Laser-Induced Fluorescence Imaging of Calcium and Barium Ion Beams in the Second Vacuum Stage of a Commercial Inductively Coupled Plasma Mass Spectrometer

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Laser-Induced Fluorescence Imaging of Calcium and Barium Ion Beams in the
Second Vacuum Stage of a Commercial Inductively
Coupled Plasma Mass Spectrometer

Alisa J. Edmund

A thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of
Master of Science

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June 2014

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ABSTRACT

Laser-Induced Fluorescence Imaging of Calcium and Barium Ion Beams in the Second Vacuum Stage of a Commercial Inductively Coupled Plasma Mass Spectrometer

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Inductively coupled plasma-mass spectrometers (ICP-MS) have become the workhorses of many analytical labs over the past few decades. Despite the instruments’ high sensitivities and low detection limits there is still a demand for improvements in several aspects of their performance. One area of improvement is in the understanding of “space charge effects.” Space charge effects are classified as problems associated with the ion beam. Problems are created when the mutual repulsions of the ions make consistent focusing of the ion beam difficult. This is particularly problematic with samples containing a low concentration analyte contained within a high salt solution matrix, resulting in lower instrument sensitivity and inaccurate results. The research presented here used laser-induced fluorescence (LIF) imaging to characterize the ion beam as it enters the mass analyzer of a commercial ICP-MS.

To perform the LIF imaging a laser system with two ring cavities was constructed to frequency double a CW titanium-sapphire laser to the calcium ion transition at 393.4 nm or to the barium ion transition at 455.4 nm. Ion beam images for both elements were taken under different instrument modes and matrix compositions. The same trends in shift and distortion of the barium ion beam with the addition of a lead matrix was observed as in previous experiments with calcium. A shift in the focal point of the ion beams of both elements was also observed in normal sensitivity mode and with the instrument’s collisional reaction interface (CRI). This work indicates that a shift in beam focusing is responsible for the change in ion transmission due to changes in matrix composition and instrument modes.

Keywords: ICP-MS, matrix effects, laser-induced fluorescence imaging
ACKNOWLEDGEMENTS

I would like to acknowledge my advisor, Dr. Paul Farnsworth. I am grateful for the opportunities I have had in his laboratory to develop educationally and personally. I would also like to acknowledge my committee members, Dr. Jaron Hansen and Dr. Scott Bergeson, for their support and encouragement. I am particularly grateful for the help and instruction from Dr. Bergeson with the laser system; this work would not be possible without his expertise. I am very appreciative of the generous financial support for this project provided by Bruker and the Brigham Young University College of Physical and Mathematical Sciences. I’m also very thankful to my family for the many ways in which they have supported me in pursuing this degree.
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1. INTRODUCTION

1.1. ICP-MS OVERVIEW

Inductively coupled plasma mass spectrometry (ICP-MS) has become a dominant analytical technique for trace elemental analysis. It is employed for analyses in many fields, such as forensics, medical, and environmental sciences [1-6]. ICP-MS is attractive due in part to its high ionization efficiency, low background levels, and superior sensitivity over other analytical techniques. ICP-MS is advantageous over other analytical techniques, such as atomic absorption spectroscopy (AAS) and ICP-optical emission spectroscopy (ICP-OES), because the operator can perform analyses in rapid succession with high selectivity and low detection limits.

ICP-MS was commercially introduced in 1983 and is considered a mature technique. Because it is considered mature the number of fundamental studies and significant advances has declined over the years, despite the need for additional improvement [6]. Despite ICP-MS being a powerful tool, analyses are complicated by matrix effects. Matrix effects are characterized by the technique reporting a value different from the “true” analyte concentration due to differences between the non-analyte (matrix) compositions of the samples and standards. An implicit assumption with external calibration methods is that the instrumental sensitivity for the analyte is independent of matrix composition. This assumption does not hold for many ICP-MS applications. Common methods for dealing with matrix effects include matrix matching, standard addition, internal standardization, and in some instruments collisional reaction cells. However, these methods are inferior in comparison to routine external calibration because they require more preparation time and resources.

The matrix effects observed in an ICP-MS are more severe than those in ICP-OES, suggesting that the ICP combined with the MS interface introduces matrix effects beyond those
solely caused by the ICP itself. Identifying the sources and mechanisms of matrix effects will provide for more effective ways of correcting for them. Study of the MS interface may also identify means of improving ICP-MS sensitivity. The study of ion transport along the path of the ion beam from the plasma to the mass analyzer in an ICP-MS has been an area of active research since the technique was first introduced.

1.1.1. ICP-MS Principle of Operation

ICP-MS instruments use a multi-stage vacuum system, as shown in Figure 1.1.; successive vacuum stages are necessary to move the ionized sample from the plasma at atmospheric pressure to the mass analyzer, which operates under high vacuum conditions (~10^{-6} Torr). The sample is introduced into the ICP as a solution; the solution is nebulized creating an aerosol and then carried by a stream of gas, commonly argon, into a quartz torch with a three turn copper coil around it. The plasma is generated as the argon gas flows through the torch while an alternating current is applied to the coil. Ionization of the argon gas is initiated by a spark from a Tesla coil. Ionization continues as the electrons are inductively heated in the oscillating magnetic field. In the plasma, collisions with electrons and argon ions ionize the sample.

Mass analysis is achieved by extracting ions from the atmospheric pressure plasma through the sampling cone into the first vacuum stage (sustained at the pressure of ~1 Torr). The ions are further extracted through a skimmer cone into the second vacuum stage (~10^{-3} to 10^{-4} Torr). The ion beam is then focused with ion optics and introduced through an additional orifice into the third vacuum stage containing the mass analyzer (~10^{-6} Torr). As the ions are extracted through the vacuum stages only a small fraction of them reach the detector.
Figure 1.1. Schematic of a conventional ICP-MS. The sample is introduced as a solution and nebulized to an aerosol (A). The aerosol is carried by Ar gas to the torch where the particles are vaporized and ionized in the plasma (B). The atomic ions are extracted through a sampling cone into the first vacuum stage (C) and then through a skimmer cone to the second vacuum stage (D). The ions are then focused and introduced to the mass analyzer (E). The analysis results are then generated by the computer (F) as a mass spectrum.

