 1) / 2$$  
(2-5)

$$M = 3.26(x / D_o)^{2/3} - 0.61(x / D_o)^{-2/3}$$  
(2-6)

By quantifying the effect of changing plasma operating conditions and matrix composition on the minimum expansion temperature (at terminal velocity position), we gain a direct understanding of the relationship between instrument operating parameter

![Graph](image)

Figure 2-32. Argon (I) axial temperature profile, standard conditions, H$_2$O sample 35% = 1.4 L/min; T1: fast-cold population; T2: slow-hot population.
choices and effect of bath gas flow behavior on observed changes in instrument sensitivity.

2.3.2.1.1 Effect of Nebulizer Rate

Figure 2-33 shows the effect of reducing nebulizer rate from 1.4 L/min (standard conditions) to 0.6 L/min. The measured Ar (I) atom population temperature corresponding to the terminal velocity position \((z = 8 \text{ mm})\) is \(316 \pm 5 \text{ K}\) compared to \(223 \pm 21 \text{ K}\) under standard conditions.

![Figure 2-33. Axial argon (I) temperature profile at 1.4 L/min (35%) and 0.6 L/min (15%) Black markers are temperatures under reduced nebulizer conditions](image-url)
A reduction in nebulizer rate from 1.4 L/min to 0.6 L/min resulted in an approximately 42% increase in first vacuum stage expansion temperature at z = 8 mm compared to a approximately 37% increase in upstream source gas kinetic (stagnation) temperature.

2.3.2.1.2 Effect of ICP Incident Power

Figure 2-34 shows the effect of reducing ICP incident power from 1250 W to 850 W. The change in fast-cold Ar (I) atom population temperature at z = 8 mm between standard conditions and reduced ICP incident powers are undetectable and within the standard deviation of the measurements.

Figure 2-34. Effect of reducing ICP power 32% from standard conditions 35% = 1.4L/min, note the absence of black markers between 12-18 mm at 850 W, T1: fast-cold population; T2: slow-hot population
2.3.2.1.3 Effect of Matrix Composition

Figure 2-35 shows the addition of 50 ppm lithium has no observable effect on either expansion minimum temperature or relative noise on the Ar (I) atom expansion temperature profile.

Figure 2-35. Effect of adding 50 ppm lithium matrix, 35% = 1.4 L/min, T1: fast-cold population; T2: slow-hot population

With the exception of the minor temperature increase effect from reducing the nebulizer rate, the lack of significant Ar (I) population temperature response to changing ICP incident power and matrix composition seems to indicate that either 1) fluorescence signal line width is insensitive to effect of changing source conditions, or 2) the
magnitude of conditions and matrix composition changes were insufficient to effect a detectible change in axial Ar (I) atom population temperature profiles.

2.3.2.2 Radial Temperature Profiles

Figures 2-36 and 2-37 are given for reference purposes. As with the radial velocity profiles, these data were collected at $z = 10$ mm downstream. Based on observed and previously discussed axial temperature profile insensitivity to changes in plasma operating conditions and matrix composition, as well as an absence of relevant discussion in the literature, the correlation between changes in radial temperature profiles to changes in plasma operation conditions or matrix composition is not well established.

Figure 2-36. Effect of reducing nebulizer rate 28% from standard conditions. 35% = 1.4 L/min, 15% = 0.6 L/min, T1: fast-cold population; T2: slow-hot population
2.4 Conclusions

It is has been shown that argon (I) metastable velocity and temperature profiles are good indicators for quantifying the effect of changing plasma operating conditions and matrix composition on plasma gas kinetic temperature and the first vacuum stage supersonic expansion. Where the first vacuum stage supersonic expansion has been adequately modeled, under standard conditions, observed laser-induced fluorescence velocity and temperature profiles agree well with theory and are consistent with data from other established plasma supersonic jet characterization methods [20,21]. What is more significant, however, is what these velocity and temperature profiles indicate about un-
modeled and poorly understood regions of the first vacuum stage supersonic expansion as well as the effect of non-standard plasma operating conditions and matrix compositions on plasma gas kinetic temperature and first vacuum stage supersonic expansion structure in analytically important locations.

Axial Ar (I) velocity profiles provide upstream plasma source information that is necessary to accurately characterize the ionization environment that sample analyte experiences. Ar (I) axial velocity profiles, and to a lesser extent, axial temperature profiles, provide unambiguous shock structure location and dimensional information about the supersonic expansion useful for placement of a second stage skimmer interface. Research by Patterson [2] indicated the presence of a shock structure just upstream of the skimmer interface located 10 mm downstream, under standard conditions, and was initially attributed to the natural emergence of the Mach disk. The unambiguous Ar (I) results discussed here provide the additional understanding that, under standard conditions, the leading Mach disk boundary forms at 10 mm downstream in an unperturbed supersonic expansion and persists for 7 to 8 mm downstream. This suggests the presence of a second stage skimmer interface may actually induce the formation a non-Mach disk shock structure prematurely and explain the observations and postulations of Patterson; Niu and Houk; and Chen and Farnsworth [1,2,22]. This revised postulate is now possible because of the early LIF-velocity/temperature method development by Patterson and others [2]. Ar (I) axial Doppler velocity profiles show a well-defined, single mode, fast-cold Ar (I) atom population that exists alone up to the leading boundary of the Mach disk and disappears in a linear fashion proportional to the linearly
proportional emergence of a slow-hot Ar (I) atom population that was not observed upstream of the Mach disk leading boundary. Axial and radial Ar (I) velocity and temperature profiles provide valuable two-dimensional clues into understanding the effects of changing plasma operating conditions and matrix composition on bath gas structure and behavior not only in the zone of silence but also in the Mach disk and barrel shock collision regions.

It has been shown that integrating the areas under the fitted Gaussian functions, used to calculate Ar (I) velocity and temperature profiles, provides previously unavailable information about the spatially dependent nature of the Mach disk atom population composition and its structural change response to changes in plasma operating conditions and matrix composition. This information has the potential to help quantify the magnitude of the problem of second stage skimmer induced shock structures on ICP-MS sensitivity and provide unambiguous data to potentially overcome the problem.

As well characterized as Ar (I) is in the first vacuum stage expansion, it would be significant to characterize the changes in Ar (I) velocity and temperature profiles in the first vacuum stage expansion as a function of Ca (II), and other ion, matrix concentration. The observation that Li ion increases neutral Ar (I) atom velocities and temperatures generates more questions and justifies additional Ar (I)-matrix effect characterization.
References


Chapter 3. Velocity and Temperature Characterization of Calcium (II) in the First Vacuum Stage of an ICP-MS

3.1 Introduction

Currently, the most common method to “optimize” ICP-MS detector response to a particular analyte in a complex mixture is an iterative and time-consuming process. Matrix matching, standard addition, gradual dilution, systematic and iterative adjustment of sample introduction parameters and plasma operating conditions are currently the practices of choice (or necessity) to improve ICP-MS performance. The problem is that ICP-MS performance cannot correctly be reduced to a simple model indicated by Equation (3-1) where $k$ is an analyte specific proportionality constant, and the effect of changing instrument settings and matrix composition, $x$, $y$, and $z$, is described as a simple linear combination of these supposedly independent variables.

\[
\text{Output} = k \ast (x+y+z) \ast \text{Input} \quad (3-1)
\]

Instead our characterization of metastable Ar (I) in the first vacuum stage expansion suggests that the relationship between ICP output entering the mass spectrometer and sample input into an ICP probably looks more like the relationship indicated by Equation (3-2) where what the mass spectrometer sees, \textit{Output}',

\[
\text{Output}' = (k_b+k_c+\ldots+k_n) \ast f(\text{Output, x, y, z}) \ast \text{Input} \quad (3-2)
\]
is the product of 1) a linear combination of non-analyte element specific proportionality constants, $k_b, k_c...k_n$; 2) a complex function depending on real ICP output, plasma operating and matrix conditions, $x, y, z$; and 3) sample introduction to an ICP, \textit{Input}. While the purpose of the research presented here is not to quantitatively determine the exact form of or values in Equation (3-2), it is our intent to show that the relationship between what the mass spectrometer receives from the interface and what the experimenter introduces to an ICP is complex and a function of non-independent experimental variables.

