Characterizing and Improving a Semiportable Mass Spectrometer System for Measurements of Noble Gas Ratios

Alice Zhou
Advisor: Rachel H.R. Stanley, Ph.D.
Department of Chemistry, Wellesley College

Submitted in Partial Fulfillment of the Prerequisites for Honors in Chemistry
April 2017
© Alice Zhou
Acknowledgements

First and foremost, nothing but the utmost gratitude for my advisor, Professor Rachel Stanley. Your patience, understanding, and unwavering support have meant the world to me. Thank you for pushing me to be a better scholar and scientist, and for teaching to trust my intuition. To say you are inspiring is an understatement; I can only hope that I will one day be able to face life with a fraction of your grace and good humor. With complete sincerity, working with you has changed my life.

Thank you to my thesis committee members, Professor Chris Arumanayagam and Professor Nolan Flynn. Your advice and encouragement throughout the process were greatly appreciated. Thank you also to Professor Yue Hu for graciously agreeing to serve as my honors visitor. I would also like to briefly recognize the three of you beyond your role as members on my committee. Chris—I almost certainly would not have pursued a degree in chemistry had it not been for your early intervention in CHEM 120. I cannot thank you enough for your mentorship, and will always look fondly back at the time spent working in your lab. Nolan—thank you for your energy and enthusiasm, and for making my foray into analytical chemistry a wonderful, memorable experience. Professor Hu—thank you for your boundless curiosity and for your astounding ability to take even my most ridiculous questions completely seriously. Your continued love of learning and ability to absorb knowledge make the thought of leaving college moderately less terrifying.

A special thank you to Professor Mala Radhakrishnan, whose tutelage bestowed upon me an appreciation for difficult problems and some degree of computational literacy. There are an infinite number of parallel universes in which I never got comfortable enough with MATLAB do research with Rachel in the first place. Your computational chemistry seminar got me started on this thesis, and your earnest joy in teaching gave me the impetus to finish it.

I would also like to extend thanks to my fellow lab members, without whom none of this would have been possible. In no particular order: Haley Pleskow ’17, Elle Friedberg ’17, Katherine Chen ’18, Brenda Ji ’18, Emily Neel ’18, Yetunde Oyenuga ’18, Helene Alt (Davis Scholar), Emma Van Scoy (Davis Scholar), Charli Klein ’19, Annie Garcia ’19, and Elizabeth Lambert ’20. I am especially indebted to Rachel’s 2016 summer students—Haley, Elle, Yetunde, and Emma—whose efforts laid the groundwork for this thesis.
And thank you to all teammates and coaches, both past and present, on the Wellesley cross country and track teams. You have made me a better version of myself, and taught me discipline, patience, and perseverance. To those of you who had faith in me when I had none to spare: I owe you one. I couldn’t have spent the last few thousand miles with a better bunch of people, and will miss you all more than you know.

Last but certainly not least, I would like to recognize my family. Mom and Dad—I am forever in debt to you both for the sacrifices you have made to hand me, to paraphrase Voltaire, the best of all possible worlds. Every day is an exercise in making the most of the opportunities I have been fortunate enough to take for granted. Emily—thanks for being the best younger sister anyone could ask for, and for sticking with me through thick and thin. I love you all and hope I’ve made you proud.
Table of Contents

Abstract .......................................................................................................................... 1

Chapter 1: Introduction ................................................................................................. 2
  1.1. Background ........................................................................................................... 2
  1.2 Case Studies: The Noble Gases as Geochemical Tracers .................................. 6
    1.2.1 Noble Gases in Ice Cores ........................................................................ 6
    1.2.2 Application of Noble Gases to Determine the Viability of CO₂ Storage ...... 6
  1.3 Henry’s Law: Atmospheric Noble Gases and Solubility Equilibria .................. 8
  1.4 Deviations from Henry’s Law Equilibrium ....................................................... 9
  1.5 Analytical Techniques in the Detection of Noble Gases .................................... 10

Chapter 2: Methods ........................................................................................................ 13
  2.1 Sample Preparation ............................................................................................. 14
    2.1.1 Flask Samples .............................................................................................. 14
    2.1.2 Bottled Samples for Accuracy Experiments .............................................. 15
  2.2 Processing Line ..................................................................................................... 16
    2.2.1 Water Flow Configuration (a, b) ................................................................. 16
    2.2.2 Gas Extraction Membrane (c) ................................................................. 17
    2.2.3 Gas Purification (d, e) ............................................................................... 18
    2.2.4 Vacuum System (f, h) ............................................................................... 21
    2.2.5 Quadrupole Mass Spectrometer (g) ............................................................. 21
  2.3 Procedures for Precision and Accuracy Experiments ......................................... 21
    2.3.1 Procedure for Precision Experiments ....................................................... 21
    2.3.2 Procedure for Accuracy Experiments ....................................................... 25
  2.4 Sample Analysis .................................................................................................... 26
    2.4.1 Mass Spectrometer .................................................................................... 26
2.4.2 Mass Spectrometer Settings

2.4.3 Elimination of Isobaric Interference

2.5 Data Analysis and Processing

2.5.1 Conversion of .csv Files to .mat Files

2.5.2 Background Correction

2.5.3 Extracting Post-Inlet Data for Calculating Noble Gas Ratios

2.5.4 Statistics

2.5.5 Overlaid Plots

Chapter 3: Results and Discussion

3.1 Precision Experiments

3.1.1 Calculating Gas Mole Ratios

3.1.2 Precision Results

3.2 Changes to Improve Measurement Precision

3.2.1 Optimization of Mass Spectrometer and Template Settings

3.2.2 Changes to Processing Line or Sampling Technique

3.3 Discussion of Precision Trends for Individual Ratios

3.4 Inlet Time Experiments and Chemical Slope Effects

3.4.1 Corrections for Chemical Slope Effects

3.5 Accuracy Experiments

3.5.1 Theoretical Warm/Cold Ratios

3.3.2 Measured Warm/Cold Ratios

3.3.3 Results of Accuracy Experiments

Chapter 4: Conclusions

References
Abstract

The five stable noble gases (He, Ne, Ar, Kr, Xe) are useful tracers of physical processes in the environment, as they are biologically and chemically inert and respond solely to physical forcing. Most instrumental systems used for measurements of the suite of noble gases are expensive, low-throughput, and require laboratory support. Here we describe the development and optimization of a low-cost, high-throughput quadrupole mass spectrometer system for the measurement of noble gas ratios in water samples. This system is based around a Hiden 201 RC residual gas analyzer, which is coupled with a Bay Instruments membrane inlet for continuous gas extraction. This work is the first of its kind to use this particular membrane for measurements of noble gases; previously, these types of membranes have only been used in the study of other, more abundant gases. We evaluate the precision and accuracy of noble gas ratios as measured with this method. Our analysis of precision indicates that this instrument could be capable of measuring environmental samples if the most precise measurements could be consistently repeated. Preliminary data from accuracy experiments, however, suggests there is room for improvement before such a setup can be used in the field. Nevertheless, there are only a few other compact membrane-inlet QMS systems in development around the world, and our setup is already capable of measuring ratios more precisely and accurately than many of these analogous systems.
Chapter 1: Introduction

1.1. Background

Occupying the last column of the periodic table and therefore characterized by filled outer valence shells, the noble gases do not readily form chemical compounds at conditions relevant to natural processes on Earth. While Kr and Xe do have an extensive chemistry, this is usually only with highly electronegative elements such as F and O, which in natural terrestrial and aquatic systems are already bound to more reactive elements than the noble gases. Despite their chemical inertness, the noble gases nonetheless differ widely in physical properties such as their solubility in liquids, ionization potential, diffusivity, and polarizability.

Noble gases are especially useful as tracers of physical processes in the environment, as they are biologically and chemically inert and thus respond solely to physical forcing. The five stable noble gases are He, Ne, Ar, Kr, and Xe; they can be distinguished from one another based on their widely varying physical properties. For instance, the diffusivities in seawater of the noble gases differ by a factor of seven, with the lightest gas (He) being the most diffusive. This can be explained in part by kinetic theory and Graham’s law of diffusion, which states that the rate of diffusion is directly proportional to $\frac{1}{\sqrt{\text{molar mass}}}$. Similarly, noble gas solubilities differ by over an order of magnitude, with Xe being the most soluble. The dissolution of noble (and other poorly soluble) gases can be conceptualized as the trapping of individual gas atoms following the cavitation of water molecules. The attractive force between water and the gas atoms is entirely electrostatic and increases with atomic radius and the dielectric constant of the noble gas. These short-range London dispersion forces result from the rapid polarization and counter-polarization of electron clouds. Large molecules in which electrons reside further from the nucleus are easier to polarize; gases with higher molecular masses possess greater dispersion and are more soluble in water. Therefore, the equilibrium ratios of noble gas concentrations in water are enriched with respect to atmospheric abundances in favor of the heavier noble gases, as shown in Table 1.
Table 1. Equilibrium percentages of gases in air and dissolved in sea water at 298K

<table>
<thead>
<tr>
<th>Gas</th>
<th>Chemical Symbol</th>
<th>Percentage in Air</th>
<th>Percentage in Seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>78.08</td>
<td>62.6</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>20.95</td>
<td>34.3</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>0.934</td>
<td>1.6</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO₂</td>
<td>0.033</td>
<td>1.4</td>
</tr>
<tr>
<td>Neon</td>
<td>Ne</td>
<td>0.0018</td>
<td>0.00097</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>0.00052</td>
<td>0.00023</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>0.00020</td>
<td>0.00038</td>
</tr>
<tr>
<td>Krypton</td>
<td>Kr</td>
<td>0.00011</td>
<td>0.00038</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>0.000015</td>
<td>0.000017</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>N₂O</td>
<td>0.000050</td>
<td>0.0015</td>
</tr>
<tr>
<td>Xenon</td>
<td>Xe</td>
<td>0.000087</td>
<td>0.000054</td>
</tr>
</tbody>
</table>

Solubilities of the heavier noble gases (Ar, Kr, Xe) have a strong, non-linear dependence on temperature, whereas the solubilities of the lighter gases in the group (He, Ne) are relatively insensitive to temperature. The strong temperature dependence of noble gas solubilities has enabled dissolved noble gas concentrations to be heavily utilized in paleothermometry. By measuring the relative abundances of noble gases in ice core sections, scientists can estimate global surface ocean water temperatures from hundreds of thousands of years ago. Changes in solubilities due to minor temperature fluctuations also force dissolved noble gases out of equilibrium saturation most of the time in the ocean; this provides much of the driving force for air-sea gas exchange.
Figure 1. a) Molecular diffusivities of the noble gases, O$_2$, and N$_2$ as a function of temperature. 
b) Solubilities of the same gases in seawater as a function of temperature. Figure reproduced from Stanley and Jenkins (2012).²

The size of individual gas molecules also has important implications in the study of sea ice dynamics. Smaller gases can fit more easily into the sea ice matrix during the crystallization of water into ice. During sea ice formation and melting, smaller gases are favorably partitioned into ice while larger gases remain dissolved in water.⁶

In general, the broad ranges in their physicochemical properties make the noble gases respond predictably to different types of physical forcing. Noble gas equilibrium concentrations reflect changes in physical conditions during air-water partitioning; these include but are not limited to changes in altitude, pressure, salinity, and temperature. Concurrent measurements of multiple noble gases allow for the investigation of a wide range of physical processes in the environment, making them indispensable tools in geochemistry and oceanography. In the ocean,
examples of such physical processes include air-sea gas exchange, ocean circulation, and sea ice melting and formation.\textsuperscript{7,8} The investigation of air-sea gas exchange allows for explicit separation of the bubble component from diffusive gas exchange, and allows scientists to characterize equilibration during deep water formation, a factor of great import in biogeochemical models. On land, measurements of noble gases in groundwater are often used for studies of groundwater-aquifer and groundwater-ocean interactions.\textsuperscript{9,10}

![Figure 2](image-url)

**Figure 2.** Schematic depicting the effect of different physical processes on saturation anomalies of He and Xe. Because of the different solubilities and diffusivities of the noble gases, different physical processes have different effects on each of the gases, allowing the gases and their ratios to be powerful tools for separating and quantifying physical processes. Figure reproduced from Stanley and Jenkins (2012).\textsuperscript{2}

In short, noble gas tracers make a significant contribution to a breadth of science problems by allowing physical changes in the environment to be tracked in a tractable way. Two case studies highlighting the use of noble gas measurements in disparate fields are presented below.
1.2 Case Studies: The Noble Gases as Geochemical Tracers

1.2.1 Noble Gases in Ice Cores

Polar ice cores serve as continuous and well-datable records of past environmental conditions and aid in the reconstruction of Earth’s climatic history over timescales of hundreds of thousands of years. For the past twenty years or so, noble gases have been used as conservative tracers to extract information from ice core archives. Noble gas analyses can be performed on two types of ice core samples. First, bubbles in polar ice trap atmospheric air, which can be extracted and analyzed for its noble gas composition. Any variations in the abundances and isotopic compositions of the noble gases can be used to infer environmental conditions at the surface of ice sheets in the distant past. For instance, researchers rely on the predictable thermal fractionation of noble gas species to create a gas isotope “thermometer”, establishing a thermochronology of ice core transects. In the second type of ice core analysis, solid particles deposited on surface snow and later incorporated into the ice matrix can also be analyzed for noble gas isotope compositions, specifically the $^{4}\text{He}/^{3}\text{He}$ signal. These studies reveal information about the provenance of terrestrial aerosols and extraterrestrial dust. In both these cases, it is the conservative nature of noble gases that ensures their fingerprints remain meaningful. That is, the total inventory of most noble gases (except for radiogenic He) is conserved, so their abundances are modulated strictly by variations in physical conditions such as mean ocean temperature and mean atmospheric temperature. Dating of polar ice cores has advanced sufficiently to allow the use of noble gas measurements to study a wide range of paleoclimatic processes, the most common of which involves constraining the magnitude of temperature changes during abrupt climate transitions in Earth’s history.