1.2. INTRODUCTION TO SPACE CHARGE-INDUCED INACCURACIES IN THE ICP-MS

The plasma passing through the sampler and skimmer cones is quasi-neutral, meaning that there are approximately equal numbers of ions and electrons. However, potentials applied to the ion optics repel the electrons, leaving only positively-charged ions. The challenge created when using an ion beam with a large number of charged species is that the mutual Coulombic repulsion by the ions distorts the shape of the beam and potentially the results of the analysis. Distortions to the ion beam due to the presence of high densities of charged species are generally classified as space charge effects. Modeling of these space charge effects, done by Tanner [7], accounted for observed mass trends in the ICP-MS. These mass–dependent space effects are most severe if a sample contains a heavy mass matrix and a much lighter analyte, a situation that
is common in samples that have complex matrices. One way to improve the function of the ICP-MS is reduction of space charge effects that occur within the second vacuum stage.

1.3. BACKGROUND

1.3.1. Researching the Second Vacuum Stage

Many researchers have investigated the first and second vacuum stages of the ICP-MS. Early experimenters placed probes [8-10] or targets to collect deposition [11-14] in the path of the ion beam to study space charge in the second vacuum stage. Using probes in the beam only measured ions and electrons but could not further determine any composition of the ion beam. On the other hand deposition experiments gave some insight into the composition of the beam, but analysis could not be taken in real time. Although these experiments provided useful information they were highly invasive and the beam was perturbed by the measurements themselves.

Other researchers have attempted to minimize space charge effects by making modifications to the ICP-MS. A three aperture interface was suggested by Ross and Hieftje in 1991 [15] and Tanner et al. in 1994 [16]. While these approaches reduced space charge effects they did so by decreasing the intensity of the ion beam transmitted to the mass spectrometer. The gains from the reduction of space charge were offset by losses in transmission efficiency through the three apertures. Houk et al. [17] added electrons with a filament behind the skimmer cone. The added electrons balanced the positive charge of the ions and minimized the radial spreading of the beam and loss of ions from space charge effects. This approach showed that with the right conditions the sensitivity of a particular ion could be improved by a factor of 2-3. Recently, Gunther et al. [18] attempted to replace the ion optics in a commercial instrument with
an ion funnel in the second vacuum stage; however, their experiments yielded a lower transmission and decreased the mass resolution of the quadrupole when compared to the original instrument configuration. Although these studies have given valuable insights into the effects of space charge, they failed to improve the overall sensitivity or accuracy of the instruments. In order to make improvements and modifications to ICP-MS a better fundamental understanding of space charges effects in ICP-MS is needed.

Non-invasive studies can be conducted using laser induced fluorescence (LIF) as a tool to characterize space charge along the path of the ion beam from the plasma to the mass spectrometer. LIF also allows the researcher to acquire data in real-time and provides good selectivity of the studied ion. It is therefore desirable over probe and deposition methods. Duersch and Farnsworth first showed the viability of this technique for studying ICP-MS and used laser excitation to characterize the ion beam 8 mm downstream from the tip of the skimmer cone with a custom built vacuum stage design [19-20]. Laser induced fluorescence has since been used extensively in our laboratory to characterize the first and second vacuum stages [19-24]. However, these experiments have been done primarily with a custom built interface. Our work here expands these fluorescence studies of space charge by using laser induced fluorescence imaging to image the ion beam in the second vacuum stage two to three millimeters before the orifice of the mass analyzer in a commercial ICP-MS.

In a previous study we successfully imaged a cross section of a Ca ion beam at the entrance to the mass analyzer in a commercial Varian 820 ICP-MS [25]. In this work we determined that the beam from a solution containing only Ca analyte behaved as predicted by SIMION simulations. The addition of three different matrices, Mg, Cs, and Pb, to Ca solutions had only minor effect on the beam profile. However, the addition of heavier matrices altered the
Ca beam trajectory and this effect was observed most prominently with Pb. This shift in the direction and location of the Ca ion beam at the entrance into the mass analyzer resulted in an order-of-magnitude decrease in the mass spectrometer signal. The work presented here expands our previous work with Ca and will present images of a Ba ion beam in normal operating modes and Ca and Ba ion beams with the Varian Collisional Reaction Interface (CRI). Imaging of two widely separated masses will give greater insight into the shifting and distortion of the ion beam due to matrix composition and different instrument modes.

1.3.2. **Instrumentation**

Commercial ICP-MS instruments featured linear extraction systems until Varian introduced their 800-line of instruments; this instrument design presents a novel right-angle ion optic geometry as shown in Figure 1.2. This ion mirror is a metal ring with four electrodes that creates a parabolic electrostatic field that bends and focuses the ions from the skimmer cone to the entrance to the mass analyzer [26]. The open ring geometry allowed us to perform LIF imaging experiments on a cross section of the ion beam before it enters the orifice of the mass spectrometer. These LIF experiments would be impossible in other previous commercial instrument with a linear system, as shown previously in Figure 1.1.

We conducted our experiments by extending the second vacuum stage with an aluminum wedge. The wedge allowed us to introduce the laser excitation and collect the fluorescence with no effect on the instrument performance. The modifications to the instrument will be described in further detail in Chapter 3. The ion beam images collected non-invasively measure the effect of space charge on ion beam formation and focusing under different instrument parameters.
Figure 1.2. Photograph of the second vacuum stage of the Varian 820 ICP-MS. The ion optic ring is shown in the center. The ion beam enters from the right through the back of the skimmer cone and extraction lenses; shown here behind the optic ring on the right. The ion beam is then reflected by the ion optic ring at a 90 degree angle to the entrance to the mass analyzer; shown here behind the optic ring on the left.

1.4. SUMMARY

Despite the inefficiencies of the ICP-MS interface, ICP-MS sensitivity is superior to other analytical instruments. Nevertheless, there are improvements in the sensitivity of this instrument that can be made. Improvements in the understanding and subsequent improvement of ICP-MS could be immediately implemented. This would save time and resources as well as improve the accuracy of routine analysis. The purpose of this work is to further the understanding of changes in ion transmission due to space charge effects in the second vacuum stage of an ICP-MS.

In this study, I investigated ion beam formation in the second vacuum stage of an ICP-MS by laser induced fluorescence. Beam cross sections were imaged 2-3 millimeters before the
entrance to the mass analyzer. Images were recorded for a range of matrix compositions and instrument modes. First, a calcium analyte ion beam under normal and high sensitivity modes of the instrument with various concentrations was studied. Second, a heavier analyte—barium was investigated under similar conditions. Finally, changes to both calcium and barium ion beams were studied when a collisional gas was introduced at the tip of the skimmer cone.

