Measurement of dissolved gas concentrations in natural waters utilizing an in-situ, membrane inlet, linear quadrupole mass spectrometer

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Measurement of Dissolved Gas Concentrations in Natural Waters Utilizing an In-Situ, Membrane Inlet, Linear Quadrupole Mass Spectrometer

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science
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Dedication

Many are the people who have been essential to the successful completion of this endeavor and to whom I dedicate this work.

First and foremost, my parent’s, Del and Emil Wenner, and my sister Ann Wenner, whose love and support never wavered though often were the times I tried their patience.

To my beloved friend Anne Wenner who saw in me things I never imagined existed and gave me the strength and confidence to pursue my dreams.

To Libby, my cherished wife, who has taught me the meaning of joy and entered my life near the end of this enterprise and never blinked through all the insanity.

To Dr. Timothy Short, as fine a mentor and friend for which one could hope, may our adventures together take us far into the future.
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In addition to those people singled out in the dedication above I would like to thank all those who provided so freely of their time and knowledge in helping me to complete this Master’s thesis.

To my major professor, Dr. Bob Byrne, whose support and persistence kept me afloat during those times I found myself drowning in a sea of doubt.

If it can be said that I am a mass spectrometrist it is to the credit of Gottfried Kibelka and his enthusiastic explanation of the finer points of membrane inlet mass spectrometry.

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To Strawn Toler whose friendship and academic acumen got me through several periods of self-doubt.

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Measurement of Dissolved Gas Concentrations in Natural Waters Utilizing an In-Situ, Membrane Inlet, Linear Quadrupole Mass Spectrometer

Peter Wenner

ABSTRACT

Since its creation in the late 19th century, mass spectrometry has evolved into one of the most versatile analytical methods in science. To chart this evolution this thesis includes a historical overview of mass spectrometry and a description of the role of mass spectrometry in oceanography. The development and deployment of underwater mass spectrometers (UMS) at the University of South Florida’s Center for Ocean Technology has made possible the collection of real-time data with greatly increased spatial and temporal density. The UMS was deployed via both remotely guided surface vehicles (GSV) and ship’s cables to monitor a suite of dissolved gases and volatile organic compounds in saltwater and freshwater environments. Spectrometer data in Lake Maggiore, Florida were acquired at a rate of 0.7-3.6 seconds/sample for 2-3 hours. The resulting multi-analyte spectrometer data were recorded in real time with the Global Positioning System (GPS) observations of an associated surface vehicle and transmitted to a remote laptop computer via a wireless Ethernet link. These data were merged to create high-resolution maps of chemical distributions. Of particular interest were the co-varying oxygen and carbon dioxide mass spectrometer signals, diagnostic of photosynthesis-respiration processes, that were collected over a 10,800 square-meter area of the lake. The UMS was also deployed on a shipborne hydrowire in Saanich Inlet, a 200-meter deep fjord in the western Canadian province of British Columbia. The
concentrations of a broad suite of dissolved gases were monitored on both downcast and upcast over a total depth range of 200 meters. Spectrometer data were acquired at a rate of 4.2 seconds/sample for the duration of the deployment. Mass spectrometer signals diagnostic of reduced species (CH₄, H₂S,) in the anoxic waters of the inlet below a depth of 100 meters were consistent with previous descriptions of the fjord’s chemistry. The UMS was deployed on a remotely guided surface vehicle on the Hillsborough River in central Hillsborough County. Spectrometer data were acquired at a rate of 0.7 seconds/sample, and geographic location was recorded by an onboard GPS during a 2,640 meter transect of the river. Prior to the deployment, the mass spectrometer was calibrated using certified gas standards. The calibration experiments correlated mass spectrometer ion intensity data with dissolved gas concentrations, whereupon the mass spectrometer data collected during the deployment were reported in units of micromole/kilogram (µmol/kg). The mass spectrometer recorded changes in gas concentrations associated with changing physical conditions and biological activity along the 2,640 meters of the river that was transited by the GSV.
Chapter One

Introduction

In the more than 100 years since its discovery, mass spectrometry has become one of the most versatile analytical methods in science. In the first half of the 20th century investigations utilizing the mass spectrometer yielded important discoveries in physics. The discovery of isotopes, and their abundances, as well as the separation of uranium-235 from uranium-238 are examples of the early contributions made by this analytical technique. The development of novel inlet systems, mass analyzers and ion detectors soon made the mass spectrometer an essential analytical tool throughout many scientific disciplines.

Mass spectrometry has been widely used in oceanographic studies to better understand biological, chemical and geological dynamics within the world’s oceans. Inductively coupled plasma-mass spectrometry (ICP-MS) is used to analyze trace metal concentrations in seawater. Isotope ratio mass spectrometry (IRMS) has been employed to determine isotopic $^{16}$O/$^{18}$O fractionation in the tests of marine planktonic organisms to reconstruct historical temperature records. Development of membrane introduction mass spectrometry (MIMS) in 1963 (Hoch & Kok, 1963) is particularly relevant to the work described in this thesis. A membrane of polydimethylsiloxane (PDMS) isolates the internal vacuum of the mass spectrometer from the environment. The PDMS membrane is ideal for use in aquatic environments as it is permeable to dissolved gases and volatile organic compounds (VOC’s) but nearly impermeable to water. The University of South
Florida underwater mass spectrometer (UMS) employs a PDMS membrane inlet system allowing for in-situ, real-time measurement of dissolved gases and VOC’s.