1.2.2 Application of Noble Gases to Determine the Viability of CO$_2$ Storage

An extensive body of evidence now supports the current warming of our climate system, with a recent assessment by the Intergovernmental Panel for Climate Change (IPCC) indicating a global surface temperature increase of 0.74 ± 0.18 °C between 1906 and 2005. It is generally accepted that increases in anthropogenic carbon dioxide (CO$_2$) emissions since the industrial revolution are a significant factor in the climate warming observed; global emissions of CO$_2$ derive largely from the burning of fossil fuels at a rate of about 25 gigatons of CO$_2$ equivalent per year. Reduction of CO$_2$ concentrations in the atmosphere could limit climate change in the
short term and possibly even ameliorate damage in the long term. The Carbon Capture and Storage (CCS) process presents a novel way to directly engineer CO₂ drawdown. CCS involves capturing CO₂ from large point source emitters such as refineries or power plants, compressing it into a supercritical fluid, and then transporting and injecting the fluid into geological formations capable of acting as natural underground storage sites. For this to work, the injected CO₂ must remain isolated from the atmosphere for relatively long timescales. While the study of noble gases in the elucidation of water-CO₂-oil interactions is still a new field, measurements of noble gases and stable isotope data can in principle provide a quantitative tool for tracing processes occurring in hydrogeological systems, with direct relevance for long term carbon sequestration.

For example, noble gases have been particularly effective in determining the source and residence time of CO₂ within natural CO₂ reservoirs. Magmatic CO₂/³He ratios exhibit a small range when compared to other crustal fluids (1 x 10⁹ to 1 x 10¹⁰), and can thus be used to both identify and quantify the amount of mantle CO₂ in a reservoir using an N-member mixing model. The marked decrease in CO₂/³He ratios measured in nine CO₂ reservoirs around the world has been used to explain the long-term fate of sequestered CO₂. As ³He is almost entirely derived from mantle outgassing, there is no source in the shallow crust that could increase [³He] after the premixed CO₂ and ³He has been introduced to the reservoir. Thus, the reduction in CO₂/³He can only be explained by a reduction in the CO₂ component relative to that of ³He. These CO₂/³He measurements are coupled with observations of increasing ⁴⁰Ne, which is strictly of atmospheric origin and is used as a tracer for formation water interaction in crustal fluids. Studies have shown that ⁴⁰Ne accumulates in formation water over time. Thus the correlation between CO₂/³He reduction and increasing ⁴⁰Ne illustrates that contact with formation water is directly controlling the removal of the CO₂ component in natural CO₂ reservoirs.
1.3 Henry’s Law: Atmospheric Noble Gases and Solubility Equilibria

Waters with a free interface to the atmosphere tend to dissolve atmospheric gas until the concentrations of the gas in both phases are in thermodynamic equilibrium. This holds for all atmospheric gases that are biogeochemically conservative, with no additional sources or sinks. Kinetic aspects of the exchange are complicated, with the simple diffusion (“stagnant film”) model now being ruled out in favor of surface renewal models.\textsuperscript{19} Gas exchange occurs fairly rapidly; a typical gas transfer rate is about 5 meters per day.\textsuperscript{20} In reality, however, the surface layer of open water bodies is not expected to have atmospheric noble gases completely in equilibrium with the atmosphere at the prevailing physical conditions, as gas transfer rates are not quite fast enough to catch up to temperature changes.

Henry’s law provides a description of gas partitioning at a free air-water interface. It assumes that the concentrations in the two phases are directly proportional to each other:

\[
\frac{C_{i \text{(gas)}}}{C_{i \text{(water)}}} = H_i(T, C_{\text{water}}, \ldots) \approx H_i(T, S)
\]

$C_{i \text{gas}}$ and $C_{i \text{water}}$ refer to the concentrations of gas $i$ in the gas and water phase, respectively, and $H_i$ is the Henry’s law constant, a dimensionless term that depends on both temperature ($T$) and the concentrations of all other dissolved species ($C_j$). Calculation of the Henry’s law constant is somewhat complicated by its dependence on the chemical interaction between solutes, but this can be neglected in most cases since solute concentrations in natural waters are sufficiently low that dissolved atmospheric gases behave like ideal gases. To simplify the equation, one can consider the total effect of all solutes on the dissolution of a gas to be a cumulative dependence of $H_i$ on salinity ($S$).

In the context of oceanographic research, most of the tabulated solubilities for He, Ne, Ar, Kr, O$_2$, and N$_2$ have been reported as a function of temperature and salinity.\textsuperscript{21} Due to the motivation behind their use, the noble gas solubilities are often expressed in terms of their equilibrium with atmospheric air, under the valid assumption that the composition of the atmosphere remains constant on time scales pertaining to gas exchange. When expressing partial pressure of a gas $p_i$, the total atmospheric pressure $p_{\text{tot}}$ must be corrected for water vapor concentration, $e_w(T)$, as well as the volume or theoretical mole fraction ($x_i$) of the gas in dry air\textsuperscript{22}. 

\[ p_i = x_i \times \left[ \sum_j p_j - e_w(T) \right] = x_i [p_{tot} - e_w(T)] \]

Local atmospheric pressures have an altitude dependence as well, as given by the barometric altitude formula:

\[ p_{tot}(h) \approx p_{tot \ at \ sea \ level} \times e^{-\frac{h}{h_{atm}}} \]

\( p_{tot}(h) \) and \( p_{tot \ at \ sea \ level} \) refer to the local and sea level pressure, \( h \) is altitude, and \( h_{atm} \) is an atmospheric scaling constant.

### 1.4 Deviations from Henry’s Law Equilibrium

The most important source of noble gases in natural waters is the dissolution of atmospheric gases according to Henry’s Law. Dissolved noble gases mainly enter bodies of water from the atmosphere through the process of gas exchange. Gas exchange is a physicochemical process primarily controlled by the difference in gas concentrations across a boundary as well as an exchange parameter, which determines the rate at which a molecule of gas can move across the liquid-atmosphere boundary. Because gas exchange usually occurs much faster than the mixing of the water immediately below the air-water interface with the bulk water, solubility equilibrium is attained at the water surface.\(^{23}\) In the ocean, equilibrium concentrations depend strongly on both the temperature and salinity of the water. In surface waters, noble gases are usually close to being in equilibrium with the atmosphere, often within \(10\%\) of the values as determined by their Henry’s Law constants.\(^{24}\) In fact, extensive measurements have shown that the noble gas concentrations of open waters closely follow expected values predicted by the solubility equilibrium according to air-water partitioning.\(^{25}\)

As mentioned above, the equilibrium concentrations of noble gases implicitly convey information about the physical properties of the exchanging water mass, particularly at the air-water interface. However, significant physical forcing such as rapid warming or cooling, ice formation or melting, and bubble injection can all lead to noticeable departures from this equilibrium. He equilibrium is further complicated by the fact that it has two additional sources: \(^4\)He is produced by alpha decay reactions, whereas \(^3\)He is produced by radioactive beta decay from atmospheric tritium (\(^3\)H).\(^{26}\)
In geochemistry, the noble gas abundance in water is typically understood as a mixture of two separate noble gas components—a well-constrained atmospheric component and a smaller non-atmospheric component. Very few processes are capable of fractionating atmospheric noble gases, and these processes are mechanistically very well understood. This essentially completely constrains air-derived noble gases. However, two non-atmospheric noble gas components are also present in most natural waters: radiogenic and terrigenic noble gases. These enter the ocean or other bodies of water through weathering processes.

Radiogenic noble gases are those generated by disintegrations of radioactive precursors and succeeding nuclear reactions. Only radiogenic $^4$He, $^3$He, and sometimes $^{40}$Ar are produced in sufficient quantities to be observed in natural waters. Rocks and minerals generate all these radiogenic isotopes by way of heavy-element decay series, whereas tritogenic He ($^3$He) is also produced by the decay of atmospheric tritium ($^3$H, half-life 4500 days).

![Diagram of Noble Gases in Water](image)

**Figure 3.** Classification of the different noble gas components found in natural waters. Terms associated with geochemical reservoirs are in rectangles, and terms associated with the processes governing noble gas abundance in ellipses. Radiogenic gases are often, but not always, of terrigenic origin. For instance, $^3$He produced by the radioactive decay of $^3$H in the atmosphere or hydrosphere is not considered terrigenic. Reproduced from Brennwald et al. (2012).

### 1.5 Analytical Techniques in the Detection of Noble Gases

The noble gases are typically analyzed using either isotope ratio mass spectrometers or magnetic sector mass spectrometers. Some methods analyze for only one or two noble gases, while other systems can analyze all five noble gases from a single sample. Most modern mass
spectrometers use electron impact sources with detection performed by Faraday cups or electron multipliers. Extraction of noble gases from aquatic samples is typically achieved by phase separation; extracted gases must then be purified and separated by a combination of chemical and physical methods.

Broadly speaking, the quantification of noble gases in water follows a sequence of three analytical steps: 1) Extraction of dissolved gases from the water, 2) Purification and separation of noble gases from the gas stream, and 3) quantitative (mass spectrometric) analysis.

Traditionally, mass spectrometric detection of multiple noble gases in natural waters involves discrete sample collection followed by analysis in dedicated laboratories. Such sample processing and analysis is time-consuming, often on the order of multiple hours per sample. Furthermore, current methods often require expensive, highly specialized instrumentation and sampling techniques, followed by subsequent lab-based quantification. As such, very few laboratories are capable of high-precision and high-accuracy (<1%) measurements of the less abundant noble gases (Ne, Kr, Xe) in natural waters. Oceanic measurements of dissolved noble gases are sparse, especially for Xe.\textsuperscript{31,32,33,34} For these reasons, it is difficult to acquire data sets that comprise a sufficiently complete suite of noble gas species at decent spatial and temporal resolutions.

Significant advancements could be made if it were possible to simultaneously analyze a suite of gases in the field, and recent developments in mass spectrometry have made such a task possible.\textsuperscript{35,36,37} For instance, high-resolution data sets of gases have recently been obtained for O\textsubscript{2}, Ar, N\textsubscript{2}O, and dimethyl sulfide.\textsuperscript{38,39}

Our focus is on the noble gases, and we describe here a relatively low-cost (~$50,000 USD) quadrupole mass spectrometer-based system for measurements of Ne, Ar, Kr, and Xe gas ratios in natural waters. We utilize the Hiden HAL 201 RC Residual Gas Analyzer (RGA) mass spectrometer, which is not specialized for this task and typically used to monitor contamination or leaks in vacuum systems. The sampling procedure involved has comparatively high throughput (~20-30 minutes per sample) by design, which allows for time-sensitive detection of gas species of interest and provides data sets with high spatial and temporal resolution. As the Hiden RGA is compact and rugged, this system would be semi-portable and could be feasibly brought to labs near field sites. At the moment, however, the precision of our system is not as good as some lab-based systems, which get better than 0.2% precision.\textsuperscript{40}
This work is noteworthy because it moves away from the “typical” noble gas analysis in several ways. Our system relies on a Bay Instruments membrane inlet system to continuously and automatically extract gases from an aqueous sample. This differs from traditional noble gas mass spectrometry systems in that there is no need for a separate gas extraction step outside the processing line. Furthermore, the noble gases are not separated from each other before inlet into the mass spectrometer, allowing for much faster analysis. Water from the sample reservoir is drawn up to an inline gas-permeable membrane; this membrane separates the water sample at atmospheric pressure from the high vacuum of the mass spectrometer system. Gases in the water sample will partition across the membrane into the region of low pressure, and are then carried to the mass spectrometer for analysis. A water flow rate of around 0.50 mL/minute results in a residence time of the water at the membrane surface sufficient for about 70% of total gas to diffuse across the membrane into the vacuum line (T. Kana, personal communication, 2015). However, it is unknown whether the gases diffuse out in a fashion representative of their molar ratios in the water sample. For instance, lighter noble gases may have higher measured relative abundances by virtue of their higher diffusivities and lower solubilities. Additionally, rates at which gases diffuse out of bulk water across the membrane and into the mass spectrometer depend on factors such as temperature, flow regime along the membrane surface, and membrane aging or fouling. Since it is notoriously difficult to achieve tight control over these operational parameters, calibration and post-processing of data is necessary. Determination of the precision and accuracy of our measurement method is also necessary to gauge the feasibility of applying the method to discrete environmental samples; precision values for gas mole ratios should ideally be < 0.5% relative standard deviation (RSD) for this purpose.