In Chapter 2 we characterized a common ICP-MS bath gas, argon, using laser-induced fluorescence of metastable Ar (I) as an indicator of the effects of changing nebulizer rates, incident ICP power, and matrix composition on source stagnation temperature, shock structure dimensions and locations, and the kinetic and thermal environment inside the first vacuum stage of an ICP-MS. In Chapter 3 we will show how these same experimental variables affect the observed velocity and temperature profiles of calcium (II) inside the first vacuum stage of our ICP-MS mock-up. By comparing and contrasting the behavior of Ca (II), atomic mass = 40.078, with Ar (I), atomic mass = 39.948, we gain important understanding of potential differences in analyte behavior due to charge, concentration, and matrix composition differences. With less than 0.5 \% difference in mass between Ar (I) and Ca (II), we can compare the effects of equal concentrations of lithium matrix without concern of significant analyte-analyte mass bias.
As discussed in Chapter 1, the dominant matrix effect on the analyte ion beam in the virtually collision-free first vacuum stage expansion is thought to be space charge [1]. Taking these facts and assumptions into account, we chose to characterize Ca (II) behavior in order to 1) compare and contrast a similar mass ion’s behavior to the behavior of the bath gas, and 2) establish a baseline for the further characterization of calcium and other analyte ion behavior under varying nebulizer rates, incident ICP powers, analyte concentrations, and matrix composition conditions.

### 3.2 Experimental Setup

The experimental setup used to characterize Ca (II) is almost identical to that used to characterize Ar (I) with a couple of notable exceptions. First, the excitation scheme is different as is shown in Figure 3-1.

![Excitation and fluorescence wavelengths of Ca (II)](image)

Figure 3-1. Excitation and fluorescence wavelengths of Ca (II)
In order to excite the Ca (II) electronic transition, changing our EOSI diode laser wavelength from 801.478 nm to 854.209 nm was required. This was accomplished by switching to an 852 nm laser diode (DMD-852-015, Newport Corporation, Irvine, CA) from our original 795 nm laser diode (DMD-795-015, Newport Corporation, Irvine, CA). In addition to changing laser diodes, changing our ICP photomultiplier tube filter to a 393.5nm, 1nm bandpass (Corion Filters, Spectra-Physics, Durham, UK) filter was required. It was desirable to use the previously calibrated and aligned Fabry-Perot etalon without significant re-alignment or re-calibration, since this task can take a skilled individual one to two days to accomplish. We were pleased to find that gross alignment or calibration of the etalon was not disturbed and only minor re-alignment of the etalon to the laser path was required. The only notable difference in switching our laser to a longer wavelength was the change in the number of interferometer fringes from eleven or twelve fringes per function generator ½ scan to eight or nine fringes per function generator ½ scan. This was due to the increase of laser wavelength from 801 nm to 854 nm. While more fringes result in a better least squares fit required to calculate the reference frequency axis, the loss of a few fringes was considered an acceptable trade-off in comparison to the time required to complete etalon calibration and realignment.

The experimental setup for the stationary population reference is slightly different because it is based on a different physical phenomenon. A “stationary” Ar (I) population was created in a Fe/Ar hollow cathode lamp and probed using the optogalvanic effect, or the change in conductivity of the hollow cathode lamp due to laser-induced excitation of metastable Ar (I) via an electronic transition. The stationary population signal for Ar (I)
is actually an absorbance/conductance curve centered at the zero velocity reference frequency. To create a stationary population reference signal for Ca (II), a more straightforward laser-induced fluorescence setup was used. Instead of detecting an optogalvanic effect signal, the laser-induced 393.366 nm fluorescence of a captive, “stationary” Ca (I) population in a Ca hollow cathode lamp (P809, Photron Pty Ltd, Australia) operated at 10 mA / 250 VDC, was filtered with a monochromator (Instruments SA, Inc., Santa Cruz, CA) and detected by a Hamamatsu fast photomultiplier tube.

Third and finally, we changed our analyte sample from pure H₂O to a 10 ppm calcium solution made from a stock 1000 ppm calcium solution. For the experiments involving changing matrix composition, a 10 ppm calcium + 50 ppm lithium solution was made from stock 1000 ppm lithium and 1000 ppm calcium solutions. Because the axial and radial profile scans required 10 minutes per data point to collect, these relatively low analyte and matrix concentrations were required to allow for up to five hours of continuous ICP operation before calcium and/or calcium/lithium salts obstructed the sampling orifice, reduced first vacuum stage pressures more than 3%, and required instrument shut-down and cleaning of the nickel cone in a 2% HNO₃ solution in an ultrasonic bath for 15 minutes. In the argon characterization experiments, continuous ICP operation could be sustained for up to ten hours for water only samples and up to six hours for 50 ppm lithium matrix experiments before the 3% pressure drop occurred. We later performed spatial profile characterizations of Ca (II) in the Mach disk region (8 mm to 20 mm downstream) with 25 ppm calcium and 25 ppm calcium + 50 ppm lithium
solutions to test for the effect of changing analyte concentration on Ca (II) behavior in the first vacuum stage expansion and plasma source gas kinetic temperature.

From what we learned about the first vacuum stage supersonic expansion from the velocity and temperature characterization of metastable Ar (I), we were able to determine which experimental variables had the most significant impact on velocity and temperature profiles, shock structure location and dimensions, and plasma source gas kinetic temperatures. It was evident from our previous results that a reduced nebulizer flow rate was a significant experimental variable that resulted in increased plasma source gas kinetic temperature as well as a thicker Mach disk with significantly different population composition. Changing incident ICP power had predictable effects on all profiles and adding 50 ppm lithium matrix generally increased Doppler velocities and calculated plasma gas kinetic temperatures, but had little effect on observed axial or radial temperature profiles.

3.3 Results and Discussion

The following data are the result of a second set of exploratory experiments designed to determine regions of analytical significance and the degree of influence that common ICP plasma operating condition and matrix composition decisions have on singly charged ions with mass similar to that of the bath gas. As discussed in the introduction to Chapter 3, 10 ppm calcium solution was our analytical sample. In the following results, the effect of ICP incident power, nebulizer rate, and matrix composition choices on Ca (II) velocity and temperature distributions is discussed and is compared to corresponding Ar I profiles.
3.3.1 Velocity Profiles for Calcium (II)

Having a mass difference of 0.3% from that of argon, Ca II should have axial and radial velocity distributions in the first vacuum stage expansion similar to Ar I and differences in behavior compared to Ar (I) will provide unambiguous evidence of space charge influence on ionic behavior in the source or the ICP-MS interface.

3.3.1.1 Axial Velocity Profiles

We first collected axial Ca (II) velocity profiles under standard conditions (1250W, 1.4 L/min nebulizer rate, 0 ppm lithium) to establish a characterization baseline. Because of the concern about analyte salt build-up on the sampling orifice we collected axial data every 1 mm for standard conditions only, and every 2 mm for experiments varying nebulizer, power, and matrix composition. The axial velocity profiles for Ca (II) and Ar (I) under standard conditions are shown in Figure 3-2. The Ca (II) terminal velocity ($v_{\text{inf}}$) at $z = 8$ mm downstream is $2400 \pm 28$ m/s which corresponds to a plasma gas kinetic temperature of $5553 \pm 28$ K, almost 500 K higher than the Ar (I) velocity based plasma gas kinetic temperature under standard conditions with pure H$_2$O analyte. This significant increase in source temperature as the result of adding 10 ppm Ca, as well as significant increases in slow-hot Ca (II) population, although not well understood, present evidence of the significance of an unexpected matrix effect on the plasma when calcium is present in the analyte sample.
3.3.1.1.1 Effect of Nebulizer Rate

Expecting Ca (II) to behave similarly to Ar (I) under reduced nebulizer rates, we attempted to collect an axial velocity profile of Ca (II) at 0.6 L/min nebulizer. Much to our surprise we observed no fluorescence. After verifying the integrity of our experimental setup and our measurements at 1.4 L/min nebulizer, we concluded that Ca (II) metastable ion was not present in detectible quantities in the first vacuum stage expansion. Based on these observations, we collected Ca (II) fluorescence at z = 8 mm downstream (location for \( V_{\text{inf}} \)) under varying nebulizer rates in order to determine the relationship between Ca (II) Doppler velocity and nebulizer rate in the zone of silence. The results of this experiment are shown in Figure 3-3.
The effect of changing nebulizer rates from 1.2 L/min to 1.4 L/min to 1.6 L/min was a surprising increase in Ca (II) fluorescence intensity, and the expected decrease in Doppler velocity. The decrease in Doppler velocity is consistent with findings of Lehn and co-workers [2] but the increase in Ca (II) fluorescence is reproducible and defies conventional wisdom. Reducing nebulizer flow rate increases plasma temperature and results in a higher degree of Ca (II) ionization, which should result in an increase in observed fluorescence, but we see the opposite. Plasma gas kinetic temperatures under varying nebulizer rates, determined from Ca (II) \( V_{\text{inf}} \) are summarized in Table 3-1.
Table 3-1. Effect of nebulizer rate on Ca (II) $V_{\text{inf}}$ & gas kinetic temperature

<table>
<thead>
<tr>
<th>Nebulizer Rate (%)</th>
<th>$V_{\text{inf}}$ @ $z = 8$ mm (m/s)</th>
<th>Eff. Gas Kinetic Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>$2454 \pm 57$</td>
<td>$5807 \pm 134$</td>
</tr>
<tr>
<td>35</td>
<td>$2395 \pm 38$</td>
<td>$5530 \pm 89$</td>
</tr>
<tr>
<td>40</td>
<td>$2179 \pm 21$</td>
<td>$4577 \pm 44$</td>
</tr>
</tbody>
</table>

$V_{\text{inf}}$: terminal velocity at $Z = 8$ mm.