This thesis describes four deployments of the UMS. The first deployment took place in Lake Maggiore, a hypereutrophic, urban lake in St. Petersburg, Florida. The UMS was deployed on a remotely operated guided surface vehicle (GSV) outfitted with an onboard GPS system to monitor spatial distributions of dissolved gas concentrations. During post-processing, GPS and mass spectrometer data were meshed to produce geo-referenced maps of ion intensity data along the track navigated by the GSV. Mass spectrometer ion intensity data were displayed as a color scale. The color scale was then superimposed upon the GPS plot to produce a plot of ion intensity vs. position on the lake’s surface. The second deployment took place in the marine waters of Bayboro Harbor/Salt Creek which borders the University of South Florida campus in St. Petersburg, FL. This deployment was conducted in the same way as was the Lake Maggiore deployment, the exception being that the mass spectrometer monitored for VOC’s. Geo-referenced maps plotting both the GPS track and mass spectrometer ion intensities for selected VOC’s were also produced for the Bayboro Harbor/Salt Creek deployment.

The third deployment took place in Saanich Inlet, located on the eastern shore of Vancouver Island, British Columbia, Canada. A series of deployments, to depths of up to 205 meters, were conducted over a four day period. Mass spectrometer ion intensity data were collected for a suite of dissolved gases and plotted as a function of depth.

In the fourth deployment, the mass spectrometer was mounted aboard the GSV along a section of the Hillsborough River in Tampa, Florida. The GSV navigated a 2,640 meter
portion of the river while the mass spectrometer collected data for argon, carbon dioxide, oxygen, methane and nitrogen. A series of calibration experiments were conducted prior to the deployment. These experiments correlated mass spectrometer ion intensity data directly to gas concentrations such that mass spectrometer data collected during the Hillsborough River deployment could be reported in units of µmol/kg.
Chapter 2

A Brief History of Mass Spectrometry

In 1898 W. Wien reported that the motion of ions could be deflected by electric and magnetic fields (Wien, 1898). The true potential of this discovery began to be realized during a series of experiments conducted by J.J. Thomson from 1910 to 1920 with a parabola mass spectrograph (Thomson, 1912). Thomson’s instrument was able to separate ions based on their mass-to-charge ratio (m/z) (Thomson, 1913). This was done by passing a collimated, positively charged ion beam through electrostatic and magnetic fields of known magnitudes. The ion beam was deflected both vertically and horizontally by the combined fields, and the path traversed by an ion in this field was dependent upon ion m/z and velocity (Thomson, 1913). Ions impacted a photographic plate where they were permanently recorded for later analysis. The instrument description is derived from the parabolic impact patterns left on the photographic plate by ions of the same m/z ratio but differing velocities. This instrument was used in Thomson’s 1912 discovery of the mass 22 isotope of neon.

Though the parabola mass spectrograph represented a spectacular advance in instrumental analysis, it lacked the ability to focus an ion beam - the only way to improve the resolving power of a mass spectrometer. Resolving power is the measure of an instrument’s ability to separate one mass from another (Smith, 1999). For ions with identical charge (z) but similar mass (m), separation (i.e., resolution) can be difficult. In 1919 F.W. Aston incorporated a velocity filter in his mass spectrograph - allowing only ions of a specific velocity to enter the flight chamber (Aston, 1919). This velocity
focusing capability produced ion impacts along a straight line on photographic plates, thus eliminating the parabola produced in Thomson’s instrument. During this same time period, A.J. Dempster achieved direction focusing, whereby deflection of ions through 180° in a magnetic field provided a resolving power of 1 part in 100 (Dempster, 1918). Another of Dempster’s innovations, use of a quadrant electrometer detector, distinguished this instrument as the first true mass spectrometer. Dempster went on to discover many isotopes and determine their abundances. Bainbridge’s further conceptual improvements, combining both velocity and direction focusing, created the double focusing mass spectrograph (Bainbridge, 1933).

Applying the principles of their earlier theoretical work, Mattauch and Herzog (Mattauch & Herzog, 1934) developed a mass spectrograph that was double-focusing for all masses (Mattauch, 1936). By careful consideration of electric and magnetic field theory and manipulation of instrument geometry, Mattauch and Herzog were able to construct an instrument that detected all ions as they impacted a linear-plane photographic plate. Of critical importance in this design was the location of the photographic plate at the exit pole boundary of the magnetic field (Roboz, 1968).

In 1940 A.O. Nier introduced his sector analyzer, which served as the design template for many future instruments (Nier, 1940). Nier replaced the large, heavy electromagnet necessary to deflect an ion 180° with a small wedge sector electromagnet that deflected ion paths by 60° (Dulski, 1999). This design innovation reduced the weight and power consumption of the electromagnet and placed the ion source and detector outside the influence of the instrument’s magnetic field (deLaeter, 2001). One of these instruments was used by Nier in the early 1940’s to separate nanogram quantities of
uranium-235 from uranium-238 (Nier, et al., 1940). The Calutron, a three-story-high version of Nier’s sector instrument, separated uranium-235 from uranium-238 for production of the first atomic bomb (Smith, 1947).