Initial attempts to measure samples using this system resulted in precision values for gas mole ratios of around 2 to 4% RSD, leaving room for improvement. This thesis describes our work on improving this initial measurement precision on both the instrumental and data processing ends. Accuracy of the method was also tested once reproducibility was deemed acceptable.

Chapter 2 describes our experimental methods in further detail. The results and discussion of experiments performed are presented in Chapter 3. Chapter 4 briefly concludes the work and outlines directions for future research.
Chapter 2: Methods

All experiments for this thesis were conducted on a custom-designed processing line. A schematic is presented in Figure 4.

Figure 4. Schematic of setup, which is split into a processing line (parts a-f) and analytical components (parts g-i). Individual components are discussed in greater detail throughout this chapter. a) Water bath/sampling inlet b) Peristaltic pump c) Gas extraction membrane d) Ethanol/dry ice slurry for condensing out water vapor, e) hot and cool getter f) rough pump g) Hiden RGA quadrupole mass spectrometer h) turbomolecular pumping system i) computer system with MASsoft 7 software.

The standard procedure for measuring dissolved noble gases is to collect a sample, extract gases from the water, and measure the extracted gases on a mass spectrometer. This thesis work entails a methods development project focused on finding some optimal configuration that allows noble gas ratios to be measured both precisely (< 0.5% relative standard deviations) and accurately (measured gas mole ratios differ by < 1% from expected values).
Meeting these goals would mean our setup can match the precision and accuracy of more specialized instrumentation dedicated to measuring noble gases; it could thus be applied to the study of noble gases in the environment.

2.1 Sample Preparation

2.1.1 Flask Samples

To limit the number of factors under consideration and allow for better reproducibility of data, we only sampled air-equilibrated laboratory water—although slight modification to the setup would allow environmental samples to be tested as well. In both precision and accuracy experiments, sampling (via either C-Flex or Viton tubing) took place directly from a reservoir of water contained inside an open three-necked round-bottom flask. A flask with three necks was necessary because of the need for separate openings for the thermometer, sampling tube, and stirrer. This flask was submerged up to its neck in a Thermo Fisher AC200 water bath for temperature control.

To create the sample, ultrapure (Milli-Q) water is poured into the flask up to water-bath level and allowed to equilibrate with the atmosphere by exposure to air for at least 48 hours. Air exposure is coupled with moderate physical stirring of the sample via a rotating plastic paddle-shaped stir rod. Stirring should be fast enough to move the water around, but not fast enough to form bubbles, which would disrupt the equilibrium concentrations of dissolved gases. One problem with the stirrer system is that variable power in the building causes stir speed to fluctuate significantly and unpredictably. When left unattended, stirring occasionally accelerates to sufficiently high speed to shred the plastic of the stir paddle, ruining both the paddle as well as the water sample, which must be replaced. For this reason, the stirrer is only turned on a few hours before the start of each experiment, when it is possible to periodically monitor its rate of rotation. Shortened stir times should not be overly detrimental, as gas diffusion rates are fast enough to approach equilibrium by exposure alone.
2.1.2 Bottled Samples for Accuracy Experiments

Briefly, accuracy can be tested by comparing gas mole ratios from a sample taken at one temperature to gas mole ratios of samples taken at a different temperature, as the solubilities of the noble gases vary in a known way with changing temperature. Since the rates of gas diffusion across the membrane surface vary with temperature as well, membrane temperature should be kept as constant as possible over all experiments to make comparison of sample ratios meaningful. For this reason, sampling cannot simply be switched between flasks held at two different temperatures.

In accuracy experiments, the water sample at the warmer temperature should be bottled and cooled to the temperature of the lower-temperature sample. Note that the reverse—bottling from the colder bath and storing samples in a warmer one—is not performed, as gases dissolved in water may exsolve upon warming. This technique relies on the assumption that once bottled, gas diffusion into or out of the bottled sample is negligible on time scales of around 1-2 days. The gas composition in bottled samples is thus expected to remain representative of the original warmer sample even after the sealed bottle has been cooled. This assumption seemed to be valid; we bottled several samples at the same temperature as the flask and saw that ratios agreed perfectly. A temperature difference of a few degrees is sufficient for noble gas ratios to be noticeably different (Table 10). We generally set the “warm bath” at 30°C and the “cold bath” at 21°C.

The bottling procedure is relatively straightforward; air-equilibrated/stirred water is drawn out of the warm bath flask using a hand pump. The hand pump is connected to a segment of plastic tubing, which is placed at the bottom of an empty sample bottle. When a plastic clip on the plastic tubing is released, water is drawn out of the flask and down to the bottle under the assistance of gravity. The pre-evacuated glass sample bottle is filled completely, with the plastic tubing being moved slowly upwards under the water line until the bottle overflows. It is important for these bottles to be filled completely with water, as gas exchange with any headspace will compromise the integrity of the dissolved gases. The bottle is immediately sealed by inserting a rubber stopper, topping it with an aluminum cap, and creating an airtight closure using a bottle crimping tool. These bottles are turned upside down and completely submerged in a beaker inside the large water bath to bring them down to the temperature of the lower-temperature sample. Storing them this way also slows diffusion of gases across the seal, since
diffusion of gases in water is much slower than diffusion of gases in air. Great care should be taken to avoid the formation of bubbles in bottles, since this will alter the ratio of noble gases in the warm samples and make warm-cold comparisons meaningless.

Finally, note that these glass bottles are not suitable for helium studies, due to the extremely high diffusivity of that species; helium has nontrivial permeation rates across glass. This is not a problem in our case since we have chosen not to measure helium.

2.2 Processing Line

2.2.1 Water Flow Configuration (a, b)
Viton tubing (a): Tubing is placed into the sample at one end and connected to the peristaltic pump at the other; the peristaltic pump then draws water out of the sample towards the membrane. Viton tubing (ID 1/32”, OD 3/32”, Shore 60 Durometer) is used for this purpose, and was chosen for its low gas permeability compared to most other forms of tubing. Approximate gas permeability data for several types of tubing compatible with peristaltic pumps is given in Table 2.

Table 2. Approximate gas permeability data for C-Flex, Tygon, and Viton tubing

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Operating Temperature</th>
<th>Durometer</th>
<th>Approx. Permeability at 25°C (cc-mmsec-cm²-cm Hg x 10⁻¹⁰)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂</td>
</tr>
<tr>
<td>C-Flex</td>
<td>-73 to 135°C</td>
<td>50(A)</td>
<td>280</td>
</tr>
<tr>
<td>Tygon (high purity)</td>
<td>-70 to 52°C</td>
<td>72(A)</td>
<td>745</td>
</tr>
<tr>
<td>Viton</td>
<td>-32 to 204°C</td>
<td>60(A)</td>
<td>79</td>
</tr>
</tbody>
</table>

Peristaltic pump (b): A Gilson MINIPULS 3 peristaltic pump is used to draw water up from the sample to the membrane contactor at a controlled, constant flow rate. A major advantage of peristaltic pumps is that they are inherently contamination-free, as the media is entirely confined to the tubing. Since the liquid sample never contacts the peristaltic pump, there are no valves, diaphragms, or seals involved. Only the tubing itself needs to be replaced in the event of wear. Thus, the peristaltic pump is low-maintenance and has little downtime compared with most other
pumping techniques. Furthermore, a peristaltic pump is non-siphoning so there is no risk of flow back to the system.

In our setup, fluid flows through the pump head, forming packets of water. Flow rate is determined by packet size and the rotation speed of rollers. We use beaded Viton tubing in the tracks, and uniform packets of sample are passed through as ten stainless steel rollers rotate, driven by a high-torque stepper motor. Peristaltic pump settings are chosen to minimize bubbles, which are sensitive to both the tuning of the pump pressure plate as well as flow rate, with slower flow yielding fewer bubbles. We generally use a flow rate of 0.50 mL/min, which when coupled with the specifications of our membrane lead to extraction of about 70% of dissolved argon (extraction efficiencies likely vary for other gases). This flow rate is checked at the beginning of each experiment by collecting and weighing the amount of water pumped through in exactly one minute.

2.2.2 Gas Extraction Membrane (c)

The membrane (Bay Instruments, S-8-75, 1 cm x 8 mm OD) is a critical component of our system and allows for the continuous extraction of dissolved gases from liquid water samples. Our membrane is a gas-permeable hydrophobic material, likely a variant of silicone, one of the most gas-permeable dense polymeric substances available. The membrane is housed inside a glass vacuum inlet, and the extracted gas stream exits the cylinder to the gas processing line by way of a glass arm near the top of the membrane housing.

Gases permeate the membrane by a solution-diffusion mechanism, whereby the rate of gas permeation is directly proportional to the product of the solubility of the gas and the rate of diffusion of the dissolved gas in the material.\(^45\) In our processing line, the peristaltic pump draws sample water through stainless steel tubing up to and along the membrane contactor. The vacuum system of the processing line ensures there is a very low partial pressure of gas outside the membrane. Since the water sample contains a comparatively high partial pressure of gases, this sets up a partial pressure difference between the inside and outside of the hollow membrane. Gas species permeate across the membrane from high to low pressure, passing through the membrane to the rest of system along a 3/8” stainless steel connection. Water pumped past the membrane simply collects in a waste beaker, which greatly improves sample throughput by eliminating the need for a separate gas extraction step. Furthermore, this allows for direct
measurements on the water sample itself—no head-space equilibration is necessary, as in gas-equilibration mass spectrometry.

The rates by which gas species diffuse from the bulk water across the membrane depend on temperature, water flow along the membrane surface, and the extent of membrane aging and fouling. This multiplicity of factors means it is very difficult to achieve tight control over all operational parameters. For most of our experiments, membrane temperature was controlled simply by submerging the membrane housing in a dewar of room-temperature water. However, the dewar water is not temperature-controlled and therefore did not always match the temperature of the water drawn up from the flask and to the membrane. Our thermocouple measurements suggest that the dewar water often fluctuates by about one degree Celsius over the course of 5-6 experiments (3 hours); the membrane temperature likely varies over this range as well. For our later experiments, the processing line was reconfigured such that the membrane housing was submerged in the large water bath. This may have improved precision, but we did not collect enough data with this particular change in place to make definitive conclusions.

2.2.3 Gas Purification (d, e)

The gas stream that is present after membrane extraction contains our species of interest (the noble gases), but also water vapor, nitrogen gas, CO₂, and other gas impurities. These should be removed or minimized before gas enters the mass spectrometer. This can be done using a combination of physical and chemical methods, which are described below in the order in which they occur.

**Ethanol/dry ice slurry (d):** Immediately after extraction, the gas stream passes through a U-shaped glass tube. This tube is almost entirely submerged in a dewar containing a slurry of absolute ethanol and finely crushed dry ice. This mixture is about -73.0°C (200K), which is well above the condensation points of the noble gases (see Table 3)⁴⁶ but low enough to condense out water vapor with reasonable efficiency.
**Table 3. Condensation points of the noble gases**

<table>
<thead>
<tr>
<th></th>
<th>Neon</th>
<th>Argon</th>
<th>Krypton</th>
<th>Xenon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point</td>
<td>-245.9°C</td>
<td>-185.8°C</td>
<td>-151.7°C</td>
<td>-106.6°C</td>
</tr>
</tbody>
</table>

Getters (e): Getters are deposits of reactive material often used for the purposes of gas purification in vacuum systems. When gas molecules strike the getter material, they combine with it either chemically or by adsorption. Absorption will also occur in the case of the hot getter; the getter material is heated and activated to promote absorption, leaving its surface free to trap more molecules. The noble gases, being inert, do not react with the getter material and pass through to the mass spectrometer. Investigators have successfully used SAES alloys St101 and St707 to purify gases for the measurement of noble gases in water and ice samples.\(^{47}\) However, we avoid using these due to their high activation temperatures (750°C), which make the system difficult to operate outside of the lab.