3.3.1.1.2 Effect of Incident ICP Power

Having established the effect of changing nebulizer rate for a 10 ppm Ca solution on the plasma gas kinetic temperature, we compared the behavior of Ca (II) to that of Ar (I) under varying power settings at $z = 8$ mm downstream. The combined results of the Ca (II) and Ar (I) power experiments are shown in Figure 3-4.

![Figure 3-4. Effect of incident power on Ca (II) & Ar (I) velocity 8 mm downstream](image)
What is significant about the results of the Ca (II) power series test is that both Ca (II) and Ar (I) exhibit similar velocities and resulting source gas kinetic temperatures above 1000 W incident ICP power with poorer agreement between 850 W and 950 W. It cannot be determined at this time if the difference between Ca (II) and Ar (I) velocities between 850 W and 950 W is real or a result of a random experimental error. Future experiments will further clarify this apparent difference.

3.3.1.1.3 Effect of Matrix Composition

Figure 3-5 shows the comparative axial velocity profiles of Ca (II) and Ar (I) with and without 50 ppm lithium matrix all under standard conditions. The addition of 50 ppm lithium matrix to the 10 ppm Ca solution resulted in a reduction in calculated plasma gas kinetic temperature from 5553 ± 28 K in the Ca only sample to 5304 ± 54 K in the Ca + Li sample. Both of these measured gas kinetic temperatures are greater than when pure water is aspirated (5061 ± 45 K). It was interesting to note that the addition of 50 ppm Li to pure water appeared to raise the measured plasma gas kinetic temperature while the addition of 50 ppm Li to a 10 ppm Ca solution appeared to lower the plasma gas kinetic temperature from that of the Ca only solution. The addition of lithium resulting in opposite gas kinetic temperature effects in the presence of neutral and charged analyte provides evidence of plasma potential affecting the velocity which ions travel through the first vacuum stage interface.
3.2.1.2 Radial Velocity Profiles

Radial Ca (II) velocity profiles provide valuable information about the structure of the ion beam as it begins to form in the first vacuum stage expansion. Similarities and differences in velocity profiles under different plasma operating and matrix conditions may further expose the mechanisms leading to matrix effects in the interface. At 10 ppm Ca concentration, fluorescence beyond 8 mm downstream was not very intense except under higher than normal nebulizer rates. As a result we were unable to detect any bimodal nature in the recorded Ca (II) fluorescence. Figure 3-6 contains the radial Ca (II) velocity profile, Ca (II) + 50 ppm Li radial velocity profile, as well as the Ar (I) radial velocity profile all under otherwise standard conditions (1250 W, 1.4 L/min nebulizer
rate) at z = 10 mm downstream. As with the axial velocity profiles, 10 ppm Ca has a higher Doppler velocity than Ar (I) with pure water. However, the addition of 50 ppm Li further increases the radial Doppler velocity of Ca (II). It is likely that the change due to the addition of Li is not significant in either axial or radial Ca (II) profiles under these conditions.

Figure 3-6. Comparison of Ca (II), Ca (II) + Li, and Ar (I) radial velocity profiles, V1: fast-cold population; V2: slow-hot population.
3.2.1.2.1 Effect of Incident ICP Power

The effect of changing incident ICP power to 850 W on axial or radial Ca (II) profiles at 10 ppm Ca concentration was not re-examined. There are sufficient similarities between the effect of power on Ar (I) and Ca (II) (see Figure 3-4) as well as insufficient Ca (II) fluorescence at 850 W to warrant further axial or radial characterization.

3.2.1.2.2 Hemispherical Expansion Validation

In order to determine if an ion and an atom follow the same hemispherical expansion in the first vacuum stage expansion, holding mass constant (< 0.5% ∆m), the radial Doppler experiment was repeated for Ca (II) from x = +2.5 mm to x = -2.5 mm in 0.25 mm increments z = 8 mm downstream under standard conditions (1250 W, 1.4 L/min nebulizer rate, 10 ppm Ca). The results of this experiment are shown in Figure 3-7 where Ca (II) Doppler velocities are compared to Ar (I) under the same conditions at the same spatial locations. After resolving the observed Doppler-shifted velocities into x and z components (V_x, V_z), we found that Ca (II) and Ar (I) had identical x velocity components (V_x, radial component) but that Ca (II) had a z velocity component (V_z, axial component) approximately 100 m/s greater than that of Ar (I) at most points within the zone of silence (-2 mm to +2 mm), as shown in Figure 3-8. These preliminary results provide evidence to support the theory that plasma potentials have a greater effect on accelerating ions through the interface than neutral atoms. It is interesting to note that while the Ca (II) ions experienced an increased velocity through the interface, the increase in velocity was entirely in the axial (V_z) direction and did not contribute to increased expansion broadening which would be evident through an increased radial
Figure 3-7. Comparison of Ca (II) and Ar (I) velocities along x-axis

Figure 3-8. Resolved Doppler velocity component vectors for Ca (II) and Ar (I)
velocity component \( (V_x) \). These results will need to be duplicated to have high confidence in the magnitude in observed Ca axial velocity component increase. In addition to characterizing the effect of plasma potential on analyte transmission velocity, this Doppler velocity shift experiment has the exciting potential to characterize the effect of space charge influences in the first vacuum stage expansion as a function of analyte and matrix composition choice under a variety of incident ICP power and nebulizer settings.

### 3.3.2 Temperature Profiles for Ca (II)

The following data represent the random component of motion, or “temperature” profiles of Ca (II) resulting from changes in nebulizer rate and matrix composition. Literature suggests there is competition between coulombic and gas kinetic forces as the primary interference mechanism in the first vacuum stage expansion depending on downstream distance, sample composition, and upstream ionizing source conditions [3]. As stated earlier, it is important to note that the temperatures reported are the result of the approximate 50% / 50% convolution of perpendicular temperatures and parallel temperatures due to the 45° excitation and collection angle in relation to the axial flow direction. As discussed earlier, at 10 ppm Ca concentration, shock structures such as Mach disk and barrel shock were not clearly evident. Our 10 ppm Ca analyte solution did not sufficiently fluoresce at the 0.6 L/min nebulizer rate or at the 850 W incident ICP power and therefore a direct comparison could not be made to Ar (I) under these conditions.
The effect of changing matrix composition on axial and radial temperature profiles provides additional characterization information that may help clarify the source effects that changing plasma operating conditions and matrix composition have on velocity profiles. The effect of changing matrix composition (adding 50 ppm Li) on the axial Ca (II) temperature profile is shown in Figure 3-9 and is compared to Ar (I) under otherwise standard conditions. The large increase in error bar size is one effect that adding Li matrix has on the spread of observed Ca II temperatures. What is interesting from the results shown in Figure 3-9 is the apparent Ca (II) insensitivity of the fast-cold population temperature profile to changes in matrix conditions in comparison to the fast-cold Ar (I) population. Significant, albeit noisy, differences in slow-hot population axial temperature

![Figure 3-9. Effect of 50 ppm Li on Ca (II) and Ar (I) axial temperature profiles T1: fast-cold population; T2: slow-hot population](image-url)
profiles for Ca (II), Ca (II) + Li, and Ar (I) indicate that dramatic differences in temperatures exist beyond the Mach disk leading boundary 12-13 mm downstream. The radial temperature profiles for Ca (II) and Ca (II)+50 ppm Li were compared to the radial temperature profile of Ar (I) at z = 10 mm downstream. The results shown in Figure 3-10

![Figure 3-10. Effect of 50 ppm Li on radial Ca II temperature profiles, T1: fast-cold population; T2: slow-hot population](image)

indicate that the presence of lithium makes little impact on the temperature of Ca (II). What is clear, however, is that the temperature increases in both Ca (II) radial profiles beyond +2 mm and −2 mm radially are due to the unfit second slow-hot population present in the barrel shock region. Future experiments with higher concentrations of Ca
(II) should give sufficient fluorescence to be able to fit two Gaussian functions to calculate T1 and T2.

3.4 Conclusions

The result of our velocity and temperature characterization of Ca (II) ion behavior in the first vacuum stage supersonic expansion represents the first unambiguous and substantial data of ionic behavior beyond the first stage interface. With a mass that is only 0.3% less than that of argon, calcium makes an ideal first ion to study in a side-by-side spatial characterization. The success of our Ca (II) characterization research has been mixed. While we have been able to draw some general conclusions about differences in Ca (II) behavior in comparison to Ar (I) behavior, the quality of our Ca (II) results can be significantly improved in future experiments. Suspecting that low Ca (II) concentration (10 ppm) is the primary culprit behind our low fluorescence and non-detectible bimodal distributions in the Mach disk and barrel shock regions, we have already begun a second set of experiments using 25 ppm Ca solutions. We believe that higher concentrations will yield stronger fluorescence and better signal to noise in our data. In addition to better quality Ca (II) Mach disk and barrel shock data, repeating the experiments at a higher Ca (II) concentration will allow us to measure the effect of changing analyte/matrix concentration ratios.