Mass spectrometry began to mature in the 1940’s as several companies developed and constructed mass spectrometers for commercial use. These early commercial instruments were used primarily by chemists in the petroleum industry to measure the abundances of small hydrocarbons in process streams (Griffiths, 2008). During this period researchers in fields other than physics came to realize the quantitative analytical potential of mass spectrometry. Physicists at this time were still primarily interested in high-precision isotope mass spectrometry, but their scope of interest began to broaden into such areas as fragmentation patterns, ionization and theoretical molecular modeling (Diaz, 1999).

In 1946 W.E. Stephens built the first time-of-flight (TOF) mass spectrometer (Stephens, 1946). Ions emanated from a pulsed source and were separated according to their $m/z$ values as they traversed a field-free path of known length. Provided that ions leave the source at the same time and with the same energy, thus the pulsed ion source, lighter ions travel the path from source to detector in less time than heavier ions.

In 1948 S.A. Goudsmit developed a helical path mass spectrometer based on the orbital period of an ion circling in a uniform magnetic field (Goudsmit, 1948). This instrument which came to be known as the “chronotron”, separated ions of different mass by measuring the time it took for different ions to travel a set number of revolutions along a helical flight path imposed by a uniform magnetic field. As in a linear time-of-flight instrument, heavier ions require a greater period of time to travel a given distance than do
lighter ions. Goudsmit’s instrument had a measurement accuracy of approximately 0.01 µsec which yielded a mass accuracy of $10^{-3}$ amu. It was an instrument of this type that was used to measure heavy elements such as $^{208}\text{Pb}$ and $^{209}\text{Bi}$ (Hays, et. al., 1951). The continuing evolution of ion cyclotron mass spectrometry culminated in 1974 with the development of Fourier transform ion cyclotron resonance (FT-ICR) which represented a major breakthrough in the field of mass spectrometry (Comisarow & Marshall, 1974).

Investigation of ion interactions in two- and three-dimensional quadrupole fields by Wolfgang Paul (Paul & Steinwedel, 1954) and coworkers in 1953 led to the development of the quadrupole mass analyzer. Although early quadrupole instruments had poor resolving power and low mass range, through use of sweeping electric potentials (Gross, 2004) they offered advantages of high transmission, light weight, small size, comparatively low-price and high scan-speed.

In 1957 the need to separate and analyze complex mixtures led to one of the most powerful tools in instrumental analysis: coupled gas chromatography-mass spectrometry (Gohlke & McLafferty, 1993). The success of this approach led to the development of other hyphenated methods: liquid chromatography-mass spectrometry (Ardrey, 2003), capillary zone electrophoresis-mass spectrometry (Tanaka, et. al., 1998) and supercritical fluid chromatography-mass spectrometry (Smith, et. al., 1982). The couplings of instrumental techniques further broadened the range of disciplines to which mass spectrometry could be applied.

Continued improvements in instrument design and performance moved mass spectrometry beyond the realm of physics into biology, chemistry, geology and materials science, as well as many other disciplines. Of particular importance were developments
taking place in ionization techniques and ion detection. Most early mass spectrometers utilized electron impact ionization (EI) to create ions. This technique limited the suite of compounds that could be analyzed by mass spectrometry. In 1984 (Fenn & Yamashita, 1984) introduction of electrospray ionization made direct transfer of ions from solution to the gas phase possible, allowing for analysis of large, non-volatile molecules such as proteins and nucleic acid polymers (Amad, et. al., 2000). Matrix assisted laser desorption ionization (MALDI) enabled the mass spectrometric analysis of large (100,000 amu) biological molecules (Karas, et. al. 1987). In this development, samples crystallized within an organic matrix were evaporated and ionized by a laser pulse. It is with MALDI-TOF instruments that peptide (Spengler, et. al., 1991) and oligonucleotide (Wang, et. al., 1997) sequencing was first accomplished.

Beyond what has been presented here is a vast array of mass spectrometric techniques and applications that make mass spectrometry one of the most versatile methods of instrumental analysis in all of science.
Chapter 3

The Role of Mass Spectrometry in Oceanography

With successive refinements, as discussed in the previous chapter, mass spectrometry became an important analytical technique in interdisciplinary realms and began to make important contributions to biological, chemical and geological oceanography (Short, et. al., 2009). Traditional oceanographic sampling techniques involve sample collection in the field, transport of samples to a land based laboratory, chemical processing and subsequent analysis. Modern instrumentation, including portable ship-based mass spectrometers now allow prompt analysis of samples at sea.

In the area of biological oceanography, mass spectrometry has been utilized for measurement of specific organic molecules in assessments of marine food web dynamics (Volkman & Tanoue, 2002), for determinations of organic matter provenance (Peters, et. al., 2005) and for assessment of past sea surface temperatures in paleoclimate reconstruction (Wakeham, 1993).

Inductively coupled plasma mass spectrometry (ICP-MS) has become an essential tool for multi-elemental analysis of trace element concentrations in seawater. Trace elements play an important role as micronutrients and toxicants for a variety of marine organisms (Morel & Price, 2003). ICP-MS is uniquely suited, as well, to provide input for models of estuarine, benthic, coastal and pelagic mass transport processes.