1.5 REFERENCES


2. LASER SETUP

2.1. DOUBLING CAVITY

2.1.1. General Setup

Preliminary experiments in our laboratory used a pulsed dye laser as the excitation source to observe the ion beam in the second vacuum stage of an ICP-MS using laser induced fluorescence (LIF). These experiments were unsuccessful because the duty cycle of the experiment was too low to get enough fluorescence signal. We then successfully imaged the ion beam with a CW titanium-sapphire laser (SolsTiS, M Squared Lasers, Glasgow, Scotland) frequency doubled to the 393.3663 nm calcium transition [1]. This chapter will describe the elements, assembly, and operation of the laser system in our laboratory patterned after the one used in previous experiments. The general setup of the frequency doubling cavities is shown in Figure 2.1.
Figure 2.1. Schematic of the laser system setup. The telescope of lenses (A) create the necessary waist for the doubling cavities (E). Approximately 4% of the beam is picked off by a beam splitter to monitor the wavelength of the fundamental beam with a wavemeter (B). A kinematically-mounted mirror (C) allows for switching between two cavities on the optical table. As part of the error locking system an electro-optical modulator (D) is placed in the beam path and a photodiode (F) collects the laser reflected off the input mirror of the frequency doubling cavity. A lens (G) collimates the light before it is sent to the ICP-MS.

The telescope (A) is comprised of two plano-convex lenses. These lenses create the waist of the laser necessary for the bowtie frequency doubling cavity. Choosing the focal length of
these lenses and their placement along the beam path will be discussed later in section 2.1.2. The wavelength is measured by a high precision wavemeter (B) (Angstrom WS/6, High Finesse, Tübingen, Germany).

All of the mirrors upstream of the doubling cavity are anti-reflection coated for 750-1100 nm (BB1-E03, Thorlabs, Newton, NJ). A mirror on a kinematic mount (C) allows for the setup of two frequency doubling cavities on the same optical table. When this mirror is on the kinematic mount it allows for the right cavity, the calcium cavity, to be used and when it is removed the left cavity, the barium cavity, is operational. Both cavities are the same design with different cavity mirrors and doubling crystals appropriate for their specified wavelengths.

An electro-optical modulator (EOM) (D) (Model 505, ConOptics, Danbury, CT) and a photodiode (F) are placed at indicated positions along the beam path as part of the cavity error locking system. The error locking system will be described in further detail in section 2.2. The frequency doubling cavity (E) is made up of four mirrors (LaserOptik, Garbsen, Germany). Mirror 1 (M1) and 2 (M2) are planar mirrors and mirror 3 (M3) and 4 (M4) are convex-concave. The radii of the curved mirrors is 100 mm. M2, M3, and M4 all have a reflectance of over 99.9% for the fundamental beam, while M1 has a reflectance of 99%. All the mirrors have a transmittance of over 97% for the doubled light. In this chapter M1 will be referred to as the input coupler or input mirror. M2 will be referred to as the piezo mirror, shown in Figure 2.2. The piezo mirror is unique because it is a 6 mm mirror mounted on a piezo-electric translator (AEO505D08F, Thorlabs, Newton, NJ). The piezo translator is mounted on a stainless steel dowel pin that is set into an aluminum cup filled with lead. The aluminum cup is then mounted in a 1” mirror mount. The lead filled cup helps to stabilize the mount when the piezo voltage is changed. The doubling crystal between M3 and M4 is a 3 x 3 x 15 mm³ LBO crystal (Castech,
Inc., Fuzhou, China). M3 and M4 have the same specifications and curvature, but mirror 4 will be referred to as the output coupler.

![Figure 2.2. Schematic of the piezo cavity mirror (M2).](image)

A lens (G) collimates the beam (LA1708-A, Thorlabs) after the output coupler in the horizontal direction to make the beam more symmetrically shaped. All the downstream mirrors for the use of the calcium cavity are coated for high reflectivity between 350-400 nm (BB1-E01, Thorlabs) while the downstream mirrors for the barium cavity are coated for 400-750 nm (BB1-E02, Thorlabs). These downstream mirrors direct the light to the ICP-MS setup, described further in Chapter 3.
2.1.2. Telescope

The position of the beam waist and telescope mirrors was determined using the ABCD law for Gaussian beams. For our ring cavity the waist needs to be 324 micrometers. The telescope lens parameters used in our setup are shown in Table 2.1.

Table 2.1. Telescope lens parameters

<table>
<thead>
<tr>
<th>Lens Parameter</th>
<th>Distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Focal length lens 1</td>
<td>50</td>
</tr>
<tr>
<td>Focal length lens 2</td>
<td>150</td>
</tr>
<tr>
<td>Position lens 1 from laser</td>
<td>251</td>
</tr>
<tr>
<td>Position lens 2 from laser</td>
<td>465</td>
</tr>
<tr>
<td>Position of waist from laser</td>
<td>2669</td>
</tr>
</tbody>
</table>

Because the size and position of the waist are so critical, we measure the beam width at several places along the beam path to confirm where and how large the beam waist is. To do this we use a power meter and a stage with a sharp edge. The distance between the stage positions at 14% and 86% of the maximum power gives the beam width for that position along the beam path. The beam waist in our setup was confirmed to be about 0.33 mm.

2.1.3. Single Pass Alignment

The next step after the telescope is aligned and the size and position of the waist is confirmed, as described in section 2.1.2, is to align the single pass of the ring cavity. Figure 2.3 shows the cavity setup and associated distances between the optics. These distances are of the utmost importance. Distances A and B must be accurate within a few millimeters; while distances C and D must be within one millimeter.
Figure 2.3. Schematic of the frequency doubling cavity. The distance between M1 and M2 (A) is 414 mm and the waist is centered between the two mirrors. The distance between M2 and M3 (B) is 294 mm. The distance between M3 and the left side of the LBO crystal face (C) and between M4 and the right side of the LBO crystal face (D) is 49.5 mm. A beam waist should be in the center of the LBO crystal.

To align the single pass of the cavity, the piezo mirror (M2), M3, the output coupler (M4), and crystal need to be put into their mounts and appropriate places. Attention must be given to make sure that the height of the laser and the optics stay the same throughout the cavity. This is important because it prevents losses and produces greater efficiency of the doubling cavity. An easy way to check the height of the beam is to put a business card in the laser beam until it burns. Do this at different points in the cavity to confirm and adjust until the beam is at a uniform height. However, caution must be taken because soot from the burned card can accumulate on the optics and crystal face. Care must be taken to not get soot on these surfaces, but if it does the optics must be carefully cleaned to prevent damage and scattering off the surfaces. Continue to check the height of the beam periodically until the cavity is aligned.
Next, the crystal is aligned using a protractor such that the angle between the crystal face and the beam reflected off of M3 are at Brewster’s angle. Brewster’s angle for the barium and calcium cavities are 58.17 degrees and 58.12 degrees respectively. Each cavity has its own Brewster’s cut lithium triborate (LBO) crystal to minimize reflections. Getting the crystal placement correct is an iterative process. It is necessary to make adjustments to the angle, then check that the distance between the crystal face and M3 are kept at the specified distance with a clear ruler. After the placement of the crystal is as good as can be accomplished by eye with the protractor, the angle is perfected by adjusting it until the reflection off the face of the crystal is minimized; it should decrease close to zero. When the crystal is aligned correctly one should see doubled light.