The recently developed St2002 nonevaporable getter, with an activation temperature around 400°C, is a better choice. This getter alloy contains Zr, V, Mg, Fe, and rare earth elements, and is preferable to St101 and St707 due to its high removal efficiency for N\(_2\).\(^{48}\) Nitrogen is extremely abundant and a typically difficult gas to remove, due to its strong triple bond. However, a simple mass scan from m/z 4 to 50 on the Faraday cup (Figure 5) confirms that N\(_2\) (m/z = 28) is removed with high efficiency. The Ar peak (m/z = 40) is by far the most abundant signal; note also the minimal O\(_2\) (m/z = 32) signal.
Figure 5. Mass spectra of air after purification with the St2002 getter. Signal of N\textsubscript{2} (m/z = 28) is greatly diminished relative to that of argon (m/z = 40). The small peak visible at m/z = 20 most likely corresponds to doubly-charged \textsuperscript{40}Ar.

Cylindrical getter pellets (6 mm diameter x 2 mm length) are placed in two metal chambers, with approximately 100 grams of getter material in each chamber. The first chamber, referred to as the “hot getter”, is heated using a custom-made coil heater connected to a Variac. The hot getter breaks C-H bonds in CH\textsubscript{4} and adsorbs all other gases except for H\textsubscript{2} and the noble gases. The second getter, referred to as the “cool getter”, is kept at room temperature and adsorbs H\textsubscript{2} gas. Each getter chamber is a long, narrow cylinder (1” OD, 4” long, \(\frac{3}{4}”\) ID). The length increases contact between the gas stream and getter pellets, further improving removal efficiency. Both getters are initially activated by heating over 400°C, and reactivation is performed as needed, typically when peak height for N\textsubscript{2} becomes comparable to the peak height of Ar. This occurs about once a month when the system is run in continuous mode, and far less frequently if the system is run in discrete mode, as was the case with our studies. Getters need only be replaced when reactivation fails to sufficiently reduce the N\textsubscript{2} peak height; at this point the getters have been fully saturated with gas.
2.2.4 Vacuum System (f, h)

Rough pump (f): An Adixen 2005 SD rotary vane vacuum pump is used to initially evacuate the processing line. Its main purpose is to create area of low pressure (about $1 \times 10^{-3}$ torr) outside the membrane region, which sets up the gas diffusion gradient.

Turbomolecular pump (h): A turbomolecular pumping system (TPS) is used to evacuate the mass spectrometer. This is used to make and maintain a higher vacuum than the rough pump is capable of, creating pressures as low as $1 \times 10^{-8}$ torr within the mass spectrometer.

2.2.5 Quadrupole Mass Spectrometer (g)

The Hiden RGA QMS is designed for residual gas analysis in ultrahigh vacuum applications, and is equipped with a dual Faraday/electron multiplier detector. Its low minimum detectable partial pressure of $5 \times 10^{-14}$ mbar makes this instrument suitable for the measurement of small sample volumes.

2.3 Procedures for Precision and Accuracy Experiments

Measurements of the noble gases must be both precise and accurate to be useful in answering questions of environmental relevance. Our experimental work aimed to improve these two properties, with most of the processing line/mass spectrometer setting optimization occurring in the summer and fall of 2016 and accuracy experiments taking place from fall of 2016 through the early months of 2017.

2.3.1 Procedure for Precision Experiments

To test instrumental precision, we run what are colloquially called “precision experiments”. These consist of a series of identical experiments (ideally >5) run in sequence, with all experimental parameters kept as constant as possible. In these experiments, we sample directly from a flask; no bottling of samples is necessary. After setting up the gas purification line, a typical set of precision experiments would follow this general procedure.

1. Open the rough pump valve for 3 minutes. This allows the rough pump to pump residual gas out of processing line; flushing it in preparation for the next sample. The configuration at the end of this step has the rough pump open, inlet valve closed, and right angle valve open.
2. Close the rough pump valve after 3 minutes has passed.
3. Start a scan on the Hiden MASSoft 7 software, using the correct template (scan settings). Simultaneously, start a stopwatch to be able to track time from start of data collection.
4. Open the inlet valve after 10 seconds has elapsed on the stopwatch. This lets gas from the sample into the mass spectrometer region. However, since the right angle valve is still open at this time, sample gas inside the mass spectrometer is immediately pumped out by the TPS. Since the pump rate is so much higher than gas inflow rate, there is only a slightly discernable increase in signal once the inlet valve is opened. The inlet valve is kept open for exactly two minutes (0:10 – 2:10 on stopwatch time). This two-minute period ensures that the gas reaching the mass spectrometer for sampling is more representative of the original gas stream evolved from the water sample. If we were to allow gas to accumulate at the very beginning of the scan, it could be the case that the more diffusive noble gases are enhanced in concentration simply because of their faster migration rates from the membrane to the inlet.

**Figure 6.** Configuration from 0:10 to 2:10 during Step 4 of the sampling procedure. The open inlet valve allows gas to flow to the mass spectrometer, but open right angle valve means gas is also pumped out before it can accumulate. The signal of gas species scanned during this time is negligible because of high pump efficiency.
5. At 2:10 on the stopwatch, close the right angle valve. Listen for a soft thump that indicates that the valve has shut completely; this almost always occurs about a half second after closing the valve switch. Closing the right angle valve shuts the mass spectrometer off from the TPS, so gas is now accumulating inside the mass spectrometer (Figure 7).

![Diagram](attachment://mass_spectrometer_diagram.png)

**Figure 7.** Configuration from 2:10-2:30 (‘inlet time’) during the sampling procedure. The open inlet valve allows gas to flow to the mass spectrometer, and the closed right angle valve means gas is no longer pumped out. Gas buildup is permitted for exactly 20 seconds.

6. Close the inlet valve *exactly* 20 seconds after the right angle valve was closed. That is, gas is only allowed to accumulate within the mass spectrometer for 20 seconds; this period is referred to as the ‘inlet time’. An inlet time of 20 seconds was determined by trial and error to be optimal for these experiments. It is long enough to let reasonable amounts of gas let in, resulting in higher signals of the noble gases and consequently better precision of ratios. Longer inlet times could potentially be damaging to sensitive components of the mass spectrometer, especially the secondary electron multiplier, which is extremely sensitive to pressure and can be stripped away if too much analyte is present.
Figure 8. Configuration from 2:30-14:30 during sampling procedure. Accumulated gas now trapped within mass spectrometer and sampled statically.

7. Collect data for 12 minutes (2:31-14:31). Upon reaching 14:31, stop scanning at the end of the current scan cycle. Save and export the data file, and reopen the right angle valve. This leaves the configuration with inlet valve closed and right angle open, which allows gas to be pumped away from the quadrupole mass spectrometer housing.

8. Pump out in this current configuration (inlet closed, right angle open) for 5 minutes. Top off the dry ice/ethanol slurry and liquid N\textsubscript{2} dewar as needed.

9. After 5 minutes, open the rough pump valve for 3 minutes (step 1). Repeat the procedure for the next sample.
2.3.2 Procedure for Accuracy Experiments

The accuracy of our method can be determined by comparing measured noble gas ratios at different temperatures to their theoretical values. The experimental procedure is fairly similar in structure to that of precision experiments, and can be summarized as follows:

1. Run at least one experiment sampling from the flask in the cooler water bath, following the procedure described above. This will provide the data for establishing the “cold” ratios that we will compare against the gas ratios in the bottled “warm” samples. See Section 2.1.2 for a discussion bottling technique.

2. As soon as the right angle valve has been reopened at the end of the flask experiment (steps 7-8 in the procedure for precision experiments), remove a bottle from the cold bath and open it using a decrimper.

3. Carefully place the opened bottle back into the cold bath; it should be submerged up to its neck but no further—we don’t want the two types of water to mix.

4. Insert the Viton sampling tubing into the bottle, making sure to sample from near the bottom of the bottle. This is done because some gas exchange will occur near the surface of the bottle within minutes after the seal is removed. The Viton tubing is usually weighted with a small metal nut near its mouth to pull it towards the bottom of the bottle.

5. When the right angle valve has been open for at least 5 minutes, open the rough pump valve for 3 minutes (Step 1 of the Precision procedure).

6. Follow the protocol for precision samples, but switch to the next bottled sample as soon as inlet time is done (Steps 5-6 of the Precision procedure). This gives the gas extracted from the next sample longer to settle before being measured. All extracted gas from the previous sample is already “locked away” in the mass spectrometer by this point, so switching to a new sample is not an issue. Repeat until done analyzing all bottle samples.

7. Run at least one more precision experiment (sampling from the flask) after the final bottled sample. This data will be used to generate cold-temperature ratios, and can provide a measure of drift if measured ratios are noticeably different from those of the initial flask experiment(s).
2.4 Sample Analysis

2.4.1 Mass Spectrometer
Our system utilizes the Hiden Analytical HAL 3F RC 201 RGA quadrupole mass spectrometer with an electron impact ionization source; this model is equipped with both a Faraday cup and secondary electron multiplier (SEM) detector. We use the SEM to detect noble gases because of their low natural abundances; the SEM can provide signal amplification roughly 1000 times higher than that of a Faraday cup. This mass spectrometer is ideal due to its native capability to vary electron energy during an experiment without loss of instrument stability. The manufacturer’s software (MASsoft Professional 7) allows a different electron energy to be used for each mass measured in a multiple ion detection (MID) experiment. This allows all five noble gases of interest to be measured using optimal electron energies for each. For instance, a reduced electron energy of 35 V is optimal for $^{22}\text{Ne}$ to minimize the formation of doubly-charged $\text{CO}_2$ (mass = 44 amu), which would interfere with $^{22}\text{Ne}$ measurements. The other noble gases are measured using higher electron energies of 55 V.

This instrument has the advantages of being relatively compact and low-cost, although like most quadrupole systems, it is limited in mass resolving power. Resolving power (R) is defined as $R = \frac{M}{\Delta M}$, where $\Delta M$ is the resolution, or the minimum peak separation needed to distinguish between two ion species. Mass resolving power is important when trying to differentiate between species with similar nominal masses but different formulas. In our case, getters remove the bulk of extraneous gas species from the gas flow such that only noble gases are let into the mass spectrometer. Since these species vary widely in mass, the low resolving power (~1 amu) of a QMS is sufficient for our purposes.

2.4.2 Mass Spectrometer Settings
Typical ion source and acquisition settings for noble gas experiments are summarized below. Each noble gas is measured using a carefully determined amplifier (range) based on its natural abundance; range is kept fixed for each mass by deselecting the ‘Auto-Range’ setting during experiment setup. The default ‘Auto-Zero’ setting is also deselected in our experiments for the purposes of minimizing acquisition time. Typically, Auto-Zero performs a zeroing (background-subtracting) function prior to measuring each selected mass during a measurement cycle, usually to correct for leakage currents and amplifier offsets. This zeroing function is a
software preset that lasts at least as long as a measurement, so turning off this setting more than halves total measurement time and greatly improves sample throughput. Disabling this feature should not adversely affect the validity of our method, as we are measuring gas mole ratios rather than absolute abundances of gas species. Additionally, we measure “half-masses”—masses at which no gas is expected, e.g. m/z = 10.5—at the same range settings as the noble gas species in order to perform our own background corrections, obviating the need for autozeroing.

Mass spectrometer settings used to measure noble gas mole ratios are shown in Table 2. A different subenvironment is used for $^{22}\text{Ne}$ (m/z = 22); this species is measured with reduced electron energy (35 V as opposed to the usual 55 V) to prevent isobaric interference in the formation of doubly-charged CO$_2$ (which also has m/z = 22). A lower emission current (500 μA instead of 1000 μA) is necessary when operating at this reduced electron energy to avoid filament overload. Note that we measure $^{38}\text{Ar}$ (m/z = 38) and later also $^{36}\text{Ar}$ (m/z = 36) rather than the most abundant argon isotope, $^{40}\text{Ar}$. This is because the $^{40}\text{Ar}$ signal is too large to be read accurately using the SEM detector at our operating pressure. The settle time describes how long the instrument waits in between measurements; this period allows for electronics to stabilize before the next measurement is performed. We use a longer settle time of 1000 ms between $^{22}\text{Ne}$ and $^{36}\text{Ar}$ to allow for greater stabilization time after a change in electron energy (35V to 55V). Dwell time refers to how long the instrument spends on a given measurement.