Of particular importance to the disciplines of geological, biological and chemical oceanography was the development of isotope ratio mass spectrometry. Harold Urey’s revolutionary work beginning in the 1930’s (Urey, 1947), along with A.O. Nier’s
development of the isotope ratio mass spectrometer in 1940 (Nier, 1940), led to the use of isotopic ratios to understand chemical pathways in the environment. Application of these techniques has enabled climatologists to construct a record of the earth’s climate.

Membrane introduction mass spectrometry (MIMS) can be used to make high frequency, real-time measurements of both dissolved gases (Hemond & Camilli, 2002) and VOC’s (Kana, et. al., 1994). Identification and quantification of dissolved gases and volatile organic compounds (VOCs) in aquatic environments provides important information about dynamic biogeochemical processes (Short, et. al, 2001). Submersible MIMS systems have been developed to enable the collection of data with high spatial and temporal resolution (Wenner, et. al., 2004). The MIMS system developed at the University of South Florida will be described in the next section of this thesis.
The University of South Florida Underwater Mass Spectrometer

The underwater MS system described here is similar in construction to the 100-amu underwater linear quadrupole system reported earlier (Short, et. al., 1999). The 200-amu instrument uses a linear quadrupole mass analyzer (Transpector CPM-200 Residual Gas Analyzer, Inficon, Inc., Syracuse, NY, USA) with a closed ion source. A new high-pressure membrane-introduction system, designed and machined at the Center for Ocean Technology, extends the depth capability of the instrument well beyond the 30-m limit imposed by the previous design (Short, et al., 2001). The high-pressure membrane-introduction probe has been pressure tested to a depth of 250 meters. A schematic of the overall underwater MS system is shown in Figure 1 and details of the high-pressure membrane probe are shown in Figure 2. Other minor differences between our current and previous designs are noted below (Short, et. al., 1999).

Figure 1. Schematic of the 200-amu linear quadrupole underwater MS system.
The underwater MS system shown in Figure 1 is modular. The main pressure vessel houses the primary vacuum system, mass analyzer, high-pressure sampling system and control electronics. A separate, smaller pressure vessel contains two diaphragm pumps. These pumps provide the backing vacuum for the turbomolecular/molecular drag pump. Table 1 summarizes the critical specifications of the system. The housing of the high pressure membrane probe (Figure 2) was machined from 3.18 cm diameter 316 stainless steel stock. Tubing (1.59 mm (OD) by 1.02 mm (ID) 316 stainless steel) was coiled around the exterior of the membrane probe housing (5 revolutions) and silver soldered in place to provide good thermal contact between coils and housing. Water flowed through this tubing and then entered the central channel of the probe housing where it flowed over

Figure 2. Schematic showing detail of the membrane housing (left) and membrane probe with the internal compression spring (right). (Graphic contributed by Richard Hildebrand of Johns Hopkins University, Applied Physics Laboratory)
the PDMS membrane. A 1-mm diameter spring (Gutekunst and Co., Metzingen, Germany) was inserted into the interior of the PDMS membrane to provide internal support at increased pressures. Two cartridge heaters (Hottwatt, Danvers, MA, USA) inserted into the back of the membrane probe housing heated the probe housing and consequently the water within the stainless steel tubing. The probe temperature was monitored via a thermocouple (Minco, Minneapolis, MN) within the probe housing. An onboard micro-controller, developed in-house, regulated power to the cartridge heaters and stabilized the probe temperature. The temperature of the sample water was adjusted to optimize analyte pervaporation relative to water vapor load across the membrane. A magnetic piston pump (Inductive Pump Corporation, Barneveld, NY, USA), constructed of stainless steel and pressure tested to 60 atm (~600 m), pulled ambient water into the sample tubing, through the membrane probe, and back to the environment. The piston pump could be adjusted to provide flow rates of 1-10 mL/min.

<table>
<thead>
<tr>
<th>Table 1. Operational specifications of the 200-amu underwater MS system.</th>
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<tbody>
<tr>
<td><strong>Type</strong></td>
</tr>
<tr>
<td><strong>Mass Range</strong></td>
</tr>
<tr>
<td><strong>Inlet System</strong></td>
</tr>
<tr>
<td><strong>Power Consumption</strong></td>
</tr>
<tr>
<td><strong>Operating Voltage</strong></td>
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<tr>
<td><strong>Deployment Time</strong></td>
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<tr>
<td><strong>Diameter</strong></td>
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<tr>
<td><strong>Length</strong></td>
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<tr>
<td><strong>Weight</strong></td>
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<tr>
<td><strong>Depth</strong></td>
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Chapter 4