What we have determined, however, is that charged species do not always behave identically to neutral species in the first vacuum stage expansion. Although Ca (II) and Ar (I) react similarly to changing nebulizer rates and incident ICP power, the similarity
ends there. The most significant finding was that charged analyte species move faster in the first vacuum stage expansion than neutral species move. This was immediately evident in our axial velocity profiles as a 100 m/s jump between Ca (II) velocity and Ar (I) velocity at z = 8 mm downstream. Determining that a 100 m/s increase in terminal velocity ($V_{\text{inf}}$) corresponded to an almost 500 K increase in plasma gas kinetic temperature, and assuming that the source temperature could not actually increase as a result of adding Ca (II), we concluded that the source plasma’s potential must be accelerating Ca (II) ions into the interface 100 m/s faster than it is neutral Ar (I) atoms. This conclusion was reinforced as a result of the Ca (II) radial Doppler test when it was calculated that while the radial vector component of velocity ($V_x$) was the same for Ca (II) and Ar (I), the axial vector component of velocity ($V_z$) showed the same 100 m/s increase in axial Ca (II) velocity over that of Ar (I). Published plasma potential data [4] and future experiments varying the charge of the analyte ion should provide a better understanding of the relationship between source plasma potential and an analyte ion’s charge, mass, and ionizing efficiency.

Future experiments involving Ca (II) should include increasing Ca (II) concentrations to better characterize ion behavior in the Mach disk and barrel shock regions; varying Ca (II)/matrix concentration ratios in order to better understand the relative effects of varying mass and charge ratios on Ca (II) velocity and temperature in the first stage expansion; and characterizing Ca (II) velocity and temperature profiles as a function of matrix element mass (Pb, Sr, etc.). It should be mentioned that any experiments involving
increased analyte/matrix concentrations must account for the effect of reduced ICP operation times due to analyte/matrix salt build-up on the sampling orifice.
References


Chapter 4. Summary and Future Directions

The velocity and temperature characterization of the first vacuum stage supersonic expansion with laser-induced atom and ion fluorescence was an overwhelming success. Building on previous atom and ion LIF work by James Patterson [1] and Becky VanWagoner, we were able to not only profile analytically important regions of the first vacuum stage expansion, but also begin to quantify the relationship between plasma operations and matrix composition on source gas kinetic temperatures and the plasma potential’s effect on ion velocities in the first stage interface. Although the results presented have inspired more questions than answers, this next generation of analytical questions represents an overall advancement of understanding of the fundamental processes causing reduced ICP-MS sensitivity through ion transmission loss and matrix effects. Atom and ion laser-induced fluorescence velocity and temperature characterization will continue to serve as one of the most effective analytical methods developed to date to study the first vacuum stage supersonic expansion and beyond.

4.1 Summary of Results

The most analytically important velocity and temperature profiles of Ar (I) metastable atom and Ca (II) ion are presented in the following sections. Where appropriate, the effects of changing plasma operating conditions and matrix composition are summarized in tables for a direct comparison of Ar (I) and Ca (II) behavior. First vacuum stage expansion regions or experimental settings requiring further characterization are so noted.
4.1.1 Significant Argon (I) Velocities

Because it is the primary plasma carrier gas for most ICP emission instruments, characterizing argon is not only important to understand the behavior of the bulk supersonic flow, but also to expand our understanding of its role in analyte ionization and reaction chemistry in the plasma source [2]. As a neutral species, it was expected that Ar (I) velocity in the first vacuum stage expansion would be affected by both changes in incident ICP power and nebulizer rate. What was not expected was the observed increase in Ar (I) velocity as a result of adding 50 ppm Li matrix to pure water. Table 4-1 summarizes the observed axial velocities and calculated gas kinetic temperatures as a result of changing plasma operating conditions and matrix composition.

<table>
<thead>
<tr>
<th>Nebulizer (L/min)</th>
<th>ICP Power (W)</th>
<th>Matrix (ppm Li)</th>
<th>( V_{\text{inf}} ) (m/s)</th>
<th>( T_{\text{stag}} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>1250</td>
<td>0</td>
<td>2295 ± 20</td>
<td>5061 ± 45</td>
</tr>
<tr>
<td>0.6</td>
<td>1250</td>
<td>0</td>
<td>2648 ± 17</td>
<td>6922 ± 45</td>
</tr>
<tr>
<td>1.4</td>
<td>850</td>
<td>0</td>
<td>2091 ± 51</td>
<td>4091 ± 102</td>
</tr>
<tr>
<td>1.4</td>
<td>1250</td>
<td>50</td>
<td>2350 ± 15</td>
<td>5307 ± 34</td>
</tr>
</tbody>
</table>

\( V_{\text{inf}} \): Ar I terminal velocity at \( z = 8 \) mm; \( T_{\text{stag}} \): source stagnation temperature

4.1.2 Significant Calcium (II) Velocities

Calcium is used frequently as an analyte and matrix element because of its high degree of ionization to Ca (II) (~99%) and Ca (III) (~1%) [3]; as well as its low ICP detection limits approaching 1 part per trillion [4]. Having a mass difference with argon of about 0.3%, it is an ideal ion for characterization comparison with argon. Table 4-2 provides a summary of analytically significant Ca (II) velocities. Since the addition of 10 ppm Ca
should not actually increase the plasma temperature, the effective gas kinetic, or stagnation temperature is reported that would produce the reported velocity for a neutral species. The change in velocity indicates the influence of plasma potential on the acceleration of the charged species through the interface.

Table 4-2. Summary of Ca (II) behavior z = 8 mm downstream

<table>
<thead>
<tr>
<th>Nebulizer (L/min)</th>
<th>Power (W)</th>
<th>Matrix (ppm Li)</th>
<th>( V_{\text{inf}} ) (m/s)</th>
<th>Eff. ( T_{\text{stag}} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>1250</td>
<td>0</td>
<td>2400 +28</td>
<td>5553 +28</td>
</tr>
<tr>
<td>1.2</td>
<td>1250</td>
<td>0</td>
<td>2454 +57</td>
<td>5807 +134</td>
</tr>
<tr>
<td>1.6</td>
<td>1250</td>
<td>0</td>
<td>2179 +21</td>
<td>4577 +44</td>
</tr>
<tr>
<td>1.4</td>
<td>1250</td>
<td>50</td>
<td>2346 +24</td>
<td>5304 +54</td>
</tr>
</tbody>
</table>

\( V_{\text{inf}} \): Ar I terminal velocity at z = 8 mm; Eff \( T_{\text{stag}} \): effective source stagnation temp. required to produce observed \( V_{\text{inf}} \) if analyte ion were neutral.

4.1.3 Significant Argon (I) Temperatures

While temperature profiles do not tell us as much about upstream plasma conditions as velocity (\( V_{\text{inf}} \)) does, temperatures indicate the degree of homogeneity in the analyte flow through the supersonic expansion. Correspondingly, temperature is a very sensitive early indicator of supersonic shock structure emergence and can provide greater insight into the effect of placing a second stage skimmer interface in proximity to a supersonic shock structure. Table 4-3 lists the minimum temperatures (z = 8 mm downstream) for Ar (I) under varying plasma and matrix conditions. A lower temperature indicates a smaller random motion component in the analyte axial motion. Minimizing the randomness of analyte motion as analyte travels into the second stage skimmer is critical to low noise at the detector.
Table 4-3. Ar (I) temperatures \(z = 8\) mm downstream

<table>
<thead>
<tr>
<th>Nebulizer (L/min)</th>
<th>Power (W)</th>
<th>Matrix (ppm Li)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>1250</td>
<td>0</td>
<td>223 ( \pm ) 21</td>
</tr>
<tr>
<td>0.6</td>
<td>1250</td>
<td>0</td>
<td>316 ( \pm ) 5</td>
</tr>
<tr>
<td>1.4</td>
<td>850</td>
<td>0</td>
<td>213 ( \pm ) 140</td>
</tr>
<tr>
<td>1.4</td>
<td>1250</td>
<td>50</td>
<td>240 ( \pm ) 28</td>
</tr>
<tr>
<td>1.4</td>
<td>1250</td>
<td>200</td>
<td>220 ( \pm ) 22</td>
</tr>
<tr>
<td>1.0</td>
<td>1250</td>
<td>0</td>
<td>288 ( \pm ) 12</td>
</tr>
</tbody>
</table>

Temperature: measure of random component of Ca II motion

4.1.4 Significant Calcium (II) Temperatures

Perhaps more important than axial Ar (I) temperatures, Ca (II) axial temperatures represent the impact of plasma operating conditions and matrix composition on the degree of analyte random motion at a point where it would be sampled by a second stage skimmer. By comparing the magnitude of these random motion indicators, better and more objective decisions can be made about instrument settings, matrix composition, and location of the second stage skimmer interface.