Finally, the output coupler position is refined, remembering that the distance between the crystal face and the output coupler needs to be accurate within one millimeter. The output coupler is aligned so the residual fundamental beam is reflected towards where the input coupler will be mounted. The doubled light can then be maximized by fine adjustments to the alignment of the crystal with the mount knobs. The doubled light is elongated in the horizontal direction. Fringes should be seen on the top and bottom of the major beam. The crystal mount is adjusted until these fringes are symmetrical. At this point the cavity is ready to be closed.

2.1.4. Closing the Cavity

Mounting the input coupler is referred to as closing the cavity. At this stage the piezo mirror, M3, and the crystal mount are not adjusted any further; only the output and input coupler are adjusted to overlap the second pass, or residual fundamental beam, onto the single pass. Initially this involves adjusting the output mirror to overlap the beam on the surface of
the input mirror followed by adjusting the input mirror and overlapping the second pass beam onto the single pass on the surface of the piezo mirror. When working in the IR range, such as with the barium cavity at 910 nm, the use of an IR viewer helps overlap the beams on the mirror surfaces. Once the beams are overlapped on both mirrors, the piezo driver is ramped using a function generator at 50 Hz with a 2 V amplitude triangle wave with a 1 V offset; this produces a 30 V amplitude, 15 V offset ramp to the piezo. There should be doubled light coming out of the output mirror. Using the adjustment knobs on the input and output mirror mounts will enable one to maximize the doubled light by sight.

Next, a photodiode is placed behind the output coupler and the output is monitored on an oscilloscope. There should be a series of peaks on the oscilloscope from the photodiode. Each peak is a mode of the cavity. The goal is to align the cavity such that there is only one strong mode. This provides the best, most efficient doubling. Using the adjustment knobs on the input and output mirror mounts to maximize one mode is also an iterative process, involving adjusting one axis and then another over and over to get a good overlap of the beams and one mode. At some time the photodiode may become saturated and it will be necessary to attenuate the beam with a neutral density filter while the signal is maximized.

Once the single mode is well maximized, the cavity should be checked for efficiency. The fast photodiode is put behind the input coupler and connected to an oscilloscope to measure the light reflected off the cavity. If the signal from the photodiode is ~80% of the maximum signal, this is excellent. While a decrease to zero would be ideal and would indicate that all of the losses are to doubling, 80% is excellent and realistic.

When the cavity is well optimized the piezo is disconnected from the function generator, the photodiode behind the output coupler is removed, and, if the locking system is setup, the
cavity is locked to measure the power output. If the power output is unsatisfactory the photodiode is put back and the cavity tuning continues further. To increase the output power the optics can be carefully cleaned. It is important that the cleaning be done as carefully as possible because it can change the alignment. However, cleaning the optics can help increase the output power because dirt on the optics can create losses due to scattering. Depending on how dirty the optics are the gains from cleaning the optics can be surprisingly large.

2.2. ERROR LOCKING SYSTEM

2.2.1. Theory of Operation

This laser system uses the Pound-Drever-Hall method [2] to lock the doubled laser beam at a desired frequency. The Pound-Drever-Hall method takes two inputs, (1) phase modulated light directed into a cavity and (2) the light reflected off the cavity detected by a fast photodiode. The phase modulated signal is sent through an oscillator and then both signals are mixed. The output of the mixer is the error signal; the error signal measures how far off resonance the cavity is. In our setup we send this error signal to a lockbox that then is connected to the frequency control of the titanium-sapphire laser to lock it to the doubling cavity. The doubled output is tuned by adjusting the voltage on the piezo driver, which shifts the resonance frequency of the cavity. With this method of frequency locking the linewidth is the same as the titanium sapphire laser’s intrinsic linewidth. The schematic for the error locking system is shown in Figure 2.4.
2.2.2. **Electronics**

The first part to create the error signal is the electro-optical modulator (EOM). The EOM is placed in the beam path of the fundamental beam before the cavity and phase modulates the beam to create sidebands to the laser. The frequency at which the EOM operates is set by a voltage-controlled-oscillator (VCO) (Mini-Circuits, Brooklyn, NY) set to operate at ~40 MHz. The output of the VCO is attenuated with a set of attenuators (VAT-3+ and VAT-15+, Mini-Circuits) to be compatible with the EOM. The amplitude of the auxiliary output of the VCO is adjusted by a combination of an amplifier (ZFL-500+, Mini-Circuits) and an attenuator (VAT-5+, Mini-Circuits) to serve as one input to a frequency mixer (ZAD-1+, Mini-Circuits). The other input to the mixer is generated by a fast photodiode (PDA10A, Thorlabs), which collects the beam reflected off the cavity input mirror. The output of the photodiode passes through a bandpass filter (SIF 40+, Mini-Circuits) and is amplified (ZFL-500+, Mini-Circuits) before being sent to the mixer. The signal from the photodiode must be phase shifted by selectively
determining the length of cable used to connect it to the mixer. The length of cables adds a delay which is analogous to adding a phase shift.

The mixer output is the error signal and is sent to the lockbox (LB1005 Servo Controller, New Focus, Irvine, CA). The output of the lock box is connected to the external reference cavity input on the ICE-BLOC controller of the Ti:Sapphire laser. The laser adjusts to give the average frequency control of the doubled light.

2.3. LOCKING AND TUNING THE CAVITY

Once the laser cavity is aligned and the error locking system is in place the cavity is ready to be locked and tuned to the desired frequency. When locking the cavity, confirm all the electronics are on (power source for error locking electronics, photodiode, EOM, piezo driver, lockbox) and that the lockbox is not engaged. Then, the titanium-sapphire laser is locked to the desired frequency; this procedure is described in detail in the Ti:Sapphire laser manual [3]. Next, the voltage on the piezo is adjusted until you observe doubled light out of the cavity. The lockbox is set to ‘LFGL lock’ and the parameters are adjusted to until stable locking parameters are found. Typical lockbox parameters for our setup are as shown in Table 2.2, however these parameters will vary between different setups. When optimal parameters are found they should not need to be adjusted often. Once the parameters are set, the lockbox is set to the ‘lock on’ setting. It is important to note that some cavity modes are stronger than others. If the desired output power is not achieved from the mode the cavity is locked to, try unlocking the lockbox and adjusting the piezo voltage again until you find a stronger mode.
Table 2.2. Typical Lock Box Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input offset</td>
<td>5 V</td>
</tr>
<tr>
<td>P-I Corner</td>
<td>100 Hz</td>
</tr>
<tr>
<td>LF Gain Limit</td>
<td>30 dB</td>
</tr>
<tr>
<td>Gain</td>
<td>4.5</td>
</tr>
<tr>
<td>Span</td>
<td>OFF</td>
</tr>
</tbody>
</table>

To tune to the desired frequency while the cavity is locked, one can simply adjust the piezo voltage. The stability of the lock and the range of voltage on the piezo will dictate how far the cavity can be tuned while locked. Our piezo has a range of 100 V and we can typically tune a maximum range of about 0.01 nm. In my experience, we typically only tune over 0.005 or 0.006 nm before the cavity and/or laser needs to be relocked due to instability of the Ti:Sapphire laser, instability of the cavity lock, or power fluctuations.