In-situ Mass Spectrometer Deployments

Bayboro Harbor and Lake Maggiore

Data presented in this section were taken from two deployments of the underwater MS. In both cases, the instrument was deployed aboard a remotely guided surface vehicle GSV) (ENG Concepts, St. Petersburg, FL, USA) (Figure 3). The 200-amu instrument was first deployed in Bayboro Harbor adjacent to the USF campus in St. Petersburg, FL, USA. The second deployment was in Lake Maggiore, a 1.41 km², hypereutrophic, urban lake within the city limits of St. Petersburg, FL, USA (CHM Hill, 1991). In both deployments, the instrument was suspended beneath the vehicle at a depth of 0.30 m and water at this depth was sampled at 5 mL/min. The forward speed of the vehicle was maintained at approximately 0.5 m/s and vehicle movements were controlled through an rf link using a hand-held controller. A GPS (Trimble BD-112) mounted aboard the surface vehicle recorded the position (latitude/longitude) of the vehicle every second. A 803.11 wireless connection enabled communication between the underwater MS and a shore-side laptop computer. Vehicle location plus MS data and operating parameters were monitored in real-time on the same laptop computer. During the Bayboro Harbor deployment, MS and GPS power was provided by two 24-V DC lead-acid battery packs. Battery capacity limited the deployment to 2-3 hours. A gasoline powered 1000-Watt Honda generator secured to the surface vehicle provided power to the underwater MS and GPS during the Lake Maggiore deployment. The use of this generator, with a 2.27-liter fuel capacity, extended the deployment time to 5 hours.
During the Bayboro Harbor deployment, the surface vehicle navigated a track across the Harbor and transited 150 meters up Salt Creek, which empties into the Harbor. The underwater MS monitored a total of seven ions, as described in Table 2. Three of these ions (78, 91, 92) are diagnostic of components in gasoline and can enter the environment via fuel spills or internal combustion engine exhaust. Another three ions (47, 83, 85) are diagnostic of chlorinated compounds found in tap water, and the seventh (62) is associated with dimethyl sulfide, a compound produced by certain planktonic organisms (Andreae, et. al., 1994). Each of the seven ions was scanned for 512 milliseconds (ms), resulting in a total scan time of 3.6 seconds (s). The MS used an electron multiplier ion detector operated at 1100 volts (V) to record ion intensities. Sample transit time (the

Figure 3. ENG Concepts guided surface vehicle deployed in Lake Maggiore
elapsed time between sample acquisition and actual measurement) was 242 seconds. All
MS data were adjusted to properly correlate MS data with geographic position.

<table>
<thead>
<tr>
<th><strong>m/z</strong> Value</th>
<th><strong>Compound</strong></th>
<th><strong>Associated with</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>Chloroform</td>
<td>Tap water</td>
</tr>
<tr>
<td>47</td>
<td>Dimethyl sulfide (DMS)</td>
<td>Plankton</td>
</tr>
<tr>
<td>62</td>
<td>Dimethyl sulfide</td>
<td>Plankton</td>
</tr>
<tr>
<td>78</td>
<td>Benzene</td>
<td>Internal combustion engine exhaust</td>
</tr>
<tr>
<td>83</td>
<td>Chloroform</td>
<td>Tap water</td>
</tr>
<tr>
<td>85</td>
<td>Chloroform</td>
<td>Tap water</td>
</tr>
<tr>
<td>91</td>
<td>Toluene</td>
<td>Internal combustion engine exhaust</td>
</tr>
<tr>
<td>92</td>
<td>Toluene</td>
<td>Internal combustion engine exhaust</td>
</tr>
</tbody>
</table>

During the Lake Maggiore deployment, the underwater MS monitored ions
diagnostic of nitrogen (m/z 28, 29), oxygen (m/z 32, 34), carbon dioxide (m/z 44, 45, 46)
and argon (m/z 40) as described in Table 3. Each of these masses was scanned for 64 ms.
The time required to scan and record the 8 ions was 650 ms. The electron multiplier
detector was operated at 900 V to record ion intensities. The sample transit time for this
experiment was 270 s. The longer sample transit time for this deployment resulted from
a longer sample inlet tube. The guided surface vehicle navigated transects in a small
embayment in the southeast corner of Lake Maggiore that encompassed approximately
53,000 m². The overall track of the measurements was approximately 1.5 km. MS
observations were synchronized with GPS measurements prior to deployment. To
coordinate the two streams of data, a digital filter (PeakFit 4.0, Systat Software Inc.,
Richmond, CA, USA) was used to match the frequencies of MS and GPS observations.
The two datasets for each experiment were then combined into one array, with 242 and 270 seconds subtracted from the time stamps of the Bayboro and Lake Maggiore MS data, respectively, to account for the sample transit times mentioned earlier. The resulting spliced datasets were plotted on digital orthographic quarter quad (DOQQ) maps representing the regions of the Bayboro Harbor and Lake Maggiore deployments (Figures 4 and 5, respectively). The positional errors of the mapped chemical tracks, including all sources of error (GPS, MS-sampling offset, and map resolution) are estimated to be ± 3 m. Further reduction of this error is difficult as the two primary contributors, GPS accuracy and DOQQ resolution, are factors over which there are no experimental controls. The MS data for m/z 62, 91 and 92 from the Bayboro Harbor deployment were plotted (Figure 6) as ion intensity vs. time of day. Ion-intensity traces for m/z 91 and 92 exhibited very similar behavior. Significant increases in intensity at approximately 11:35 a.m. and 11:50 a.m. indicated enhanced toluene concentrations. The m/z 91:92 ratio is close to the value for toluene reported in the National Institute of Standards and Technology (NIST) database (NIST, 1998). The m/z 62 signal had two significant peaks, the first of which occurred at approximately 11:55 a.m. and the second, slightly smaller,
at approximately 11:58 a.m. The \textit{m/z} 62 trace cannot be attributed to a specific chemical species. The MS fingerprint of dimethyl sulfide has significant peaks at \textit{m/z} 47 and 62, with the \textit{m/z} 62:47 ratio equal to approximately one. The Bayboro Harbor data showed no increase in the \textit{m/z} 47 ion intensity in the region of the \textit{m/z} 62 ion-intensity peaks. Additional analyses are required to identify the species responsible for \textit{m/z} 62 peaks in the absence of peaks at \textit{m/z} 47. It should be noted that underwater MS, as applied here, serves as a method to screen for the presence of VOC’s. The instrumentation is not currently capable of positively identifying individual VOC species in the environment.