Table 4-4. Ca (II) temperatures \(z = 8\) mm downstream

<table>
<thead>
<tr>
<th>Nebulizer (L/min)</th>
<th>Power (W)</th>
<th>Matrix (ppm Li)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>1250</td>
<td>0</td>
<td>289 ( \pm ) 41</td>
</tr>
<tr>
<td>1.2</td>
<td>1250</td>
<td>0</td>
<td>326 ( \pm ) 97</td>
</tr>
<tr>
<td>1.4</td>
<td>1250</td>
<td>50</td>
<td>272 ( \pm ) 34</td>
</tr>
<tr>
<td>1.6</td>
<td>1250</td>
<td>0</td>
<td>253 ( \pm ) 14</td>
</tr>
</tbody>
</table>

Temperature: measure of random component of Ca II motion
4.2 Recommendations for Future Study

The velocity and temperature characterization of a neutral atom, Ar (I), and a singly charged ion, Ca (II), in the first vacuum stage supersonic expansion of an ICP-MS, have provided a substantial foundation upon which to build future characterization and matrix effect modeling studies. In order to confidently move on to characterizing other atoms and ions, there is still more characterization work to do for Ca (II). The following sections suggest, based on the quality of the results from these reported experiments, that Ca (II) characterization requires replication at a higher concentration, due to low analyte signal to noise. I also suggest new experiments that will study the effects of charge and mass in changed matrix composition on Ar (I), Ca (II), and other ion velocities and temperatures.

4.2.1 Increased Concentration of Ca

Our Ca (II) characterization at 10 ppm Ca suffered from low fluorescence signal to noise and, as a result, told us little about the subtle changes in ion population velocity and temperature throughout the expansion and in the Mach disk and barrel shock regions. Already, these previously discussed Ca (II) characterization experiments are being repeated at 25 ppm Ca in order to be able to adequately fit the fluorescence to single and dual Gaussian functions to yield more detailed shock structure information about Ca (II) in the first vacuum stage expansion. Based on initial results, we observe the bimodal character of the Ca (II) fluorescence and are eager to compare the population distribution of Ca (II) to that of Ar (I).
4.2.2 Effect of Atomic Mass Ratio on V and T

After a thorough characterization of Ca (II), one of the first new experiments that warrant attention is the effect of changing the atomic mass ratio of analyte to matrix (A/M) elements (at equal concentrations). The results of this experiment should increase understanding about the effect, or lack of effect, of mass bias in the first vacuum stage. Already having observed the effect of plasma potential on the velocity of Ca (II) in the first vacuum stage expansion as compared to neutral Ar (I), it would be interesting to characterize the behavior of other Period 2 elements, such as barium, at constant analyte and matrix concentrations. Careful consideration will need to be made regarding the ionization efficiency of the analyte and matrix species to ensure an approximately equal population of each in the plasma and in the first vacuum stage expansion.

4.2.3 Effect of Concentration Ratio on V and T

A follow-on experiment to the A/M mass ratio experiment described in section 4.2.2 could involve varying the A/M concentration ratio of the same analyte/matrix ions used before. Having previously characterized the effect of the A/M atomic mass ratio effect at equal concentrations, varying A/M concentration ratio will further our understanding of the effect of relative abundance of analyte and matrix species in the plasma and first vacuum stage on observed velocities and temperatures.
4.2.4 Effect of Charge Ratio on $V$ and $T$

Finally, having thoroughly characterized the relative effects of mass (holding charge constant) and concentration (correcting for mass bias), it should be possible to quantify the effect of changing analyte charge on Ar (I) and analyte velocity and temperature profiles by carefully selecting matrix elements with different charges but well characterized mass bias differences. This fourth experiment, combined with the results of the previous three, should provide a comprehensive set of results clearly delineating the individual effects of atomic mass, concentration, and charge analyte/matrix ratios on velocities and temperatures in the first vacuum stage, as well as any influences on source plasma gas kinetic temperatures.

4.3 Final Summary

Through laser-induced fluorescence based velocity and temperature characterization of the first vacuum stage supersonic expansion, it is clear that the effect of changing plasma operating conditions and matrix composition on analyte behavior is not simple. Evidence of the influence of plasma potential on the trajectories of analyte ions on their way to the second-stage skimmer interface and mass detector warrants significant future study. The unambiguous link between plasma operating conditions and the plasma gas kinetic temperature in an ICP-MS has been established, but by no means thoroughly characterized, and requires additional characterization to produce an analytically useful prediction model. The relationship between plasma operating conditions, matrix composition, and charged species behavior has been established, but requires significant
characterization to isolate and quantify the effects of analyte/matrix mass, concentration, and charge ratios on analyte behavior in the interface region of an ICP-MS.
References


Appendix A: Sample Experimental Data Formats

Shown are examples of data in raw ASCII data and final Excel® / Mathcad® Fitting formats.

A.1 ASCII “*.log” File Raw Data Format

A sample of raw data for axial standard conditions Ar (I) measurement at z = 8 mm. There are approximately 12000 lines of data; one line for every 0.05 seconds of scanning at 10 mHz (10^3 Hz) (approximately 10 minutes per 5 triangle wave cycles).

<table>
<thead>
<tr>
<th>Time (s)</th>
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<th>OGE(V)</th>
<th>Funct(V)</th>
<th>ICP(V)</th>
</tr>
</thead>
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</tr>
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<td>-0.015</td>
</tr>
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<td>0.737</td>
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<tr>
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<td>1.393</td>
<td>0.005</td>
<td>0.737</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Figure A-1. ASCII log file format Ar (I)
A.2 Formatted Data Format

After trimming to five complete cycles and formatting, there are five repeating sets of columns (Inter, OGE, Funct, ICP) with one Frequency column to input to Mathcad®.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Inter(V)</th>
<th>OGE(V)</th>
<th>Funct(V)</th>
<th>ICP(V)</th>
<th>Inter(V)</th>
<th>OGE(V)</th>
<th>Funct(V)</th>
<th>ICP(V)</th>
</tr>
</thead>
<tbody>
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<td>0.015</td>
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<td>0.01</td>
<td>-1.692</td>
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Figure A-2. Trimmed & formatted Ar (I) Excel® data, ready for Mathcad® fitting for z = 8 mm axial Ar (I) under standard conditions.
Appendix B: Mathcad® Gaussian Function Fitting Worksheets

Shown in Figures B-1 through B-7 are the pages of the Mathcad® worksheet used to fit the z = 8 mm standard condition axial Ar (I) data to a single Gaussian function to determine velocity and temperature. Figures B-8 through B-17 are the pages of the Mathcad® worksheet used to fit two Gaussian functions and integrate relative areas of each to determine velocity, temperature, and relative area for the fast-cold population and the slow-hot population in the Mach disk or barrel shock regions. Figures B-8 through B-17 show the actual dual Gaussian fit for Ar (I) under standard conditions at z = 15 mm downstream.
B.1 Single Population Gaussian Function Fitting Worksheet

This reads in the data from an excel spreadsheet. The starting row and column are specified when the component is defined. The first column in the spreadsheet contains a frequency axis based on the calibration of the etalon. Columns 3, 7, 11, 15, and 19 contain the data from the hollow cathode lamp. Columns 5, 9, 13, 17, and 21 contain the calcium fluorescence data. 'data' is an array, and data<n> refers to column n+1 in that array (the beginning subscript for Mathcad is 0).

\[ k_1 := 4 \ln(2) \]

\[ \text{data}_{0,0} = -713.47 \]

\[ x := \text{data}(0) \]

\[ y := \text{data}(2) \]

\[ y_a := \text{data}(6) \]
\[ y_b := \text{data}(10) \]
\[ y_c := \text{data}(14) \]
\[ y_d := \text{data}(18) \]

\[ y_2 := \text{data}(4) \]
\[ y_{2a} := \text{data}(8) \]
\[ y_{2b} := \text{data}(12) \]
\[ y_{2c} := \text{data}(16) \]
\[ y_{2d} := \text{data}(20) \]