**Table 4. Ion source settings**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Focus</td>
<td>-65 V</td>
</tr>
<tr>
<td>Cage</td>
<td>3 V</td>
</tr>
<tr>
<td>Electron Energy</td>
<td>35 V for $^{22}\text{Ne}$, 55 V for all other species</td>
</tr>
<tr>
<td>Emission Current</td>
<td>500 μA for $^{22}\text{Ne}$, 1000 μA for all other species</td>
</tr>
<tr>
<td>Multiplier</td>
<td>1200 V</td>
</tr>
</tbody>
</table>
Table 5. Acquisition settings for Multiple Ion Detection (MID) experiments

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mass (m/z)</th>
<th>Dwell time (ms)</th>
<th>Settle time (ms)</th>
<th>Range (Torr)</th>
<th>Electron energy (V)</th>
<th>Emission current (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{22}$Ne</td>
<td>22</td>
<td>4000</td>
<td>1000</td>
<td>1E-11</td>
<td>35</td>
<td>500</td>
</tr>
<tr>
<td>$^{36}$Ar</td>
<td>36</td>
<td>2000</td>
<td>500</td>
<td>1E-7</td>
<td>55</td>
<td>1000</td>
</tr>
<tr>
<td>$^{38}$Ar</td>
<td>38</td>
<td>2000</td>
<td>1000</td>
<td>1E-9</td>
<td>55</td>
<td>1000</td>
</tr>
<tr>
<td>$^{84}$Kr</td>
<td>84</td>
<td>8000</td>
<td>500</td>
<td>1E-9</td>
<td>55</td>
<td>1000</td>
</tr>
<tr>
<td>$^{129}$Xe</td>
<td>129</td>
<td>4000</td>
<td>500</td>
<td>1E-11</td>
<td>55</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 6. Acquisition settings for background half-masses

<table>
<thead>
<tr>
<th>Mass (m/z)</th>
<th>Associated Noble Gas(es)</th>
<th>Dwell time (ms)</th>
<th>Settle time (ms)</th>
<th>Range (Torr)</th>
<th>Electron energy (V)</th>
<th>Emission current (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5</td>
<td>$^{22}$Ne</td>
<td>1000</td>
<td>4000</td>
<td>1E-11</td>
<td>35</td>
<td>500</td>
</tr>
<tr>
<td>25.5</td>
<td>$^{36}$Ar</td>
<td>1000</td>
<td>4000</td>
<td>1E-7</td>
<td>55</td>
<td>1000</td>
</tr>
<tr>
<td>75.5</td>
<td>$^{38}$Ar, $^{84}$Kr</td>
<td>1000</td>
<td>500</td>
<td>1E-9</td>
<td>55</td>
<td>1000</td>
</tr>
<tr>
<td>121.5</td>
<td>$^{129}$Xe</td>
<td>1000</td>
<td>500</td>
<td>1E-11</td>
<td>55</td>
<td>1000</td>
</tr>
</tbody>
</table>

2.4.3 Elimination of Isobaric Interference

Doubly-charged CO$_2$ has the same mass-to-charge ratio as $^{22}$Ne (m/z = 22). However, theoretical calculations show that electron energy must be at least 37 V to strip two electrons from CO$_2$. Therefore, $^{22}$Ne is intentionally measured at a lower electron energy of 35 V to prevent formation of doubly-charged CO$_2$. $^{20}$Ne, which is about 10 times more abundant than $^{22}$Ne, is not measured at all due to isobaric interference from singly-charged $^{18}$O-H$_2$O, which has a lower ionization potential than $^{20}$Ne. Although most water vapor is condensed out during passage through the ethanol-dry ice cold trap, not all of it is removed. Water vapor that enters the mass spectrometer would contribute to the peak height at m/z = 20. Doubly-charged $^{40}$Ar is another concern; $^{40}$Ar is by far the most abundant noble gas isotope and would also interfere with measurements of the $^{20}$Ne isotope.
2.5 Data Analysis and Processing

MASSoft 7 is capable of exporting .csv files at the end of each experiment; these files include information about scan settings (increment, dwell time, settle time, etc.) and the environment (multiplier, electron energy, cage voltage, etc.) as well as the ion current for all masses scanned at various time increments. We use MATLAB (R2016b) for further data analysis, so it is necessary to first convert the exported .csv file into a .mat file. Although MATLAB can read data from .csv files, files with a .mat extension are preferred because they are ‘native’ to the program and data can be loaded from or written to these files directly through MATLAB commands. These files present a way to keep MATLAB-formatted data persistent on the hard drive. Additionally, the .mat files are useful since we often perform further statistics on or analysis with the data.

A summary of our most commonly utilized scripts is presented below. These are available upon request (email azhou3@wellesley.edu).

2.5.1 Conversion of .csv Files to .mat Files

Each experiment has a .csv file associated with it, and each exported .csv file must be converted separately to a native .mat file. We have written a script that incorporates the popular hdrload.m file, which can be found on the Mathworks Central File Exchange. Essentially, the hdrload script is necessary to extract relevant data because the exported .csv file contains a default text header—namely, the information about scan and environment settings. Hdrload will split the .csv file into two outputs: the first is a text array containing the header information, and the second is a data matrix of the same dimensions as the data in the original file, i.e. one row per line of ASCII data in the file. However, hdrload has one major limitation in that no line of the text header can begin with a number. The original .csv files begin (cell A1) with the number of scans, which is indeed read as a number. For this reason, a letter must be manually placed before the number of scans prior to running this script.

After hdrload loads in the data as a matrix, we extract the ion current data associated with each mass. We save just the time data and each ion current array, including that of the half masses, which will be used for background correction. These arrays are concatenated and saved as a .mat file, which serves as the basis for further data manipulation.
2.5.2 Background Correction

Background half-masses are subtracted from the measured signal of each noble gas in order to “zero” measurements for species of interest. This is necessary because there is nonzero ion current even when no ions are hitting the detector. The signal for the background mass chosen at each gain setting is used as a measurement of instrumental noise at that gain level. To perform background correction, we subtract the average signal of each background mass from that of noble gases measured on the same gain (Table 6). Zeroing is done with the average signal of each background mass rather than individual data points because there is significant point to point fluctuation in background mass signals due to the inherent noisiness of very small signals. Subtracting averages removes any systematic biases due to instrumental noise.

2.5.3 Extracting Post-Inlet Data for Calculating Noble Gas Ratios

After extracting ion current data and storing it in a .mat file, we must determine noble gas ratios as well as the mean, standard error, and percent errors of ratios across experiments. As outlined in the sampling procedure, gas accumulation within the vacuum system does not occur until after 2 minutes (2:11-2:31). Ratios should not be determined from gas measurements made prior to or during this rise time. Only values after equilibration, when the ion current has plateaued, should be used. Previously, a threshold time index had been determined separately for each gas species in every experiment by looking at a preliminary ion current plot and estimating where the rise levelled off. This was both time-consuming and prone to error—for example, how flat was “flat enough”? Ion currents generally evened out as time progressed, but discarding too much of the earlier values meant a smaller pool of data to work with.

I developed a simple script called ‘plateaufinder.m’ to automate this process. Initially, this utilizes both the ‘max’ and ‘diff’ commands in MATLAB to find the index of maximum difference of each ion current array. This corresponds to the time at which the ion current slope is steepest, which occurs roughly halfway through the inlet time. Since the plateau must start after this point, all data in the time and ion current arrays prior to this indexing point can be ignored. Data points after the steepest rise are stored in new arrays for further manipulation, and the associated time arrays are shortened correspondingly. It was found that a threshold value of 0.02 returned the best precision overall for several sets of test data. The script finds the first point on the ion current series for which relative fluctuations in post-inlet current are less than the
threshold value. That is, a region is considered “flat enough” if the difference between two adjacent points is less than 2% of the maximum possible rise of the plot. This assumes that there are no significant fluctuations in ion current after the first flat region, which is almost always the case. The script also generates ion current plots with a marker denoting the threshold point so the user can visually check the amount of post-inlet data extracted. We keep all data after and including the threshold point and discard the rest. Only post-inlet values are used for all further processing and statistics.

2.5.4 Statistics

Once post-inlet ion current data for each noble gas species has been extracted, the correct background signals are subtracted (see 2.5.2 for description of background correction). Gas mole ratios are found by taking the appropriate ratios of averaged, background-corrected noble gas signals. The relative standard deviation for each set of ratios is then calculated as a measure of precision.

2.5.5 Overlaid Plots

Our statistics return the relative standard deviation of gas mole ratios across experiments, but sometimes it is useful or informative to see how the ion currents themselves compare. In theory, ion current serves as a proxy for gas abundance within the mass spectrometer, although this is complicated somewhat by the fact that emission currents, electron energy, and range are not always identical for the species we measure. This code loads in .mat files; the user can input an arbitrary number of file names, but it usually only makes sense to compare experiments from a single day. The script then plots the ion currents of each mass across all experiments on a separate figure. That is, it will generate a figure with overlaid ion current measurements for $^{22}\text{Ne}$ across all experiments loaded, a separate figure for ion current measurements of $^{36}\text{Ar}$, and so on. In total, this will generate 5 figures, one for each noble gas species of interest. By looking at the ion current plots, we can see if there are systematic ion current trends across experiments. Ideally, plots would truly look overlaid, meaning the ion current vs. time response is identical across consecutive experiments for a given mass-to-charge ratio. However, we typically see “splitting” of these ion currents, indicating some variation in or drift across measurements.
Chapter 3: Results and Discussion

A total of 30 sets of experiments were run from 10/13/16 to 2/14/17. Each experiment typically consisted of measuring around 5-6 samples, resulting in a total of 165 values recorded for each of the noble gas ratios. Most (17) of these experiments were “precision experiments” (71 precision samples in total), 6 experiments were accuracy experiments, and 5 were inlet time experiments to determine chemical slope (matrix) effects. Several additional experiments were performed in the process of ruling out certain sampling methods. For example, 3 sets of preliminary “accuracy” experiments involved switching between the cold bath and warm bath without bottling samples, but this procedure returned poor data and was not used after the bottling technique was implemented.

3.1 Precision Experiments

For precision experiments, usually only one set of experiments was run on any given day. Each set consisted of at least 5-6 discrete samples run in sequence, taking a total of around 3 hours after initial setup of the processing line. Most statistics are only considered for data within each experimental set, as it is not meaningful to compare ratios across different days, or even across experiments conducted on the same day if separated by more than a few hours. This is because fluctuations in instrument response, water sample gas compositions, room temperature, voltages supplied, etc. all vary enough from day to day to make calculations of reproducibility on those time scales impractical.

It is important to note that we determine the mole ratios of gases rather than their actual concentrations. Obtaining individual concentrations for gas species of interest is not possible without knowing the amount of gas introduced to the mass spectrometer. In our current setup, there is no way of quantifying total gas volume extracted from the water sample by the membrane. Nonetheless, noble gas mole ratios are generally sufficient to quantify physical processes.\(^{50,51}\) Mole ratios are calculated using average signal intensities for each species of interest; the Hiden software automatically converts and reports detected current to pressure (torr), although these pressure values are not truly indicative of the physical pressures of each gas species in the mass spectrometer. The raw signal intensities and calculated ratios for each of the noble gases in the mass spectrometer are likely to differ slightly from their concentrations and
ratios in the sample. The reason for this is twofold. First, the partial pressures of gases in the gas stream are likely to differ from the relative concentrations of dissolved gases in the water sample. The mechanism of gas extraction using our membrane is not well-understood, but gas extraction is neither complete nor equally efficient for all dissolved gases, with certain species partitioning more efficiently across the membrane. Furthermore, there could be differences in the physical rate of gas delivery to the mass spectrometer, favoring enhanced delivery of the lighter, more diffusive gases. We implement a buildup time of 2 minutes (0:10-2:10, see Section 2.3.1) in the sampling procedure, which is sufficiently long to minimize this bias. Secondly, within the mass spectrometer itself, there will be variations in the ease of ionization and detection of each species, resulting in signals that don’t perfectly reflect the relative amounts of each gas species measured. These problems are inherent to gas extraction and the operation of mass spectrometers, respectively.

### 3.1.1 Calculating Gas Mole Ratios

In our precision experiments, ratios are calculated from the raw signal intensity (ion current profile), without adjustment to molar abundances in air or water. Prior to the start of collecting $^{36}$Ar data on 11/8/16, the six ratios tabulated were $^{22}$Ne/$^{129}$Xe, $^{36}$Ar/$^{129}$Xe, $^{84}$Kr/$^{129}$Xe, $^{22}$Ne/$^{84}$Kr, $^{38}$Ar/$^{84}$Kr, and $^{22}$Ne/$^{38}$Ar. We report all ratios as lighter gas/heavier gas for consistency; relative precision (% RSD) values remain the same if ratios are inverted.