Lake Maggiore is hypereutrophic because of extreme nutrient loading from urban storm water run-off, and, at the time of this investigation, was scheduled for extensive dredging to remove nutrient-laden sediment. The underwater MS was deployed to acquire data relating to dissolved gas concentrations in a stressed freshwater environment. MS data for \textit{m/z} 32 (oxygen) and \textit{m/z} 44 (carbon dioxide) from the Lake Maggiore deployment are shown in Figure 7 as ion intensity vs. time of day. Ion intensities for a second isotopic form of oxygen (\textit{m/z} 34) and carbon dioxide (\textit{m/z} 45) were also recorded to verify identifications of the \textit{m/z} 32 and \textit{m/z} 44 peaks (Figure 8). Between approximately 10:15 a.m. and 11:03 a.m. the \textit{m/z} 32 and \textit{m/z} 34 signal intensities show distinct inverse relationships to those of \textit{m/z} 44 and \textit{m/z} 45. There are 13 significant minima in \textit{m/z} 32 ion intensity in this region of the data. Eight of these minima correspond to ion-intensity maxima in the \textit{m/z} 44 signal. This co-variation in the \textit{m/z} 32 and \textit{m/z} 44 signal intensities could be evidence of fine-scale spatial variations in photosynthesis and respiration by lake organisms (Jumars, 1993). In those regions of the lake where respiration dominates photosynthesis, one would expect to see a decrease in
dissolved oxygen coupled with an increase in dissolved carbon dioxide. Additional work is necessary to confirm that this co-variation in the $m/z$ 32 and $m/z$ 44 signal intensities

Figure 4. DOQQ map of Bayboro Harbor showing (a) $m/z$ 91 (toluene) signal intensity mapped over the GPS plotted track of the guided surface vehicle; (b) $m/z$ 62 (dimethyl sulfide) signal intensity mapped over the GPS plotted track of the guided surface vehicle.
Figure 5. DOQQ map of deployment area in Lake Maggiore showing (a) m/z 32 (oxygen) signal intensity mapped over the GPS plotted track of the guided surface vehicle; (b) m/z 44 (carbon dioxide) signal intensity mapped over the GPS plotted track of the guided surface vehicle.
Figure 6. Data acquired by the 200-amu underwater MS system during the Bayboro Harbor deployment. The m/z 91 and m/z 92 signals are diagnostic of toluene and m/z 62 is diagnostic of dimethyl sulfide.

is attributable to organic/inorganic transformations of particulate/dissolved carbon (organic carbon/dissolved CO₂) with attendant covariations in dissolved oxygen.

The ion intensity for argon (m/z 40) was also recorded during the Lake Maggiore deployment (Figure 8). Argon is biologically inactive and its ion intensity should remain stable during deployments in waters that are approximately isothermal. The absence of significant changes in the m/z 40 signal indicated that all MS system components were functioning normally. The underwater MS data for m/z 91 (Figure 4a) and m/z 62 (Figure 4b) were displayed on a DOQQ map of Bayboro Harbor. Mapping of the Bayboro Harbor data correlated the m/z 62 and m/z 91 time series data in Figure 6 to geographic locations within the harbor. All m/z values that were monitored by the underwater MS could be mapped as well. As discussed above, the identity of the compound responsible for the increase in m/z 62 was impossible to determine without additional analyses. Both
areas of increased m/z 91 and m/z 92 intensity (Figure 6) are likely toluene signals associated with the exhaust of boats that had traversed the path of the surface vehicle/MS.

The Lake Maggiore underwater MS data for carbon dioxide (Figure 5a) and oxygen (Figure 5b) were displayed on a DOQQ map of Lake Maggiore. The pattern of oxygen and carbon dioxide concentrations in Lake Maggiore were associated with specific locations at the time of the measurements. General conclusions about the relative significance of benthic and water column biogeochemical contributions to the observed signals require additional supporting data (e.g., chlorophyll, particulate organic carbon.

Figure 7. Data acquired by the 200-amu underwater MS system in Lake Maggiore. The m/z 32 signal is diagnostic of oxygen and m/z 44 is diagnostic of carbon dioxide.
Figure 8. Data acquired by the 200-amu underwater MS system deployed in Lake Maggiore. The signals of two isotopic forms of carbon dioxide (m/z 44 and 45), oxygen (m/z 32 and 34) and argon (m/z 40) are shown. Degradation of all signals between time 9:40 a.m. and 10:10 a.m. is caused by out-gassing associated with the MS start-up.

measurements, etc.), and additional underwater MS calibrations that allow transformation of ion intensities to in situ gas concentrations.