Figure B-1. Page 1 of single Gaussian fit worksheet
\[ F(z,u) = \begin{bmatrix} -k_1 \frac{(z-u_2)^2}{(u_3)^2} \\ u_0 + u_1 e \\ 1 \\ -k_1 \frac{(z-u_2)^2}{(u_3)^2} e \\ e \\ -k_1 \frac{(z-u_2)^2}{(u_3)^2} \\ u_1 e \\ -k_1 \frac{(z-u_2)^2}{(u_3)^2} \\ u_1 e \end{bmatrix} \]

\[ F_m(z,u) := \begin{bmatrix} -k_1 \frac{(z-u_2)^2}{(u_3)^2} \\ u_0 + u_1 e \\ 1 \\ -k_1 \frac{(z-u_2)^2}{(u_3)^2} e \\ e \\ -k_1 \frac{(z-u_2)^2}{(u_3)^2} \\ u_1 e \\ -k_1 \frac{(z-u_2)^2}{(u_3)^2} \\ u_1 e \end{bmatrix} \cdot \begin{bmatrix} 2 \cdot k_1 \frac{(z-u_2)}{(u_3)^2} \\ 2 \cdot k_1 \frac{(z-u_2)}{(u_3)^2} \\ 2 \cdot k_1 \frac{(z-u_2)}{(u_3)^2} \\ 2 \cdot k_1 \frac{(z-u_2)}{(u_3)^2} \end{bmatrix} \]

\[ \lambda \] is the fluorescence wavelength, the rest of these are fundamental constants.

\[ \lambda := 801.4651 \cdot 10^{-9} \cdot m \]
\[ c := 2.998 \cdot 10^8 \cdot m \cdot sec^{-1} \]
\[ h := 6.6260755 \cdot 10^{-34} \cdot \text{joule} \cdot \text{sec} \]
\[ f_m := \frac{c}{\lambda} \]
\[ k := 1.380541 \cdot 10^{-23} \cdot \text{joule} \cdot \text{K}^{-1} \]
\[ N_0 := 6.0221367 \cdot 10^{23} \cdot \text{mole}^{-1} \]
\[ m_{\text{ca}} := \frac{39.948 \cdot \text{gm}}{N_0} \]

The calls below are calls to the fitting function. There is one call for each curve. The results are stored in vectors P, PA, PB etc. The first parameter in the function call is the vector containing the x data. The second parameter is the vector containing the y data. The third parameter is the vector of guesses. The fourth parameter is the array of functions.

Figure B-2. Page 2 of single Gaussian fit worksheet
This next section simply plots the fits on the same axes as the raw data. This step is essential because it tells you immediately if your fit has converged.

\[ P := \text{genfit}(x, y, \text{vg}, F) \quad \text{P2} := \text{genfit}(x, y2, \text{vg2}, F) \]

\[ \text{PA} := \text{genfit}(x, ya, \text{vg}, F) \quad \text{P2A} := \text{genfit}(x, y2a, \text{vg2}, F) \]
\[ \text{PB} := \text{genfit}(x, yb, \text{vg}, F) \quad \text{P2B} := \text{genfit}(x, y2b, \text{vg2}, F) \]
\[ \text{PC} := \text{genfit}(x, yc, \text{vg}, F) \quad \text{P2C} := \text{genfit}(x, y2c, \text{vg2}, F) \]
\[ \text{PD} := \text{genfit}(x, yd, \text{vg}, F) \quad \text{P2D} := \text{genfit}(x, y2d, \text{vg2}, F) \]

This next set of calls simply reconstructs the curves by a calls to the first function in \( F \), with the fit parameters supplied in the \( P \) vectors.

\[ g(x) := F(x, P)_0 \quad g2(x) := F(x, P2)_0 \]
\[ ga(x) := F(x, PA)_0 \quad g2a(x) := F(x, P2A)_0 \]
\[ gb(x) := F(x, PB)_0 \quad g2b(x) := F(x, P2B)_0 \]
\[ gc(x) := F(x, PC)_0 \quad g2c(x) := F(x, P2C)_0 \]
\[ gd(x) := F(x, PD)_0 \quad g2d(x) := F(x, P2D)_0 \]

This next section simply plots the fits on the same axes as the raw data. This step is essential because it tells you immediately if your fit has converged.

Figure B-3. Page 3 of single Gaussian fit worksheet.
Figure B-4. Page 4 of single Gaussian fit worksheet
The next section calculates the velocities and temperatures from the fitted equations. The pertinent equations can be found in James Patterson's thesis and in Ingle and Crouch.

Figure B-5. Page 5 of single Gaussian fit worksheet
vel := \left( P_2 - P_2' \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \sqrt{2} \\
Temp := \left( \frac{P_3 \cdot 10^6 \cdot \text{sec}^{-1}}{2} \cdot \frac{c}{f_m} \right)^2 \cdot \frac{m_{ca}}{2 \cdot \text{ln}(2) \cdot k} \\
\text{vel} = 2.262 \times 10^3 \frac{\text{m}}{\text{s}} \\
\text{Temp} = 202.158 \text{K} \\
vel_A := \left( P_{A_2} - P_{A_2}' \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \sqrt{2} \\
Temp_A := \left( \frac{P_{A_3} \cdot 10^6 \cdot \text{sec}^{-1}}{2} \cdot \frac{c}{f_m} \right)^2 \cdot \frac{m_{ca}}{2 \cdot \text{ln}(2) \cdot k} \\
\text{vel}_A = 2.298 \times 10^3 \frac{\text{m}}{\text{s}} \\
\text{Temp}_A = 226.937 \text{K} \\
vel_B := \left( P_{B_2} - P_{B_2}' \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \sqrt{2} \\
Temp_B := \left( \frac{P_{B_3} \cdot 10^6 \cdot \text{sec}^{-1}}{2} \cdot \frac{c}{f_m} \right)^2 \cdot \frac{m_{ca}}{2 \cdot \text{ln}(2) \cdot k} \\
\text{vel}_B = 2.279 \times 10^3 \frac{\text{m}}{\text{s}} \\
\text{Temp}_B = 237.834 \text{K} \\
vel_C := \left( P_{C_2} - P_{C_2}' \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \sqrt{2} \\
Temp_C := \left( \frac{P_{C_3} \cdot 10^6 \cdot \text{sec}^{-1}}{2} \cdot \frac{c}{f_m} \right)^2 \cdot \frac{m_{ca}}{2 \cdot \text{ln}(2) \cdot k} \\
\text{vel}_C = 2.274 \times 10^3 \frac{\text{m}}{\text{s}} \\
\text{Temp}_C = 228.517 \text{K} \\
vel_D := \left( P_{D_2} - P_{D_2}' \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \sqrt{2} \\
Temp_D := \left( \frac{P_{D_3} \cdot 10^6 \cdot \text{sec}^{-1}}{2} \cdot \frac{c}{f_m} \right)^2 \cdot \frac{m_{ca}}{2 \cdot \text{ln}(2) \cdot k} \\
\text{vel}_D = 2.294 \times 10^3 \frac{\text{m}}{\text{s}} \\
\text{Temp}_D = 226.454 \text{K} \\

Figure B-6. Page 6 of single Gaussian fit worksheet
\[
\text{Temps} := \begin{pmatrix}
\text{Temp} \\
\text{TempA} \\
\text{TempB} \\
\text{TempC} \\
\text{TempD}
\end{pmatrix}
\quad \text{vels} := \begin{pmatrix}
\text{vel} \\
\text{velA} \\
\text{velB} \\
\text{velC} \\
\text{velD}
\end{pmatrix}
\]

\[
\text{Avetemp} := \text{mean(Temps)} \quad \text{etemps} := \text{Stdev(Temps)}
\]

\[
\text{Avvel} := \text{mean(vels)} \quad \text{evels} := \text{Stdev(vels)}
\]

\[
\text{Avetemp} = 224.38 \text{K} \quad \text{Avvel} = 2.281 \times 10^3 \frac{\text{m}}{\text{s}}
\]

\[
\text{etemps} = 13.255 \text{K} \quad \text{evels} = 14.764 \frac{\text{m}}{\text{s}}
\]

\[
\text{Temps} = \begin{pmatrix}
202.158 \\
226.937 \\
237.834 \\
228.517 \\
226.454
\end{pmatrix} \quad \text{vels} = \begin{pmatrix}
2.262 \times 10^3 \\
2.298 \times 10^3 \\
2.279 \times 10^3 \\
2.274 \times 10^3 \\
2.294 \times 10^3
\end{pmatrix} \frac{\text{m}}{\text{s}}
\]

Figure B-7. Page 7 of single Gaussian fit worksheet.
B.2 Dual Population Gaussian Function Fitting Area Integration Worksheet

\[
\text{data} := \text{O:\pbflab\Neil's Research}
\]

This reads in the data from an excel spreadsheet. The starting row and column are specified when the component is defined. The first column in the spreadsheet contains a frequency axis based on the calibration of the etalon. Columns 3, 7, 11, 15, and 19 contain the data from the hollow cathode lamp. Columns 5, 9, 13, 17, and 21 contain the calcium fluorescence data. 'data' is an array, and data\^[n] refers to column n+1 in that array (the beginning subscript for Mathcad is 0).