Beginning 11/8/16, the mass spectrometer’s software (MASsoft Pro 7) was configured to measure $^{36}$Ar ($m/z = 36$) as well. The switch to measuring two isotopes of argon ($^{36}$Ar and $^{38}$Ar) was done in attempt to improve the precision of argon measurements. $^{40}$Ar, which is the most abundant argon isotope (99.6% natural abundance), was not measured, as its signal would have been too high for the global amplifier settings. The nine ratios calculated after this change were $^{22}$Ne/$^{129}$Xe, $^{36}$Ar/$^{129}$Xe, $^{38}$Ar/$^{129}$Xe, $^{84}$Kr/$^{129}$Xe, $^{22}$Ne/$^{84}$Kr, $^{36}$Ar/$^{84}$Kr, $^{38}$Ar/$^{84}$Kr, $^{22}$Ne/$^{36}$Ar, and $^{22}$Ne/$^{38}$Ar, with new ratios bolded.

Raw mass spectrometer data consists of a time series of extracted ion current profiles for each of the noble gas isotopes of interest: $^{22}$Ne, $^{36}$Ar (from 11/8 onwards), $^{38}$Ar, $^{84}$Kr, and $^{129}$Xe. Signals for background half-masses ($m/z$ = 10.5, 25.5, 75.5, 121.5) are also recorded for use in background corrections. Average signals of each noble gas species are used to calculate gas mole ratios; this processing is carried out in MATLAB. The ‘plateaufinder’ script is first used to find
and extract only the ion current data after the end of gas inlet (accumulation), marked by closure of the inlet valve. We then take the average of post-inlet ion currents for each noble gas isotope and subtract the average background signal of each corresponding half-mass. Note that there is no need to distinguish between pre- and post-inlet data for the half-masses, as they do not correspond to any actual species and are instead a measure of the instrumental noise associated with each gain setting. The average background signal for each half-mass is subtracted off the average signal of noble gases species measured on the same gain. Gas mole ratios are then calculated by pairwise division of average, background-corrected ion currents.

Suppose we wanted to calculate a $^{22}\text{Ne}/^{129}\text{Xe}$ ratio. The pseudocode for such a procedure would look something like this:

\[
\text{adjusted}_{22} = (\text{average ion current post-inlet for } m/z \ 22) - (\text{average ion current of } m/z \ 10.5)
\]
\[
\text{adjusted}_{129} = (\text{average ion current post-inlet for } m/z \ 129) - (\text{average ion current of } m/z \ 121.5)
\]
\[
22\text{ to } 129\text{ ratio} = \frac{\text{adjusted}_{22}}{\text{adjusted}_{129}}
\]

Precision of measurements is defined to be the relative standard deviation (RSD) of each ratio across a set of experiments. Because the noble gases measured have different abundances and physical properties, their measured ratios will have varying precisions and accuracies. Both precision and accuracy are reported for all gas combinations, since the utility of each gas ratio in the study of environmental processes depends on specific gases and thus on the precision and accuracy of each gas ratio. These metrics also serve as the starting point for the quantification of the reproducibility and measuring capability of our instrumental system. For use in seawater studies, RSD values for noble gas ratios should ideally be under 1 percent.

### 3.1.2 Precision Results

The majority of experiments done for this thesis were strictly precision experiments. These experiments were particularly important in the early stages of this work, which involved optimization of instrument settings and processing line design. A summary of RSD values for 14 precision experiments run are given in Table 7. In total, these 14 experiments involved measuring noble gas ratios for 71 samples.
Table 7. Minimum and average RSD values across precision experiments

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Minimum RSD (%)</th>
<th>Average RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{22}\text{Ne}/^{129}\text{Xe}$</td>
<td>0.40</td>
<td>2.00</td>
</tr>
<tr>
<td>$^{36}\text{Ar}/^{129}\text{Xe}$</td>
<td>0.74</td>
<td>1.56</td>
</tr>
<tr>
<td>$^{38}\text{Ar}/^{129}\text{Xe}$</td>
<td>0.60</td>
<td>1.63</td>
</tr>
<tr>
<td>$^{84}\text{Kr}/^{129}\text{Xe}$</td>
<td>0.10</td>
<td>0.95</td>
</tr>
<tr>
<td>$^{22}\text{Ne}/^{84}\text{Kr}$</td>
<td>0.30</td>
<td>1.43</td>
</tr>
<tr>
<td>$^{36}\text{Ar}/^{84}\text{Kr}$</td>
<td>0.45</td>
<td>1.24</td>
</tr>
<tr>
<td>$^{38}\text{Ar}/^{84}\text{Kr}$</td>
<td>0.48</td>
<td>1.14</td>
</tr>
<tr>
<td>$^{22}\text{Ne}/^{36}\text{Ar}$</td>
<td>0.48</td>
<td>2.04</td>
</tr>
<tr>
<td>$^{22}\text{Ne}/^{38}\text{Ar}$</td>
<td>0.30</td>
<td>1.82</td>
</tr>
</tbody>
</table>

On average, precision of most ratios is not tight enough to be ideal (< 1% RSD) for studies of environmental samples. Interestingly, the precision of $^{84}\text{Kr}/^{129}\text{Xe}$ was surprisingly good given that $^{84}\text{Kr}$ and $^{129}\text{Xe}$ are the two least abundant species measured. On the other hand, ratios involving $^{22}\text{Ne}$ appeared to be less precise than other ratios. This may be due to its small signal, as $^{22}\text{Ne}$ is measured with a lower cathode voltage than the other species (and is a less abundant isotope to begin with). Furthermore, neon is most sensitive to bubbles, and its measurements would be adversely affected if there were problems with bubbling or low-level leaks at any point in the processing line. Finally, the precision of ratios with $^{38}\text{Ar}$ tend to be slightly better than those involving $^{36}\text{Ar}$. This may be due to the very high natural abundance of $^{36}\text{Ar}$ (0.3365%) compared to $^{36}\text{Ar}$ (0.0632%) and all other noble gas isotopes studied; linearity corrections may not apply as well for $^{36}\text{Ar}$ as for the other species, which are closer to each other in abundance. Trends for individual ratios over time are discussed in Section 3.3.

Despite subpar precision overall, it is worth pointing out that the minimum RSD values for all nine noble gas ratios were in fact quite good. If these values had been consistently obtained, ratios would have been considered precise enough for use in environmental studies. There were several sets of experiments in which precisions for most ratios were very good. However, no single day where existed where all ratios were the most precise—these were spread over experiments. The discrepancy between the minimum and average precision of noble gas ratios can be attributed to several days of experiments with high RSD values. Unfortunately,
many of those experiments occurred on days where no discernable change to the procedure existed. To move forwards with these studies, we must find a way to reliably reproduce our best-precision experiments.

3.2 Changes to Improve Measurement Precision

To improve precision, several changes were made to either the mass spectrometer scan settings or the physical processing line itself. Mass spectrometer scan settings were optimized early on in this work. These steps saw marked initial improvements. For example, we went from losing signal of certain noble gas species to consistently measuring all isotopes of interest. Other changes were instated later to improve noble gas ratios; most notably, we added $^{38}$Ar into the scan routine.

3.2.1 Optimization of Mass Spectrometer and Template Settings

Secondary Electron Multiplier Emission Adjustments

Our first attempted experiments often resulted in the unexpected loss of $^{36}$Ar ($m/z = 36$) and $^{84}$Kr ($m/z = 84$) signals. Preliminary discussions with Hiden staff suggested that this behavior likely stemmed from an issue with the secondary electron multiplier (SEM) detector when operating within certain $m/z$ ranges. To test this, we conducted SEM scans across 2-100 amu, with 10+ cycles of 20 scans per mass. One important consideration was that scanning at too high of an emission damages the SEM, as too many ions incident on the its surface will result in increased rates of degradation. Therefore, it was necessary to first check signal produced using the native Faraday cup detector, which is limited in sensitivity and dynamic range but far more robust. A simple rule of thumb is that at a given emission value, the SEM signal for any given species will about 1000 times higher than that generated by the Faraday cup.

Settings were adjusted to keep Faraday signal under 5E-3 and SEM signal under 5E-6; higher currents would likely be damaging. We were forced to use a global emission for these troubleshooting steps, since they necessitated Profile Mode scans. In MASsoft 7, Profile Mode does not allow for adjustments to emission settings in between masses, as the MID mode does. Since $^{36}$Ar is the most abundant gas we measure and thus gives the highest-signal peak at a given emission setting, it was sufficient to find an emission value that maximized $^{36}$Ar ($m/z = 36$) while keeping the Faraday cup signal for that species under 5E-3. An emission of 1200 was found to be optimal, with $^{36}$Ar signal under 5E-3 and all other peaks visible and well-formed.
After this adjustment, all noble gases of interest (m/z = 22, 36, 84, 129) were once again detected in a Multiple Ion Detection (MID) experiment using MASsoft 7 acquisition settings from summer research. Preliminary average signals for each of the species are listed below.

**Table 8. Preliminary signals for noble gas species at the beginning of the year.**

<table>
<thead>
<tr>
<th>Mass</th>
<th>Average Signal (Arbitrary Units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>4.31E-11</td>
</tr>
<tr>
<td>38</td>
<td>4.05E-9</td>
</tr>
<tr>
<td>84</td>
<td>5.12E-10</td>
</tr>
<tr>
<td>129</td>
<td>3.70E-11</td>
</tr>
</tbody>
</table>

**Mass Calibration**

Mass calibration is more of a fine-tuning adjustment but is still an important step, since it sets the exact m/z value that the mass spectrometer uses to scan for each of the noble gas species. Note that these values need not be integer values; in fact, it is often advantageous to scan a few hundredths of an atomic mass unit away. The HAL 201 RC RGA has a resolution of 0.01, which is the minimum permissible scan increment for the device. Since mass calibration scans are more effective with greater analyte abundances, we temporarily switched the inlet to a fused silica capillary (2 m x 0.05 mm ID) and sampled directly from air rather than air-equilibrated water. The scan point for each species should be set at the m/z value corresponding to the highest signal, although the scan point should also be at a flat region of the species profile. For the mass calibration, we used Profile Mode instead of the typical MID mode to check settings for one noble gas at a time, selecting a small window around each of the exact integer masses as a starting point. Scan resolution was in increments of 0.01 amu. Settings and conclusions for the mass calibration are presented in Table 9 below.
Table 9. Mass calibration results.

<table>
<thead>
<tr>
<th>Species</th>
<th>Acquisition Gain</th>
<th>Dwell Time</th>
<th>Scan Range</th>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{22}\text{Ne}$</td>
<td>1E-11</td>
<td>200% (of default dwell time, which is different for each gain and contained within look-up tables in the MSIU’s microcomputer)</td>
<td>21-23 amu</td>
<td>Signal at 22.00 is both high and flat. Continue scanning for $^{22}\text{Ne}$ at m/z = 22.0</td>
</tr>
<tr>
<td>$^{38}\text{Ar}$</td>
<td>1E-10</td>
<td>200%</td>
<td>37-39amu</td>
<td>Signal at 38.00 is high and flat, but drops sharply off at higher m/z values. Continue scanning for $^{38}\text{Ar}$ at m/z = 38.0</td>
</tr>
<tr>
<td>$^{84}\text{Kr}$</td>
<td>1E-10</td>
<td>500% (since peaks were very jagged with the lower dwell time of 200%)</td>
<td>83-85 amu</td>
<td>Signal at 84.00 is followed by a sharp drop in signal to the immediate right. Perform all future scans for $^{84}\text{Kr}$ at m/z = 83.98 to be safe.</td>
</tr>
<tr>
<td>$^{129}\text{Xe}$</td>
<td>1E-13</td>
<td>200%</td>
<td>128-130 amu</td>
<td>Signal at 129.0 looks good, although begins to drop off somewhat at higher m/z value. Continue scanning for $^{129}\text{Xe}$ at m/z = 129.00</td>
</tr>
</tbody>
</table>

Our mass calibration scans indicated that current template settings were already near-optimal for scanning for our noble gas isotopes of interest. Following this step, inlet was switched back to the membrane inlet system for regular experiments (sampling gases from water).
New Template: Addition of $^{36}$Ar to the scan routine

On 11/8/16, the MASsoft scan template was changed to measure $^{36}$Ar (m/z = 36) as well. Measured noble gas isotopes were now $^{22}$Ne, $^{36}$Ar, $^{38}$Ar, $^{84}$Kr, $^{129}$Xe. Briefly, $^{36}$Ar measurement settings were similar to those for $^{38}$Ar, although dwell time for m/z = 36 was doubled from 1000 ms to 2000 ms. Additionally, the settle time for the m/z = 36 was shortened to 500 ms from the default value of 1000 ms. The addition of $^{36}$Ar to our scan template was done to improve precision of ratios involving Ar, as previously the precision for ratios involving $^{38}$Ar was on average worse than that of other ratios. The RSD values for ratios with $^{38}$Ar were consistently above 1% or even 1.5%, whereas they were often under 1% for other noble gas ratios.