2.4. REFERENCES


3. FLUORESCENCE IMAGING OF BARIUM AND CALCIUM ION BEAMS

3.1. INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) is an especially sensitive analytical technique because the plasma source creates an intense beam of analyte ions. One challenge associated with such an intense ion beam is that the mutual coulombic repulsion by the ions makes consistent focusing of the beam difficult. In an ICP-MS the total ion flux varies with sample matrix, even when the concentration of a target analyte remains fixed. The resultant changes in charge density can affect ion beam focusing and ion transmission into the mass analyzer. These “space charge” effects are thought to be a source of matrix effects that are unique to analyses by ICP-MS.

In our previous work we imaged a cross section of a Ca ion beam at the entrance to the mass analyzer in a commercial Varian 820 ICP-MS [1]. The uniqueness of this particular mass spectrometer is its patented 90 degree reflecting optics. An electrostatic field created by a ring lens reflects and focuses the ion beam into the mass analyzer. This unique open ring geometry allowed us to optically excite selected atomic species with a sheet of laser radiation directed orthogonal to the direction of the ion beam and collect the resulting fluorescence with a CCD camera mounted at an angle of 70 degrees relative to the ion beam. Optimal fluorescence collection orthogonal to the laser sheet and parallel to the ion beam was not possible due to space restrictions in this commercial instrument.

In the initial study we determined that the beam from a solution containing only Ca analyte behaved as predicted by SIMION simulations. However, the addition of matrices altered the beam trajectory, particularly with the addition of heavier matrices, while the matrix additions
had only minor effect on beam shape. The most prominent effect was observed with the Pb matrix, which caused an order-of-magnitude drop in the Ca signal intensity of the mass spectrometer due to a shift in the direction and location of the Ca ion beam at the entrance into the mass analyzer. This work extends our original work with Ca to a heavier element, Ba. Having data at two widely separated masses will aid in understanding beam behavior, particularly because the Ca ions are embedded in a high intensity beam of argon ions.

Another challenge associated with ICP-MS is the overlap of ions that have the same mass-to-charge ratio. Some methods of dealing with these spectral overlap interferences have been to change the plasma conditions [3] or to use collisional induced dissociation or reactions with a secondary gas with multipole collisional cells [4]. However, changing the plasma conditions can decrease the ionization efficiencies of the ions of interest. Also, some secondary reaction gases such as ammonia are corrosive and expensive. Therefore, there is need for improvement to make counteracting spectral overlap interferences less cumbersome and more broadly applicable. In addition to the 90 degree ion optics, the Varian 820 has a unique collisional reaction interface (CRI) that introduces a secondary gas of He or H₂ to one or both of the interface cones [2]. This work looks at the effect the CRI gas, when introduced at the tip of the skimmer cone, has on the ion beam formation.

3.2. EXPERIMENTAL

3.2.1. ICP-MS

These experiments were performed on a Varian 820 ICP-MS. Bruker (Fremont, CA) purchased the Varian ICP-MS line in 2010 and this instrument is now marketed as the Bruker Aurora M90. All experiments record beam cross sections under the two instrument operating
modes, normal sensitivity and high sensitivity, as well as with the collisional reaction interface (CRI). The high sensitivity mode applies higher voltages to the extraction lens and ion optics compared to the normal sensitivity mode. Instrument parameters for the two modes are shown in Table 3.1 and the parameters for the CRI experiments are shown in Table 3.2 and 3.3.

Table 3.1. ICP-MS parameters for barium normal and high sensitivity experiments

<table>
<thead>
<tr>
<th></th>
<th>Ca Normal sensitivity</th>
<th>Ba Normal Sensitivity</th>
<th>Ba High Sensitivity</th>
</tr>
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<tbody>
<tr>
<td>Plasma Flow</td>
<td>16 L/min</td>
<td>16 L/min</td>
<td>16 L/min</td>
</tr>
<tr>
<td>Auxiliary Flow</td>
<td>1.2 L/min</td>
<td>1.2 L/min</td>
<td>1.8 L/min</td>
</tr>
<tr>
<td>Sheath Gas</td>
<td>0.2 L/min</td>
<td>0.2 L/min</td>
<td>0.22 L/min</td>
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<tr>
<td>Nebulizer Flow</td>
<td>0.99 L/min</td>
<td>0.99 L/min</td>
<td>0.91 L/min</td>
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<tr>
<td>RF Power (kW)</td>
<td>1.4 kW</td>
<td>1.4 kW</td>
<td>1.4 kW</td>
</tr>
<tr>
<td>First Extraction Lens</td>
<td>– 2 V</td>
<td>– 2 V</td>
<td>– 530 V</td>
</tr>
<tr>
<td>Third Extraction Lens</td>
<td>– 198 V</td>
<td>– 190 V</td>
<td>– 590 V</td>
</tr>
<tr>
<td>Mirror Lens Left</td>
<td>30 V</td>
<td>30 V</td>
<td>55 V</td>
</tr>
<tr>
<td>Mirror Lens Right</td>
<td>26 V</td>
<td>26 V</td>
<td>64 V</td>
</tr>
<tr>
<td>Mirror Lens Bottom</td>
<td>38 V</td>
<td>42 V</td>
<td>77 V</td>
</tr>
<tr>
<td>Entrance Lens</td>
<td>0 V</td>
<td>0 V</td>
<td>1 V</td>
</tr>
<tr>
<td>Fringe Bias</td>
<td>– 2.3 V</td>
<td>– 2.3 V</td>
<td>– 3 V</td>
</tr>
<tr>
<td>Entrance Plate</td>
<td>– 68 V</td>
<td>– 68 V</td>
<td>– 60 V</td>
</tr>
</tbody>
</table>
Table 3.2. ICP-MS parameters for calcium CRI experiments