\[
\begin{align*}
\text{data}_{1,0} &= -484.382 \\
k_1 &:= 4 \cdot \ln(2) \\
k_2 &:= \frac{\sqrt{\pi}}{2 \cdot \ln(2)}
\end{align*}
\]

\[
x := \text{data}^\langle 1 \rangle \\
y := \text{data}^\langle 2 \rangle \\
y_a := \text{data}^\langle 3 \rangle \\
y_b := \text{data}^\langle 4 \rangle \\
y_c := \text{data}^\langle 5 \rangle \\
y_{d} := \text{data}^\langle 6 \rangle \\
y_2 := \text{data}^\langle 7 \rangle \\
y_{2a} := \text{data}^\langle 8 \rangle \\
y_{2b} := \text{data}^\langle 9 \rangle \\
y_{2c} := \text{data}^\langle 10 \rangle \\
y_{2d} := \text{data}^\langle 11 \rangle
\]

Figure B-8. Page 1 of dual Gaussian fit & area integration worksheet
lambda is the excitation wavelength, the rest of these are fundamental constants.

\[
\begin{align*}
\lambda &= 801.478 \times 10^{-9} \, \text{m} \\
c &= 2.998 \times 10^8 \, \text{m/s} \\
h &= 6.6260755 \times 10^{-34} \, \text{joule-sec} \\
f_{m} &= \frac{c}{\lambda} \\
k &= 1.38054 \times 10^{-23} \, \text{joule/K} \\
N_0 &= 6.0221367 \times 10^{23} \, \text{mole}^{-1} \\
m_{ca} &= \frac{39.948 \, \text{gm}}{N_0} \\
\end{align*}
\]

\[F(z,u)\] is an array of equations. The first equation is the function we want to fit, a general gaussian. It has four adjustable parameters: \(u0\) is the value of the baseline, \(u1\) gives the amplitude, \(u2\) gives the shift from the origin, and \(u3\) gives the width. The remaining four functions are the partial derivatives our gaussian function with respect to \(u0\), \(u1\), \(u2\), and \(u3\) respectively. \(\text{vg}\) is a vector containing guesses for the starting values of the four parameters. If these initial guesses are too far off, the fitting function won’t converge and you get garbage. Note that there are two sets of guesses, one for each curve in a scan.

\[F(z,u) := \begin{bmatrix}
-k1 \frac{(z-u2)^2}{(u3)^2} \\
u0 + u1 \cdot e^{\frac{1}{(u3)^2}} \\
-k1 \cdot (z-u2)^2 \\
-\frac{e}{(u3)^2} \\
-k1 \frac{(z-u2)^2}{(u3)^2} \\
u1 \cdot e^{\frac{-2k1 \cdot (z-u2)}{(u3)^2}} \\
-k1 \frac{(z-u2)^2}{(u3)^2} \\
u1 \cdot e^{\frac{-2k1 \cdot (z-u2)}{(u3)^3}}
\end{bmatrix}\]

\[\text{vg} := \begin{bmatrix} 0 \\ 1.5 \\ 4500 \\ 1000 \end{bmatrix}\]

Figure B-9. Page 2 of dual Gaussian fit & area integration worksheet
The calls below are calls to the fitting function. There is one call for each curve. The results are stored in vectors P, PA, PB etc. The first parameter in the function call is the vector containing the x data. The second parameter is the vector containing the y data. The third parameter is the vector of guesses. The fourth parameter is the array of functions.

\[
\begin{bmatrix}
- k_1 \left( \frac{(z-u_{12})^2}{(u_{13})^2} \right) & - k_1 \left( \frac{(z-u_{15})^2}{(u_{16})^2} \right) \\
u_{10} + u_{11} e & 1 \\
- k_1 \left( \frac{(z-u_{12})^2}{(u_{13})^2} \right) e & - k_1 \left( \frac{(z-u_{12})^2}{(u_{13})^2} \right) e \\
u_{11} e & \frac{(z-u_{12})^2}{(u_{13})^2} \\
- k_1 \left( \frac{(z-u_{12})^2}{(u_{13})^2} \right) \cdot 2 k_1 \left( \frac{(z-u_{12})^2}{(u_{13})^2} \right) \\

\end{bmatrix}
\]

The calls below are calls to the fitting function. There is one call for each curve. The results are stored in vectors P, PA, PB etc. The first parameter in the function call is the vector containing the x data. The second parameter is the vector containing the y data. The third parameter is the vector of guesses. The fourth parameter is the array of functions.

\[
F_1(z, u_{11}) :=
\begin{bmatrix}
- k_1 \left( \frac{(z-u_{12})^2}{(u_{13})^2} \right) & - k_1 \left( \frac{(z-u_{15})^2}{(u_{16})^2} \right) \\
u_{10} + u_{11} e & 1 \\
- k_1 \left( \frac{(z-u_{12})^2}{(u_{13})^2} \right) e & - k_1 \left( \frac{(z-u_{12})^2}{(u_{13})^2} \right) e \\
u_{11} e & \frac{(z-u_{12})^2}{(u_{13})^2} \\
- k_1 \left( \frac{(z-u_{12})^2}{(u_{13})^2} \right) \cdot 2 k_1 \left( \frac{(z-u_{12})^2}{(u_{13})^2} \right) \\

\end{bmatrix}
\]

\[
\begin{bmatrix}
0 \\
1.5 \\
2500 \\
.5 \\
3000 \\
2000 \\
\end{bmatrix}
\]

\[
vg_2 :=
\begin{bmatrix}
1000 \\
2000 \\
\end{bmatrix}
\]

Figure B-10. Page 3 of dual Gaussian fit & area integration worksheet
This next section simply plots the fits on the same axes as the raw data. This step is essential because it tells you immediately if your fit has converged.

\[
\begin{bmatrix}
0.012 \\
1.632 \\
4.255 \times 10^3 \\
1.068 \times 10^3 
\end{bmatrix}
\]

This next set of calls simply reconstructs the curves by a calls to the first function in \( F \), with the fit parameters supplied in the \( P \) vectors.

\[
\begin{align*}
\text{g}(x) &= F(x, P)_0 \\
g_2(x) &= F_1(x, P_2)_0 \\
g_a(x) &= F(x, P_{A})_0 \\
g_{2a}(x) &= F_1(x, P_{2A})_0 \\
g_b(x) &= F(x, P_{B})_0 \\
g_{2b}(x) &= F_1(x, P_{2B})_0 \\
g_c(x) &= F(x, P_{C})_0 \\
g_{2c}(x) &= F_1(x, P_{2C})_0 \\
g_d(x) &= F(x, P_{D})_0 \\
g_{2d}(x) &= F_1(x, P_{2D})_0
\end{align*}
\]

This next section simply plots the fits on the same axes as the raw data. This step is essential because it tells you immediately if your fit has converged.

Figure B-11. Page 4 of dual Gaussian fit & area integration worksheet
Figure B-12. Page 5 of dual Gaussian fit & area integration worksheet
The next section calculates the velocities and temperatures from the fitted equations. The pertinent equations can be found in James Patterson's thesis and in Ingle and Crouch.

Figure B-13. Page 6 of dual Gaussian fit & area integration worksheet
vel := \left( P_2 - P_{2'} \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \cdot \sqrt{2} \quad \text{vel} = 2.272 \times 10^3 \text{ m/s}

vel2 := \left( P_2 - P_{2'} \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \cdot \sqrt{2} \quad \text{vel2} = 1.051 \times 10^3 \text{ m/s}

\text{Temp} := \left( \frac{P_3 \cdot 10^6 \cdot \text{sec}^{-1} \cdot c}{2 \cdot f_m} \right) \cdot \frac{m_{ca}}{2 \cdot \text{ln(2)} \cdot k} \quad \text{Temp} = 281.354 \text{K}

\text{Temp2} := \left( \frac{P_{26} \cdot 10^6 \cdot \text{sec}^{-1} \cdot c}{2 \cdot f_m} \right) \cdot \frac{m_{ca}}{2 \cdot \text{ln(2)} \cdot k} \quad \text{Temp2} = 4.03 \times 10^3 \text{ K}

Calculate the areas of the curves. This is a simple analytical integral of the Gaussians calculated by the fitting procedure.