Ultimately, precision for new ratios involving $^{36}$Ar did not seem to be much better than their corresponding $^{38}$Ar ratios, and the overall precision of ratios with Ar did not improve much when this change was instated. However, we kept scanning for $^{36}$Ar anyways because precision did not worsen with this change, and we thought it might be advantageous to have more data. Measuring both argon isotopes would prove to be informative in later accuracy experiments—ratios involving $^{38}$Ar were much closer to theoretical values than ratios involving $^{36}$Ar.

3.2.2 Changes to Processing Line or Sampling Technique

Reduction of Membrane Bubbling

After adjusting mass spectrometer settings to fix missing signals, we were able to run experiments in which all species of interest were detected. However, precision was poor overall; certain ratios had RSD values ranging from 2% to 5%. When checking the wetline, we noticed the formation of bubbles in the membrane and hypothesized that there could be some problem with the tubing or stainless steel connections before the sample reached the membrane. The extent of bubbling decreased when 1) the initial portion (sample to membrane) of stainless steel tubing was replaced with C-Flex thermoplastic tubing, and 2) a machinist smoothed out the edges of the stainless steel connectors to eliminate a small burr that had originally prevented full contact. Further improvements were observed when the new C-Flex tubing was connected to the bottom of the membrane housing, rather than the top, as it had been before. No more bubbles were seen in following experiments (10/19/16 onwards). Precision improved immediately afterwards, with RSD values ranging between 0.3-3.0% on 10/19 and 0.4-2.3% on 10/20.
Exercising the Right Angle Valve

After generating and comparing overlaid plots of ion current, we decided to “exercise” (close and then immediately reopen) the right angle valve at least five times prior to running the first experiment of each day. The right angle valve, when closed via our pneumatic switch system, prevents the turbomolecular pump from evacuating the mass spectrometer chamber. We had observed that the right angle valve often took upwards of 3-4 seconds to slide shut in the first experiment of the day but always closed within half a second in subsequent experiments.

Overlaid plots showed that noble gas signals around the inlet time of the first sample in a set of precision experiments typically differed noticeably from those of subsequent samples. This was thought to be at least somewhat related to the lag time in right angle valve closure during the first experiment of each set. When the right angle valve stays open for an additional few seconds in the first experiment, the gas stream is pumped away for a few seconds longer.
Figure 9. Overlaid plots of signal for a) m/z = 22 and b) m/z = 129, from experiments run on 10/19/16 (before the rule to exercise the right angle valve was instated). An initial bump in Experiment 1’s ion current was observed for all species measured except $^{22}\text{Ne}$, which is shown for the sake of comparison.
For all experiments starting 11/1/16 onwards, we required that the right angle valve be exercised at least five times before the start of the first experiment. Exercising was only done when the inlet valve and rough pump valve were both closed to prevent accidental leakage of gas into the mass spectrometer.

This change was effective in reducing or eliminating the strange “peaking” behavior for all noble gas signals, as evidenced by future overlaid plots.

![Figure 10](image)

**Figure 10.** Overlaid plot of m/z = 129 signals for experiments run on 11/1/16, after the right angle valve was exercised. Note the absence of the hump seen in the m/z = 129 overlaid plot from 10/19/16 (Figure 9).

**Replacing C-Flex with Viton Tubing**

C-Flex tubing was changed to fluoroelastomer Viton tubing (60A Durometer, 1/32” ID x 3/32” OD x 1/32” wall), which is the same material used in the tubing that goes through the roller tracks of the peristaltic pump. We hoped this would make measured noble gas ratios more representative of their actual ratios post-extraction from the water sample, as Viton is much more impermeable to gas diffusion than C-flex (see Table 2). This switch did not appreciably change noble gas signals or the RSD of ratios, suggesting that the new tubing had little effect on gas diffusion over the distance between the sample and membrane. Although precision was not
noticeably improved, we decided to continue using the Viton tubing due to its high durability and potential for limiting diffusion.

**Improving Membrane Temperature Consistency**

Recent literature on gas extraction membranes suggested that the rates at which different gases partition across the membrane are highly sensitive to temperature. Any changes in membrane temperature over the course of an experiment could alter the amounts of each gas reaching the mass spectrometer, and hence the reported noble gas ratios. Since the membrane temperature was controlled only by submerging its glass housing in a dewar of room-temperature water (usually around 23.5-24.5°C, as recorded by constant thermocouple measurements), we hypothesized that the membrane cooled slightly over the course of experiments as the 21°C water sample flowed past it. We hypothesized that bringing the water bath and sample up to room temperature could mitigate this effect, so the water bath setpoint was increased to 24°C from 21°C.

The first set of precision experiments with the water bath setpoint at room temperature (24°C) resulted in extremely good precision. The gas ratios on the day of the change (1/27/17) all had RSD values < 1%. This suggested that improvements to precision might be possible if the membrane temperature could be kept constant throughout a set of experiments. However, precision for the following set of experiments (1/28/17) was poor reason with this new change.

**Moving the Membrane to the Water Bath**

Adjusting the water bath/sample temperature to match measured room temperature was not an ideal way to keep membrane temperature constant, as this required constant changes to the bath setpoint, and temperature of the water bath and sample always took a few hours to equilibrate after these changes. We decided to overcome this problem by physically rerouting the membrane housing so it could rest inside the water bath. This involved the most dramatic change to the processing line of the entire thesis project. A piece of electropolished, ¼ inch OD stainless steel tubing was bent to the correct specifications so that the membrane could be moved inside the water bath.
Figure 11. New stainless steel tubing bent to extend membrane housing towards the water bath. Note that in this picture, the membrane itself is not visible (it is submerged inside the water bath at the far right edge of the picture). The U-shaped tube and dewar to the immediate left of the water bath comprise the first step of the gas purification process, in which water vapor is condensed out by means of an ethanol/dry ice slurry.

Moving the gas extraction membrane to the water bath also greatly extended the distance between the membrane and mass spectrometer, so changes to the experimental procedure had to be made to accommodate for the new setup. Briefly, these changes involved extending the settling time for gas from 2 minutes to 5 minutes and the pump-out time from 3 minutes to 5 minutes. Experiments for this thesis ended before any conclusions could be made regarding the efficacy of the new membrane setup.
3.3 Discussion of Precision Trends for Individual Ratios

**Figure 12.** $^{22}\text{Ne}/^{129}\text{Xe}$ ratios over time (for precision experiments only). Precision can be visualized by looking at the vertical spread of each group of points. Changes instated are marked as follows: (a) 11/1/16 – Started to exercise right angle valve (b) 11/8/16 – Began scanning for m/z = 38 (c) Water bath/sample temperature increased to 24°C to more closely match room temperature.

The $^{22}\text{Ne}/^{129}\text{Xe}$ ratio had a wide spread of RSD values, ranging from 0.40% on 10/25/16 to 5.15% on 1/28/2017. Graphically, we see that ratios were more precise in the earlier experiments, with the largest spread (worst precision) on 1/28/17. Note that two experiments—one 15s inlet time experiment and a 20s inlet time experiment—were run on 1/13/17, generating two sets of ratios.
Figure 13. $^{36}\text{Ar}^{129}\text{Xe}$ ratios over time for precision experiments.

No ratios exist for dates before 11/15/16 since m/z = 36 was yet not scanned for. One set of experiments was run on 11/8/16 with old template settings and is omitted from the figure above; its RSD was not recorded in the table to the right because that experiment was run as a trial to optimize template settings.
Precision for $^{36}\text{Ar}/^{129}\text{Xe}$ ratios was poor to begin with, prompting the attempt to improve argon ratios by scanning for $^{38}\text{Ar}$ as well. Once again, experiments on 1/28/17 resulted in particularly poor precision, even though no intentional changes in procedure occurred.

**Figure 14.** $^{38}\text{Ar}/^{129}\text{Xe}$ ratios over time for precision experiments.

**Figure 15.** $^{84}\text{Kr}/^{129}\text{Xe}$ ratios over time for precision experiments.
As mentioned earlier, precision of $^{84}\text{Kr}/^{129}\text{Xe}$ ratios was good compared to other ratios, despite the low natural abundances of both $^{84}\text{Kr}$ and $^{129}\text{Xe}$. This may be because these two species have similar physicochemical characteristics and can thus partition across the membrane in comparable ways. Any slight environmental or instrumental changes that result in differences in membrane permeation would therefore not affect these two gases too differently with respect to each other.

**Figure 16.** $^{22}\text{Ne}/^{84}\text{Kr}$ ratios over time for precision experiments.

Precision for $^{22}\text{Ne}/^{84}\text{Kr}$ ratios was generally acceptable; there were several days in which RSD values were at or under 1%. Additionally, these ratios had values which were generally consistent across time, differing markedly only on 1/28/17.
Figure 17. $^{36}\text{Ar}/^{84}\text{Kr}$ ratios over time for precision experiments.

There is considerable variation in the values of $^{38}\text{Ar}/^{84}\text{Kr}$ ratios across different days, although we were unable to determine why this was the case. Another interesting observation was that the value of this ratio seemed to be extremely sensitive to inlet time, as evidenced by comparing results of a) 20s inlet time experiments in the morning of 1/13/17 and b) 15s inlet time experiments conducted in the evening of the same day. Much larger $^{36}\text{Ar}/^{84}\text{Kr}$ ratios for the 20s inlet time suggest that either $^{36}\text{Ar}$ signal is preferentially enriched or $^{84}\text{Kr}$ signal is suppressed at higher sample volumes.

The observation that ratios differ when different volumes of sample are let into the mass spectrometer is indicative of chemical slope (matrix) effects, discussed in section 3.4. Note that RSD was slightly better with the longer inlet time of 20s, which is consistent with the principle that higher signal leads to less relative variance. We hypothesize that the magnitude of the inlet time effect is more noticeable for this ratio than many others because of the high relative natural abundance of $^{36}\text{Ar}$, which causes selection pressures to become more pronounced. Note that RSD on 1/13/17 was slightly better with the longer inlet time of 20s, which is consistent with the principle that higher signal leads to less relative variance.
A direct comparison with $^{36}\text{Ar}/^{84}\text{Kr}$ ratios shows that $^{38}\text{Ar}/^{84}\text{Kr}$ ratios almost always have slightly better precision. There is a slight upwards drift in $^{38}\text{Ar}/^{84}\text{Kr}$ ratios over time, although ratios seemed to be fairly consistent over the last few experiments. The value of this ratio is less sensitive to inlet time, as experiments run on 1/13/17 have much more similar ratios than they did in the $^{38}\text{Ar}/^{84}\text{Kr}$ case (see Figure 17). Much larger $^{38}\text{Ar}/^{84}\text{Kr}$ ratios for the 20s inlet time suggest that either $^{38}\text{Ar}$ signal is preferentially enriched or $^{84}\text{Kr}$ signal is suppressed at higher sample volumes.

**Figure 18.** $^{38}\text{Ar}/^{84}\text{Kr}$ ratios over time for precision experiments.
This ratio is one of the more consistently imprecise combinations, with %RSD values being <1% for only two days of experiments. We are currently not certain why this is the case.

Figure 19. $^{22}$Ne/$^{36}$Ar ratios over time for precision experiments.
Figure 20. $^{22}\text{Ne}/^{38}\text{Ar}$ ratios over time.

These ratios had poor precision initially, which led us to measure $^{36}\text{Ar}$. Unfortunately, as seen above in Figure 19, $^{22}\text{Ne}/^{36}\text{Ar}$ ratios were imprecise as well. Furthermore, the values of these $^{22}\text{Ne}/^{38}\text{Ar}$ ratios were not consistent, as they drifted down throughout the experiments conducted in the earlier months.
3.4 Inlet Time Experiments and Chemical Slope Effects

The chemical slope effect, often also called the matrix effect, is a well-documented phenomenon in which detection limits are compromised by either molecule-molecule collisions within the mass spectrometer or competition for ionization between the analytes of interest. The adverse effect on detector response and recorded signal is usually attributed to reduced ionization efficiency for analytes of interest. While the mechanism for ion suppression in a quadrupole system is not fully understood, the degree of ion suppression is often dependent on the concentration of the analyte(s) monitored.\textsuperscript{52}

When analyzing a sample for a suite of noble gases, one must consider the chemical slope effect of each noble gas species on the others. Since ion suppression has the potential to affect the analytical parameters of any scan, we evaluated the extent of this effect as part of our method validation. To do so, we performed a series inlet time experiments in which we changed the accumulation time of the gas stream in the mass spectrometer by varying inlet times between 14 seconds and 20 seconds. Although we were unable to quantify actual gas volumes, the inlet times should be directly proportional to the amount of gas sampled. Inlet times were varied in a non-systematic manner to prevent conflation with instrumental drift. A sequence we frequently used in inlet time experiments was 20s, 14s, 17s, 15s, 18s, with an additional 20s inlet time experiment run at the end for the purposes of comparison with the first sample. In the absence of chemical slope effects, we would expect noble gas ratios to be invariant with sampled gas volume (of course, raw signal should be higher for longer inlet times). However, it was clear that the ratios themselves changed with inlet time when gas mole ratios were plotted against average signals.