In situ measurements by an underwater MS can eliminate many problems inherent in traditional sampling methods and provide data with spatial and temporal resolutions that are difficult to obtain by other means. High-density data mapping can be a powerful tool in both aquatic biogeochemical process studies and studies aimed at the identification of point sources for anthropogenic chemicals. The PDMS membrane is highly permeable to
small, volatile, non-polar molecules, making it an ideal interface for the types of compounds examined in this section. Development of different types of MS-sample-introduction interfaces will be required for analysis of other types of aqueous chemical species. Future plans include the development of a solid phase micro extraction (SPME) interface for analysis of larger, somewhat more polar and less volatile molecules. This will greatly expand the types of compounds that are detectable using underwater MS. Additional work was undertaken in February 2007 to establish quantitative relationships between MS ion intensities and analyte concentrations. The results of some portions of that work will be presented later in this chapter.
Saanich Inlet

Saanich Inlet is located on the eastern shore of Vancouver Island in the Canadian province of British Columbia (Figure 9a). The inlet has a surface area of 65 km$^2$ and a maximum depth of 225 meters (Binqiu, 1989). A sill, located at a depth of 70 meters at the northern mouth of the inlet, isolates basin waters (Figure 9b) such that for about 8 months of the year the bottom waters are anoxic, contain no nitrate or nitrite, and significant concentrations of free hydrogen sulfide (H$_2$S) are present (German & Elderfield, 1989).

In April 2004 members of the USF Mass Spectrometry Group collaborated with colleagues from the University of Victoria (Victoria, British Columbia) and the Woods Hole Oceanographic Institute (Woods Hole, Massachusetts) in evaluations of in-situ instrumentation for measurement of dissolved gas concentrations, specifically methane. During the dates of April 13-16, 2004 the underwater MS system was deployed in Saanich Inlet four times. Deployments took place aboard the University of Victoria’s Marine Sciences Vessel, John Strickland. The MS system, along with a CTD probe (Applied Microsystems Ltd, Sydney, British Columbia, Canada) that provided temperature, salinity and depth measurements, was coupled to a steel cable (Figure 10) and lowered to depth using an onboard deck crane. A 220 meter tether connected the MS system to both the ship’s power and an onboard laptop computer. The tether allowed for real-time data transmission and overall system control, and delivered power to the MS system from the ship’s onboard power supply. The data presented here were collected during a deployment of the MS system to a depth of 200 meters on April 13, 2004.
Figure 9. Saanich Inlet location and bathymetry: (a) chart showing location of Saanich Inlet, Satellite and Swanson Channels, note α-β transect; (b) bathymetry of Saanich Inlet, Satellite and Swanson Channels along transect α-β.
The approximate location of the deployment, as recorded by the ship’s GPS system, was latitude: 48°37’04.7” and longitude: 123°29’18.9” (Figure 9a). The m/z values used to monitor dissolved gas species for the April 13, 2004 deployment are listed in Table 4. During this deployment the electron multiplier was set to 900 volts and the mass spectrometer dwell time for each m/z was set to 64 ms, resulting in a scan time of approximately 0.90 seconds.
Table 4. Mass-to-charge (m/z) values, diagnostic of dissolved gas species, scanned by the 200-amu mass spectrometer during the April 13, 2004 Saanich Inlet deployment.

<table>
<thead>
<tr>
<th>m/z Value</th>
<th>Detected Ions</th>
<th>Isotopic Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>C(^+)</td>
<td>(^{12}\text{C})</td>
</tr>
<tr>
<td>14</td>
<td>CH(_2)^+ , N(^+)</td>
<td>(^{12}\text{C}^2\text{H}^+\text{H}, (^{14}\text{N})</td>
</tr>
<tr>
<td>15</td>
<td>CH(_3)^+ , N(^+)</td>
<td>(^{12}\text{C}^3\text{H}^2\text{H}, (^{15}\text{N})</td>
</tr>
<tr>
<td>16</td>
<td>CH(_4)^+ , O(^+)</td>
<td>(^{12}\text{C}^4\text{H}^3\text{H}^2\text{H}, (^{16}\text{O})</td>
</tr>
<tr>
<td>28</td>
<td>N(_2)^+</td>
<td>(^{14}\text{N}^{14}\text{N})</td>
</tr>
<tr>
<td>29</td>
<td>N(_2)^+</td>
<td>(^{18}\text{N}^{15}\text{N})</td>
</tr>
<tr>
<td>32</td>
<td>O(_2)^+</td>
<td>(^{16}\text{O}^{16}\text{O})</td>
</tr>
<tr>
<td>34</td>
<td>O(_2^+), H(_2)S(^+)</td>
<td>(^{16}\text{O}^{18}\text{O}, (^{1}\text{H}^{12}\text{S})</td>
</tr>
<tr>
<td>40</td>
<td>Ar(^+)</td>
<td>(^{40}\text{Ar})</td>
</tr>
<tr>
<td>44</td>
<td>CO(_2^+)</td>
<td>(^{12}\text{C}^{16}\text{O}^{16}\text{O})</td>
</tr>
<tr>
<td>45</td>
<td>CO(_2^+)</td>
<td>(^{14}\text{C}^{16}\text{O}^{16}\text{O})</td>
</tr>
</tbody>
</table>