<table>
<thead>
<tr>
<th></th>
<th>H$_2$ 100 mL</th>
<th>H$_2$ 150 mL</th>
<th>He 100 mL</th>
<th>He 180 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Flow</td>
<td>18 L/min</td>
<td>19 L/min</td>
<td>20 L/min</td>
<td>21 L/min</td>
</tr>
<tr>
<td>Auxiliary Flow</td>
<td>1.8 L/min</td>
<td>1.8 L/min</td>
<td>1.8 L/min</td>
<td>1.8 L/min</td>
</tr>
<tr>
<td>Sheath Gas</td>
<td>0.15 L/min</td>
<td>0.15 L/min</td>
<td>0.15 L/min</td>
<td>0.15 L/min</td>
</tr>
<tr>
<td>Nebulizer Flow</td>
<td>0.98 L/min</td>
<td>0.98 L/min</td>
<td>0.98 L/min</td>
<td>0.98 L/min</td>
</tr>
<tr>
<td>RF Power</td>
<td>1.45 kW</td>
<td>1.45 kW</td>
<td>1.45 kW</td>
<td>1.45 kW</td>
</tr>
<tr>
<td>Mirror Lens Left</td>
<td>44 V</td>
<td>44 V</td>
<td>51 V</td>
<td>36 V</td>
</tr>
<tr>
<td>Mirror Lens Right</td>
<td>25 V</td>
<td>25 V</td>
<td>45 V</td>
<td>37 V</td>
</tr>
<tr>
<td>Mirror Lens Bottom</td>
<td>49 V</td>
<td>49 V</td>
<td>30 V</td>
<td>17 V</td>
</tr>
<tr>
<td>Entrance Lens</td>
<td>– 6 V</td>
<td>– 10 V</td>
<td>0 V</td>
<td>– 10 V</td>
</tr>
<tr>
<td>Fringe Bias</td>
<td>– 10 V</td>
<td>– 10 V</td>
<td>– 10 V</td>
<td>– 10 V</td>
</tr>
<tr>
<td>Entrance Plate</td>
<td>– 74 V</td>
<td>– 74 V</td>
<td>– 50 V</td>
<td>– 40 V</td>
</tr>
<tr>
<td>Pole Bias</td>
<td>– 3 V</td>
<td>– 6 V</td>
<td>– 4 V</td>
<td>– 10 V</td>
</tr>
<tr>
<td>Skimmer Gas Source</td>
<td>H$_2$</td>
<td>H$_2$</td>
<td>He</td>
<td>He</td>
</tr>
<tr>
<td>Skimmer Flow</td>
<td>100 mL/min</td>
<td>150 mL/min</td>
<td>100 mL/min</td>
<td>180 mL/min</td>
</tr>
</tbody>
</table>
### Table 3.3. ICP-MS parameters for barium CRI experiments

<table>
<thead>
<tr>
<th></th>
<th>H$_2$ 100 mL</th>
<th>H$_2$ 150 mL</th>
<th>He 100 mL</th>
<th>He 180 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Flow</td>
<td>22 L/min</td>
<td>23 L/min</td>
<td>24 L/min</td>
<td>25 L/min</td>
</tr>
<tr>
<td>Auxiliary Flow</td>
<td>1.8 L/min</td>
<td>1.8 L/min</td>
<td>1.8 L/min</td>
<td>1.8 L/min</td>
</tr>
<tr>
<td>Sheath Gas</td>
<td>0.15 L/min</td>
<td>0.15 L/min</td>
<td>0.15 L/min</td>
<td>0.15 L/min</td>
</tr>
<tr>
<td>Nebulizer Flow</td>
<td>0.98 L/min</td>
<td>0.98 L/min</td>
<td>0.98 L/min</td>
<td>0.98 L/min</td>
</tr>
<tr>
<td>RF Power</td>
<td>1.45 kW</td>
<td>1.45 kW</td>
<td>1.45 kW</td>
<td>1.45 kW</td>
</tr>
<tr>
<td>Mirror Lens Left</td>
<td>44 V</td>
<td>44 V</td>
<td>51 V</td>
<td>36 V</td>
</tr>
<tr>
<td>Mirror Lens Right</td>
<td>25 V</td>
<td>25 V</td>
<td>45 V</td>
<td>37 V</td>
</tr>
<tr>
<td>Mirror Lens Bottom</td>
<td>53 V</td>
<td>47 V</td>
<td>30 V</td>
<td>20 V</td>
</tr>
<tr>
<td>Entrance Lens</td>
<td>– 6 V</td>
<td>– 10 V</td>
<td>0 V</td>
<td>– 10 V</td>
</tr>
<tr>
<td>Fringe Bias</td>
<td>– 10 V</td>
<td>– 10 V</td>
<td>– 10 V</td>
<td>– 10 V</td>
</tr>
<tr>
<td>Entrance Plate</td>
<td>– 74 V</td>
<td>– 74 V</td>
<td>– 50 V</td>
<td>– 40 V</td>
</tr>
<tr>
<td>Pole Bias</td>
<td>– 3 V</td>
<td>– 6 V</td>
<td>– 4 V</td>
<td>– 10 V</td>
</tr>
<tr>
<td>Skimmer Gas Source</td>
<td>H$_2$</td>
<td>H$_2$</td>
<td>He</td>
<td>He</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>150</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Skimmer Flow</td>
<td>mL/min</td>
<td>mL/min</td>
<td>mL/min</td>
<td>180 mL/min</td>
</tr>
</tbody>
</table>

Modifications to the second vacuum stage of the instrument are presented in Figure 3.1. Under normal use of the commercial instrument the second vacuum stage turbo pump (C) is connected to the copper block (A). In our setup we have added a bored-out aluminum wedge (B) with two windows: (1) a two-inch window on the front to collect the fluorescence signal and (2) a 0.5-inch angled window in the top to introduce the laser. With the addition of the wedge between the turbo pump and the copper block we have not observed any change in the pressure or operation of the second vacuum stage.
3.2.2. Laser

Fluorescence was excited by a CW titanium-sapphire laser (SolsTiS, M Squared Lasers, Glasgow, Scotland) frequency doubled to the Ca II 4s $^{2}S_{1/2} – 4p \ ^{2}P_{3/2}$ transition at 393.4 nm or to the Ba II 6s $^{2}S_{1/2} – 6p \ ^{2}P_{3/2}$ transition at 455.4 nm. The frequency doubling cavities are described in detail in Chapter 2. These lines produce strong direct line fluorescence at 854.2 nm and 614.1 nm, respectively. We used a precision wavemeter (Angstrom WS/6, High Finesse, Tübingen, Germany) to monitor the wavelength of the Ti:sapphire laser during the experiments.