A total of 5 inlet time experiments were run (11/21/16, 11/29/16, 12/10/16, 1/15/17, 1/16/17). In these experiments, gas ratios followed a clear linear dependence on inlet time. Points for Experiment 1 were always discarded because of deviations from linearity; plots of data from a representative experiment (1/16/17) are shown below.
Figure 21. Results of inlet time experiments on 1/16/17; inlet times were varied from 14s to 20s in some non-systematic order. Noble gas ratios are plotted against the average signal of the more abundant gas, except when ratios involve $^{129}\text{Xe}$, in which case ratios are plotted against the average $^{129}\text{Xe}$ signal instead.

Although it is difficult to pinpoint the exact cause(s) of these chemical slope effects, we can say with certainty that these effects discriminate more strongly against the rarer gases at low pressures (sample volumes) than at high pressures. Given the gas abundance series of $^{38}\text{Ar} > ^{84}\text{Kr} > ^{22}\text{Ne} > ^{129}\text{Xe}$, we notice that ratios of less abundant:more abundant gas (ex: Ne:Ar-38) slope downwards, while ratios of more abundant/less abundant (e.x. Kr:Xe) gases slope upwards. Slopes for each of the ratios were calculated using a simple linear regression model in MATLAB and saved for future reference.

3.4.1 Corrections for Chemical Slope Effects

Slopes associated with each of the inlet time plots were extracted using a linear fitting function in MATLAB. Since several days of inlet time experiments were run, each with slightly different ratio vs. inlet time slopes, there was some flexibility involved in choosing which slope values to use when applying corrections. We finally decided to average the slopes from 12/10/16, 1/15/17, and 1/16/17; doing so reduced the error terms associated with most slope values. Nine
total average slopes were generated (one for each noble gas ratio); these slopes were used to correct for the chemical slope effect.

Although inlet times were not varied within precision experiments, human operation of the pneumatic valve system could lead to slight variations in the timing of gas accumulation, and thus possible chemical slope effects. Corrections were applied for each set of precision experiments in the following way. First, an arbitrary sample was chosen to serve as the reference sample for the set. We often set Experiment 2 as the reference. After choosing a reference, \( \frac{\text{sample ratio}}{\text{reference ratio}} \) was calculated for each gas ratio across all experiments. Then the “true ratio” (i.e., the expected ratio at a given inlet time without the presence of chemical slope effects) can be approximated as:

\[
\text{True ratio} = \text{measured ratio} + \text{slope of ratio} \times (1 - \frac{\text{sample ratio}}{\text{reference ratio}}).
\]

For an example of how this would work in practice, consider the \( ^{38}\text{Ar} /^{129}\text{Xe} \) ratios in a series of inlet time experiments. As seen in Figure 21, there is a strong upwards slope in \( ^{38}\text{Ar} /^{129}\text{Xe} \) values with increasing inlet time. However, in the absence of chemical slope effects, these ratios should be constant. Our chemical slope corrections scale all \( ^{38}\text{Ar} /^{129}\text{Xe} \) ratios to that of the 20-second inlet time, marked with a dashed line in Figure 22 below. These “true ratios” reflect what the ratios would be if chemical slope effects were nonexistent. To obtain the true ratio value from a measured ratio, represented by points in Figure 16 below, we add a term equal to \( [\text{slope of ratio} \times (1 - \frac{\text{sample ratio}}{\text{reference ratio}})] \), the magnitude of which is exactly the difference between the measured ratio and the reference ratio. For example, the magnitude of the correction for the first point is shown with a red arrow in the figure below.
Figure 22. Explanatory figure for chemical slope corrections. Measured ratios are plotted as dots and normalized to gas concentrations of the reference experiment, such that the reference or highest-signal experiment has value of ‘1’. This normalization step makes the chemical slope correction applicable to all sets of experiments as long as the reference is chosen properly.

When chemical slope corrections were applied to precision experiments, RSD values improved somewhat for 22:129, 36:129, 38:128, 84:129, and usually 38:84. The other three ratios—36:84, 22:36, and 22:38—either did not change appreciably or worsened slightly. However, for the sake of consistency, all noble gas ratios in experiments done for this thesis were corrected for chemical slope effects. Values reported in this paper all reflect ratios post-chemical slope correction.

Chemical slope corrections are crucial for accuracy experiments, since the decreased solubility of gases at higher temperatures means that warm-water samples will always contain a lower concentration of dissolved gases than the cooler samples they are compared to. In these experiments, the reference ratios are taken to be the average of flask (cold sample) ratios, which have higher abundances of dissolved gas species than the bottled samples. Otherwise, corrections are applied in the same manner described above.
3.5 Accuracy Experiments

3.5.1 Theoretical Warm/Cold Ratios

We can use Henry’s law to determine the equilibrium molality of any inert gas. For example, using Ne:

$$[X]_{\text{Ne, equilibrium}} = p_{\text{Ne, air}} \times H_{\text{Ne}}(T, \text{ salinity})$$

Here $[X]_{\text{Ne}}$ is the molar concentration of neon that is dissolved in water at equilibrium (mol kg$^{-1}$) and $p_{\text{Ne}}$ is the partial pressure of Ne in dry air (atm). $H_{\text{Ne}}$ is the Henry’s Law solubility coefficient of Ne (mol kg$^{-1}$ atm$^{-1}$). This solubility coefficient is a function of the temperature and salinity of the water sample and scales with isotopic abundances. For most of our accuracy experiments, warm-water samples were bottled at 30°C and analyzed in conjunction with a flask of water at 21°C. The expected gas mole ratios at each of these temperatures were calculated using MATLAB scripts written by Roberta C. Hamme (Scripps Institute of Oceanography, currently at the University of Victoria). These scripts return the solubility (μmol/kg) of each noble gas species in water at 1 atm pressure, given a temperature and salinity (salinity = 0 in our experiments with laboratory water). A table of theoretical values calculated in this manner is included below. We calculate measured warm/cold ratios of each noble gas ratio and compare it to the theoretical values to validate the accuracy of our measurements.

For example, the theoretical warm/cold value for $^{22}\text{Ne}/^{129}\text{Xe}$ at 21°C vs. 30°C would be calculated using

$$\frac{(^{22}\text{Ne}/^{129}\text{Xe})_{\text{at 30°C}}}{(^{22}\text{Ne}/^{129}\text{Xe})_{\text{at 21°C}}}.$$  

Table 10. Theoretical solubilities of the noble gases (μmol/kg) in distilled water at 1 atm air

<table>
<thead>
<tr>
<th></th>
<th>Neon</th>
<th>Argon</th>
<th>Krypton</th>
<th>Xenon</th>
</tr>
</thead>
<tbody>
<tr>
<td>21°C</td>
<td>0.0083</td>
<td>13.6813</td>
<td>0.0030</td>
<td>$4.2027 \times 10^{-4}$</td>
</tr>
<tr>
<td>30°C</td>
<td>0.0078</td>
<td>11.6462</td>
<td>0.0025</td>
<td>$3.1998 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

3.3.2 Measured Warm/Cold Ratios

Six sets of accuracy experiments were run in total, with all experiments comparing flask water at 21°C to AEW that had previously been bottled at 30°C. The first and last samples of any set of accuracy experiments were always 21°C flask samples, with bottled samples run in the
middle. When deciding which flask ratios to set as the “cold” ratios, it was observed that all nine ratios drifted downwards between the first flask and the last flask, perhaps due to instrumental drift. Instead of setting the cold ratio values to be the average of the flask ratios, we opted for a more rigorous correction. We assumed flask ratios dropped in a linear fashion with time, and used the MATLAB ‘interp1’ function to interpolate what the flask (“cold”) ratios would have been at the time of each bottle (warm ratio) measurement. We then divided each bottle ratio by its corresponding interpolated flask ratio to obtain the measured warm/cold values.

For example, the measured warm/cold ratio for $^{22}\text{Ne}/^{129}\text{Xe}$ would be

$$\frac{^{22}\text{Ne}/^{129}\text{Xe}}{^{22}\text{Ne}/^{129}\text{Xe}} \text{bottle [warm]} \bigg/ \frac{^{22}\text{Ne}/^{129}\text{Xe}}{^{22}\text{Ne}/^{129}\text{Xe}} \text{interpolated flask [cold]}.$$ 

Warm/cold ratios were averaged across all bottles in a set of experiments. The accuracy for each ratio was determined by taking the percent difference between theoretical warm/cold values (as calculated using Hamme’s MATLAB scripts) and average measured warm/cold values.

### 3.3.3 Results of Accuracy Experiments

Figure 23 shows a summary of percent differences between measured warm/cold ratios and their theoretical counterparts for all six days of accuracy experiments. These are grouped roughly based on how good the accuracy was, with ratios with poorer accuracy in the left column and ratios with better accuracy in the right column.

Kr/Xe was the only ratio for which percent differences were all negative, although this should not be taken as a conclusive statement since only 6 accuracy experiments were performed in total. On average, Days 1 and 2 (12/2/16 and 12/6/16, respectively) resulted in more accurate ratios than the rest, Some bubbles were observed in bottled samples for Day 3 (12/8/16) and Day 6 (2/14/17), which may help explain the poorer accuracy in measurements. If the bubbles resulted from air diffusing through the bottle seal, they would affect the gas compositions of the less soluble dissolved gases more than those of the more soluble dissolved gases. This could explain why Ne/Xe, Ne/Kr, and Ne/Ar deviated more from theoretical values on those days. However, Kr/Xe, which involves the two most soluble noble gases, also had very large percent differences. Interestingly, although $^{38}\text{Ar}$ did not result in the most precise ratios, the most accurate ratios all involved this species.
Figure 23. Percent differences between measured and theoretical warm/cold ratios across 6 accuracy experiments. Days listed on the x-axis are 12/2/16, 12/6/16, 12/8/16, 1/20/17, 1/24/17, 2/14/17 (in that order). Note y-axes are not equal.
Chapter 4: Conclusions

The precision and accuracy experiments conducted in our laboratory have shown that our system, consisting of a residual gas analyzer mass spectrometer with membrane gas extraction, is not yet ready to measure noble gas ratios in aquatic samples. Our ratios sometimes have RSD values above 1.5%, which is above the desired <1% cutoff for the measurement of noble gas ratios in seawater. Future efforts will focus on keeping precision as low as on our best days, as those precisions were suitable for measurements of discrete environmental samples. The accuracy of our method is also not yet at the necessary values, with some ratios often differing from theoretical calculations by as much as 5% or more. Since the range of saturation states of dissolved noble gases in seawater is only about 5-15%, measurement accuracies need to be around an order of magnitude smaller to be considered accurate enough.

During this process, we learned much about the optimization of this mass spectrometer/membrane inlet combination, which can be applied to future work with our system or similar setups. Moreover, our research has reinforced our belief that the gas extraction membrane plays a significant role in determining measured noble gas ratios. A better theoretical understanding of how individual gases partition across membranes, as well as how partitioning changes with different flow regimes and membrane temperatures, would benefit researchers interested in using membrane inlet mass spectrometry for the detection of dissolved gases. One immediate future direction should be to find some way to measure and manipulate membrane temperatures. That way, we could determine with more exactness how the membrane partitions various gases under different temperature conditions. Similarly, it might be informative to manipulate peristaltic pump settings, especially the flow rate, as well as various timings during the analysis procedure.

Corrections for chemical slope effects and instrumental drift could also be expanded to be far more rigorous. For example, it would have been better to have performed more inlet time experiments, which would allow us to make statements about the variation in time of chemical slopes. If the extent of the chemical slope effect differs significantly from day to day, it would be worthwhile to find out which factors influence it and how. Finally, future work should focus on using additional methods to test the accuracy of our measurements. For example, we could test different bottling procedures, or instead of using bottles, sample directly from the warm bath.
References