\text{fasta} := P_2 \cdot P_3 \cdot k2 \quad \text{slowa} := P_{2'} \cdot P_{2'} \cdot k2

velA := \left( P_{A2} - P_{2A} \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \cdot \sqrt{2} \quad \text{velA} = 2.286 \times 10^3 \text{ m/s}

velA2 := \left( P_{A2} - P_{2A} \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \cdot \sqrt{2} \quad \text{velA2} = 1.034 \times 10^3 \text{ m/s}

\text{TempA} := \left( \frac{P_{A2} \cdot 10^6 \cdot \text{sec}^{-1} \cdot c}{2 \cdot f_m} \right) \cdot \frac{m_{ca}}{2 \cdot \text{ln(2)} \cdot k} \quad \text{TempA} = 287.081 \text{K}

\text{TempA2} := \left( \frac{P_{A26} \cdot 10^6 \cdot \text{sec}^{-1} \cdot c}{2 \cdot f_m} \right) \cdot \frac{m_{ca}}{2 \cdot \text{ln(2)} \cdot k} \quad \text{TempA2} = 4.049 \times 10^3 \text{ K}

\text{fastaA} := P_{2A} \cdot P_3 \cdot k2 \quad \text{slowaA} := P_{2A} \cdot P_{2A} \cdot k2

velB := \left( P_{B2} - P_{2B} \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \cdot \sqrt{2} \quad \text{velB} = 2.293 \times 10^3 \text{ m/s}

velB2 := \left( P_{B2} - P_{2B} \right) \cdot 10^6 \cdot \text{sec}^{-1} \cdot \text{lambda} \cdot \sqrt{2} \quad \text{velB2} = 1.127 \times 10^3 \text{ m/s}

\text{TempB} := \left( \frac{P_{B2} \cdot 10^6 \cdot \text{sec}^{-1} \cdot c}{2 \cdot f_m} \right) \cdot \frac{m_{ca}}{2 \cdot \text{ln(2)} \cdot k} \quad \text{TempB} = 247.261 \text{K}

Figure B-14. Page 7 of dual Gaussian fit & area integration worksheet
TempB2 := \( \frac{P2B_6 \cdot 10^6 \cdot \sec^{-1}}{2} \frac{c}{f_m} \) \frac{m_{ca}}{2 \cdot \ln(2) \cdot k} \quad \text{TempB2} = 3.979 \times 10^3 \text{ K}

fastaB := P2B_1 \cdot P2B_3 \cdot k2 \quad \text{swaB} := P2B_4 \cdot P2B_6 \cdot k2

velC := \( \left( P2C_2 - P2C_2 \right) \cdot 10^6 \cdot \sec^{-1} \cdot \lambda \cdot \sqrt{2} \) \quad \text{velC} = 2.265 \times 10^3 \text{ m/s}

velC2 := \( \left( P2C_2 - P2C_5 \right) \cdot 10^6 \cdot \sec^{-1} \cdot \lambda \cdot \sqrt{2} \) \quad \text{velC2} = 1.048 \times 10^3 \text{ m/s}

TempC := \( \frac{P2C_3 \cdot 10^6 \cdot \sec^{-1}}{2} \frac{c}{f_m} \) \frac{m_{ca}}{2 \cdot \ln(2) \cdot k} \quad \text{TempC} = 331.316 \text{ K}

TempC2 := \( \frac{P2C_6 \cdot 10^6 \cdot \sec^{-1}}{2} \frac{c}{f_m} \) \frac{m_{ca}}{2 \cdot \ln(2) \cdot k} \quad \text{TempC2} = 3.984 \times 10^3 \text{ K}

fastaC := P2C_1 \cdot P2C_3 \cdot k2 \quad \text{swaC} := P2C_4 \cdot P2C_6 \cdot k2

velD := \( \left( PD_2 - PD_2 \right) \cdot 10^6 \cdot \sec^{-1} \cdot \lambda \cdot \sqrt{2} \) \quad \text{velD} = 2.26 \times 10^3 \text{ m/s}

velD2 := \( \left( PD_2 - PD_5 \right) \cdot 10^6 \cdot \sec^{-1} \cdot \lambda \cdot \sqrt{2} \) \quad \text{velD2} = 1.066 \times 10^3 \text{ m/s}

TempD := \( \frac{P2D_3 \cdot 10^6 \cdot \sec^{-1}}{2} \frac{c}{f_m} \) \frac{m_{ca}}{2 \cdot \ln(2) \cdot k} \quad \text{TempD} = 256.341 \text{ K}

TempD2 := \( \frac{P2D_6 \cdot 10^6 \cdot \sec^{-1}}{2} \frac{c}{f_m} \) \frac{m_{ca}}{2 \cdot \ln(2) \cdot k} \quad \text{TempD2} = 3.835 \times 10^3 \text{ K}

fastaD := P2D_1 \cdot P2D_3 \cdot k2 \quad \text{swaD} := P2D_4 \cdot P2D_6 \cdot k2

Figure B-15. Page 8 of dual Gaussian fit & area integration worksheet
Figure B-16. Page 9 of dual Gaussian fit & area integration worksheet

```
Temps := (TempA, TempB, TempC, TempD)
vels := (velA, velB, velC, velD)
Temps2 := (TempA2, TempB2, TempC2, TempD2)
vels2 := (velA2, velB2, velC2, velD2)

fastas := (fastaA, fastaB, fastaC, fastaD)
slowas := (slowaA, slowaB, slowaC, slowaD)

Avetemp := mean(Temps) etemps := Stdev(Temps)
Avetemp2 := mean(Temps2) etemps2 := Stdev(Temps2)
Avvel := mean(vels) evels := Stdev(vels)
Avvel2 := mean(vels2) evels2 := Stdev(vels2)
Avefasta := mean(fastas) efastas := Stdev(fastas)
Aveslowa := mean(slowas) eslowas := Stdev(slowas)
```
Avetemp = 280.671 K
Avvel = $2.275 \times 10^3 \frac{m}{s}$
etemps = 32.843 K
evels = $13.84 \frac{m}{s}$

$$\begin{bmatrix} 281.354 \\ 287.081 \\ 247.261 \\ 331.316 \\ 256.341 \end{bmatrix} K$$
$$\begin{bmatrix} 2.272 \times 10^3 \\ 2.286 \times 10^3 \\ 2.293 \times 10^3 \\ 2.265 \times 10^3 \\ 2.26 \times 10^3 \end{bmatrix} \frac{m}{s}$$

$Avetemp_2 = 3.975 \times 10^3 K$
$Avvel_2 = 1.065 \times 10^3 \frac{m}{s}$
etemps_2 = 84.186 K
evels_2 = $36.203 \frac{m}{s}$

$$\begin{bmatrix} 4.03 \times 10^3 \\ 4.049 \times 10^3 \\ 3.979 \times 10^3 \\ 3.984 \times 10^3 \\ 3.835 \times 10^3 \end{bmatrix} K$$
$$\begin{bmatrix} 1.051 \times 10^3 \\ 1.034 \times 10^3 \\ 1.127 \times 10^3 \\ 1.048 \times 10^3 \\ 1.066 \times 10^3 \end{bmatrix} \frac{m}{s}$$

$Avefasta = 511.11$
$Aveslowa = 2.495 \times 10^3$
efastas = 45.849
eslowas = $51.163$

$$\begin{bmatrix} 560.221 \\ 526.211 \\ 452.898 \\ 542.475 \\ 473.745 \end{bmatrix}$$
$$\begin{bmatrix} 2.445 \times 10^3 \\ 2.5 \times 10^3 \\ 2.576 \times 10^3 \\ 2.458 \times 10^3 \\ 2.495 \times 10^3 \end{bmatrix}$$

Figure B-17. Page 10 of dual Gaussian fit & area integration worksheet
Appendix C: First Stage Vacuum Expansion Vector Calculation Equations

Assume that the expansion is symmetric with respect to the Z-axis. Consider two points with \(z_1 = z_2\) and \(x_1 = -x_2\).

\[
V_{\text{obs}1} = V_1 \cos (\theta_D + \theta_V) \\
V_{\text{obs}2} = V_2 \cos (\theta_D - \theta_V)
\]

\[
\frac{V_{\text{obs}1}}{\cos(\theta_D + \theta_V)} = \frac{V_{\text{obs}2}}{\cos(\theta_D - \theta_V)}
\]

\[
\cos (\theta_D - \theta_V) = \cos \theta_D \cos \theta_V - \sin \theta_D \sin \theta_V
\]

\[
\cos (\theta_D + \theta_V) = \cos \theta_D \cos \theta_V + \sin \theta_D \sin \theta_V
\]

\[
sin \theta_D = \cos \theta_D = \frac{\sqrt{2}}{2}
\]

\[
\frac{V_{\text{obs}1}}{(\cos \theta_V - \sin \theta_V)} = \frac{V_{\text{obs}2}}{(\cos \theta_V + \sin \theta_V)}
\]

\[
V_{\text{obs}1} \cos \theta_V + V_{\text{obs}1} \sin \theta_V = V_{\text{obs}2} \cos \theta_V - V_{\text{obs}2} \sin \theta_V
\]

\[
(V_{\text{obs}2} + V_{\text{obs}1}) \sin \theta_V = (V_{\text{obs}2} - V_{\text{obs}1}) \cos \theta_V
\]

\[
\tan \theta_V = \frac{(V_{\text{obs}2} - V_{\text{obs}1})}{(V_{\text{obs}2} + V_{\text{obs}1})}
\]

\[
V = \frac{V_{\text{obs}1}}{\cos(45 + \theta_V)} = \frac{V_{\text{obs}2}}{\cos(45 - \theta_V)}
\]

\[
V_z = V \cos \theta_x
\]

\[
V_x = V \sin \theta_x
\]

Figure C-1. Calculations of \(V_z\) and \(V_x\) from Doppler \(V_{\text{obs}}\)