3.2.3. Optics

Plano-concave and plano-convex cylindrical lenses shaped the laser into a 1 mm x 10 mm sheet. The sheet was directed into the second vacuum stage through the 0.5-inch angled window on the wedge and placed about 2 mm in front of the orifice of the mass spectrometer. The fluorescence was collected by a CCD camera (iDus DU440A BV, Andor, Belfast, Northern Ireland) with a magnification of 0.37 using a pair of achromatic lenses. A long-pass filter (LG-790, Corion, Hollison, MA) and a narrow band interference filter (CVI, Albuquerque, NM) with
a center wavelength of 854.3 nm or 614.2 and a bandwidth of 1.1 or 1 nm, for calcium and barium respectively, were positioned between the lenses to reject laser scatter and allow the fluorescence signal to the CCD.

### 3.2.4. Solutions and Gases

The CRI experiment images were recorded for two solutions: 50 mg L$^{-1}$ Ca and 171 mg L$^{-1}$ Ba and two CRI, high purity gases: 99.999% helium and 99.995% hydrogen (Airgas, Radnor, PA). Images were recorded for CRI gas flow rates of 100 and 150 mL/min for hydrogen and 100 and 180 mL/min for helium. These flow rates were chosen because 100 mL/min is a typical flow rate and 150 and 180 mL/min are the maximum flow rates employed with this instrument.

The barium normal and high sensitivity experiments recorded images for four different solutions: 171 mg L$^{-1}$ Ba and 171 mg L$^{-1}$ Ba combined with 1.5 mM Mg, Cs, or Pb. These concentrations were chosen to be equimolar to our previously published calcium study [1]. All solutions were made using calcium nitrate, barium nitrate (J.T. Baker Chemical Co., Phillipsburg, NJ), magnesium nitrate (Mallinckrodt Inc., St. Louis, MO), lead nitrate, and cesium chloride (Spectrum Chemical Manufacturing Corp., New Brunswick, NJ) dissolved in trace metal grade nitric acid (Thermo Fisher Scientific Inc., Waltham, MA) diluted to 2% with 18 MΩ deionized water (Millipore, Billerica, MA).

### 3.2.5. ICP-MS optimization

#### 3.2.5.1. Ba High and Normal Sensitivity

The ICP-MS parameters were optimized using the instrument’s auto-optimization feature. Then, the calcium or barium solution was introduced and small adjustments to the ion optic ring
voltages were made manually to maximize the analyte signal. Because the concentrations used for this experiment are much higher than typically used with ICP-MS we decreased the detector voltage from 2400 V to 2000 V and monitored the minor isotopes, $^{43}\text{Ca}$ (natural abundance = 0.135%) or $^{130}\text{Ba}$ (natural abundance = 0.106%), to prolong the life of the detector.

3.2.5.2. CRI Images

The ICP-MS parameters were optimized manually by one of Bruker instrument’s primary research and developers Iouri Kalinitchenko. First, he iteratively optimized the ICP-MS voltages with the manufacturer’s tuning solution without any CRI gas. Then, the analyte signal was optimized with the calcium or barium solutions. Finally, the CRI gas was introduced and the analyte signal was maximized to find the optimum ion optic voltages.

3.2.6. Imaging

Each frame was taken as a one-minute exposure at 0.001 nm intervals over the Doppler width of the fluorescence excitation profile. The frames over the fluorescence profile are summed to make the total ion beam images. A blank, background image was taken while a 2% nitric acid solution containing no analyte was introduced into the ICP. Due to fluctuations in laser power over the course of the experiments the images were normalized by the ratio of the signal of the background laser scatter to the signal of the frame’s laser scatter. A point on the upper left side of the orifice was chosen to compare laser scatter in each frame and background image. We chose this portion of the image because it was in the path of the laser beam and showed laser scatter with no analyte present; this portion of the image was also sufficiently separated in distance from the portion of the image containing the analyte ion beam fluorescence. According to our calculations the signal increases linearly with laser power. Therefore, we
normalized the images by multiplying each frame by the normalization factor and then subtracting the background image.

3.3. RESULTS AND DISCUSSION

3.3.1. Ba High and Normal Sensitivity

The barium and calcium composite ion beams and cross sections under normal sensitivity mode are presented in Figure 3.2. We acknowledge that the striations observed across the images from the upper left to the lower right are artifacts introduced by laser beam inhomogeneities. The calcium ion beam was reproduced under the same conditions as our published study. It agrees well with our previous findings and small differences, such as the smaller fluorescence signal, can be attributed to laser power. In our previous study the laser system used produced twice the power as the current system. This explains why the fluorescence signal is half what it was in our previous study. Overall, the ion beam was reproduced well. From the beam cross sections it is obvious that the Ba ion beam is focused farther to the left by the ion optics compared to the calcium beam. The barium beam is approximately 1.5 mm to the left of the calcium beam. This confirms our predictions made in the previous study. In our previous study we used SIMION to predict the beam trajectory of this instrument. This model showed that heavier ions would be focused more to the left than the calcium beam. From the cross sections it is also apparent that the Ba ion beam is broader than the Ca ion beam. The FWHM of the Ba and Ca beams are 1.8 and 2.3 mm respectively.
Figure 3.2. Composite images (a) of Ca (i) and Ba (ii) and cross sections of the beams (b). Each image is a composite of frames at 0.001 nm increments across the Doppler width of the fluorescence excitation profile.

The total ion beam and cross sections for the four barium test solutions are presented in Figure 3.3. The FWHM of the Ba ion beam diameter is approximately 2.3 mm and the addition of matrices does not significantly affect the diameter. From the beam cross sections it is evident that the addition of lead shifts the position of the Ba ion beam. The beam is shifted approximately 1 mm to the right. This compares well to our previously published calcium study in which we saw a shift in the position of the calcium ion beam of 1.2 mm to the right with the addition of lead. However, in the case of barium this position shift helps to slightly increase the flux to the mass spectrometer, while our previous study showed the position shift of the calcium ion beam decreased the flux. This difference can be explained by the different focal points of the barium and calcium normal sensitivity ion beams because the focal point of the barium ion beam
is on the left side of the orifice while the calcium ion beam is focused to the right side of the orifice. Therefore, a lateral shift to the right will focus the larger barium ion beam towards the center of the orifice and calcium farther to the right of the orifice where some ions will not be transmitted to the mass analyzer.

Figure 3.3. Ba composite images (a) under normal sensitivity mode and cross sections of the beams (b). Each image is a composite of 5 frames from 910.811nm to 910.815nm.

The barium total ion beam under high sensitivity mode is presented in Figure 3.4. The high sensitivity beam is 1.7 mm FWHM, making it significantly more compact than the normal sensitivity mode ion beam. This, in addition to the 5.6 times higher fluorescence signal of the high sensitivity image, explains the more than order of magnitude increase in MS signal with high sensitivity mode. This is similar to the increase between normal and high sensitivity mode operation observed in the previous study. As stated in our previous work, the higher extraction
voltages employed with the high sensitivity mode reduce charge density inside the skimmer and therefore reduce space charge effects in this system. This allows for the more compact focusing of the ion beam and higher ion flux to the MS.

**Figure 3.4.** Ba high sensitivity composite ion beam and cross section.

### 3.3.2. CRI Images

Composite ion beams for the Ca and Ba with different CRI gases and flow rates are presented in Figures 3.5 and 3.6. The false color scales are the same within a figure, but the barium CRI image signals are 30 times greater than that of calcium. From these images it is apparent that the lighter calcium ions are much more affected by introduction of the CRI gas than barium. Barium gives a fairly consistent beam shape and higher fluorescence signal than calcium even with the higher CRI gas flow rates. Also, the addition of CRI gas shifted the position of the beam to right compared to the ion beams under normal sensitivity mode conditions. From the center of the normal sensitivity barium beam to the center of the CRI barium beams the shift is approximately 4.8 mm to the right. In comparison, the shift of the CRI calcium beams is approximately 2.9 mm to the right from center to center.
The cross sections of the beams are presented in Figure 3.7. The FWHM beam diameters are summarized in Table 3.4. The beam focusing under CRI conditions gave a less well defined beam compared to the normal sensitivity ion beams. The mass spectrometer orifice is 4 mm in diameter and large beam diameters support the order of magnitude or greater decrease in MS signal characterized by the use of the CRI even after optimization.
Table 3.4. FWHM beam diameters of CRI composite ion beams

<table>
<thead>
<tr>
<th>Run</th>
<th>FWHM beam width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba H₂ 100 mL/min</td>
<td>4.7 mm</td>
</tr>
<tr>
<td>Ba H₂ 150 mL/min</td>
<td>3.7 mm</td>
</tr>
<tr>
<td>Ba He 100 mL/min</td>
<td>4.4 mm</td>
</tr>
<tr>
<td>Ba He 180 mL/min</td>
<td>3.7 mm</td>
</tr>
<tr>
<td>Ca H₂ 100 mL/min</td>
<td>4.3 mm</td>
</tr>
<tr>
<td>Ca H₂ 150 mL/min</td>
<td>2.8 mm</td>
</tr>
<tr>
<td>Ca He 100 mL/min</td>
<td>3.9 mm</td>
</tr>
<tr>
<td>Ca He 180 mL/min</td>
<td>4.1 mm</td>
</tr>
</tbody>
</table>

Figure 3.7. Cross sections for Ca and Ba CRI composite ion beams

However, this is not unexpected because the collisions with a secondary gas change the kinetic energies of the ions. The ion optic voltages change to compensate for the change in kinetic energies of the ions. The ion optic voltages change to compensate for the change in
kinetic energies, however, focusing of the beam becomes more difficult. This is apparent in the
less well defined beam and decrease in MS signal. The change in kinetic energies of the ions
might also help explain the larger fluorescence profiles of the CRI images. The velocity
distributions of the Ca and Ba ion beams with hydrogen gas at a flow rate of 100 mL/min are
presented in Figures 3.8 and 3.9 and the distributions of the Ca and Ba normal sensitivity ion
beams are presented in Figures 3.10 and 3.11. The wavelength reported on each image is the
wavelength of the fundamental beam as monitored by the wavemeter. From these images it is
apparent that the calcium velocity distribution is broader than barium as might be expected due
to their mass difference. It is also obvious that the addition of the CRI gas significantly broadens
the energy spread of ions entering the mass analyzer.

Figure 3.8. Ca CRI velocity distribution for H₂ at 100 mL/min. The wavelength on each image is
the wavelength of the fundamental beam.
3.4. CONCLUSIONS

We have demonstrated images of the ion beam with ions of two widely separated masses. We have confirmed similar trends in shift and distortion of the ion beam that we observed with
Ca are observed with Ba as well. The lateral shift in the ion beam position due to space charge effects seen previously with Ca was also observed with addition of a Pb matrix to Ba. Former predictions by a SIMION model that the ion optics focus the heavier analyte ions to the left and the lighter ions to the right were confirmed as barium ions were shifted left relative to the calcium ions. Barium also showed a larger beam width than that of calcium.

Further, we have validated the focusing abilities of the Varian instrument with the addition of a second gas with the instrument’s collisional reaction interface. Our current results further support our previous study and suggest that improvements in the performance and decrease in matrix effects can be achieved by improved focusing of the ion beam.

3.5. REFERENCES


4. CONCLUSION

4.1. SUMMARY

The goal of this work was to image and characterize the ion beam in the second vacuum stage of a commercial ICP-MS. To accomplish this we constructed a laser setup similar to the one used in our previous Ca study [1] with two frequency doubling cavities to study Ca and Ba. We have successfully imaged the ion beams of these two widely separated masses under normal and high sensitivity instrument modes. Comparison of the Ba and Ca normal sensitivity beams confirmed that heavier elements like Ba are focused by the ion optics more to the left while the lighter Ca ions are focused to the right side of the orifice as predicted by SIMION calculations in our previous study. Also, Ba showed a larger FWHM beam diameter compared to Ca. The addition of different equimolar matrices showed that a heavy Pb matrix caused a position shift of the ion beam in Ba similar to the lateral shift observed previously with Ca.

In addition, we have imaged and characterized Ca and Ba ion beams with the Varian instrument’s collisional reaction interface (CRI). We found that ion optics formed a larger, less well defined beam with the addition of the collision gas with the CRI. Also, the focal point of the ion beam was significantly shifted to the right of the orifice compared to the ion beam under normal sensitivity modes. Our results indicate that the change in ion transmission due to a change in matrix composition and instrument mode is caused by a change the focusing of the ion beam.

4.2. FUTURE WORK

Further experiments to confirm how the matrix ions interact with the analyte ion beam would be useful. Our setup with some minor alterations is equipped to image Ca and Ba ion
beams in rapid succession. An experiment that imaged both ion beams with a solution containing equimolar concentrations of Ca and Ba would give more precise understanding of how the mass separated “matrix” species interacts with the “analyte” ion beam.

Also, we are interested in imaging the ion beam when parameters upstream, such as the first vacuum stage pressure and skimmer cone orifice diameter, are altered. Characterizing the beam formation and focusing of the ion beams when these parameters are changed would give more insight into optimal conditions and possible improvements for better instrument performance.

4.3. REFERENCES