Figures 11 through 15 display the vertical trends associated with temperature, methane (m/z 15), carbon dioxide (m/z 44), oxygen (m/z 32) and hydrogen sulfide plus \(^{18}\text{O}^{16}\text{O}\) (m/z 34). The most abundant peak in the mass spectrum of methane occurs at m/z 16. It is not practical, however, to monitor this value for trends in methane concentration as the m/z 16 signal is overwhelmed by atomic oxygen derived from fragmentation of CO\(_2\), H\(_2\)O and O\(_2\) at the MS ion source. The next most abundant peak in the methane mass spectrum occurs at m/z 15 corresponding to the CH\(_3\) ionization fragment of methane. The absence of substantial interferences makes m/z 15 the best ion for monitoring trends in methane concentration.

The vertical temperature profile in Figure 11 shows a ~5.5\(^{\circ}\)C drop in temperature (from 13.5\(^{\circ}\)C to 8.5\(^{\circ}\)C) in the first 25 meters. From 85 meters to 125 meters the temperature increased from 8.5\(^{\circ}\) to 9.5\(^{\circ}\)C. Below 125 meters the temperature was essentially constant. In Figure 12 the m/z 15 ion intensity (diagnostic of CH\(_4\)) remains fairly constant through the first 100 meters. A sharp increase in m/z 15 intensity is seen below 100 meters as increasingly anoxic conditions stabilize reduced species such as
methane and H$_2$S. A chemocline depth at 100 meters is also seen in the ion intensity plot of carbon dioxide (Figure 13). A gradual increase in m/z 44 intensity between 70 and 100 meters gives way to a sharp increase at 100 meters. Between 100 and 125 meters the carbon dioxide plot increases more gradually and then decreases between 125 and 200 meters, possibly indicating that methanogenic bacteria are converting CO$_2$ to methane in the bottom waters and sediments of the fjord.

Figure 14 displays the ion intensity plot associated with oxygen at m/z 32. The ion intensity exhibits a steady decline with increasing depth between 25 and 100 meters, with only small changes below this depth. The ion intensity plot for H$_2$S plus $^{18}$O$^{16}$O (both m/z 34), is displayed in Figure 15. The m/z 34 trend closely tracks that of m/z 32 from the surface to a depth of 140 meters. From 140 to 200 meters the m/z 34 intensity plot steadily increases whereas the m/z 32 plot remains relatively constant. This increase in the m/z 34 ion intensity plot is attributable to the presence of H$_2$S in the deep waters of Saanich Inlet. Although the PDMS membrane of the MS system inlet is relatively impermeable to H$_2$S, in appreciable quantities, much like H$_2$O, it will migrate across the PDMS membrane and enter the mass spectrometer.

The data presented here from the April 2004 deployments of the USF MS system demonstrated MS system capabilities to provide data of unprecedented spatial and temporal density at depths up to 200 meters. The ion intensity measurements obtained during this work allowed qualitative comparison of trends in gas concentrations but not absolute concentration measurements. The next section of this thesis describes MS calibrations that relate ion intensities directly to gas concentrations.
Figure 11. Temperature profile (Deg C), from surface to 200 meters depth, during MS system deployment in Saanich Inlet on April 13, 2004.

Figure 12. Methane (m/z 15) profile, from surface to 200 meters depth, during MS system deployment in Saanich Inlet on April 13, 2004.

30
Figure 13. Carbon dioxide (m/z 44) profile, from surface to 200 meters depth, during MS system deployment in Saanich Inlet on April 13, 2004.

Figure 14. Oxygen (m/z 32) profile, from surface to 200 meters depth, during MS system deployment in Saanich Inlet on April 13, 2004.
Figure 15. Hydrogen sulfide and oxygen isotope ($m/z$ 34) profile, from surface to 200 meters depth, during MS system deployment in Saanich Inlet on April 13, 2004.
Calibration of Mass Spectrometer Data

Field deployments of the USF underwater MS system, described in previous sections of this chapter, have shown that mass spectrometers can be used in-situ to produce data that are diagnostic of biogeochemical processes. However, dissolved gas data are of limited use unless MS observations are reported directly in terms of concentrations. In order to address this problem certified gas standards were used for calibration of the UMS. Subsequently, mass spectrometer data obtained in field studies along a 2,640 meter section of the Hillsborough River were expressed in units of µmol/kg.

A portable calibration system was constructed for use with certified gas standards that were obtained from Airgas, Inc. (Radnor, PA). The composition of the calibration standards are given in Table 5. Equilibrations with certified gases, and subsequent calibrations, were conducted using two 2,000 mL volumetric flasks. Standardized dissolved gas solutions were produced in Flask One. This flask, containing approximately 1,500 mL of Hillsborough River water and a magnetic stir bar, was placed atop a waterproof magnetic stirrer. Both the flask and the magnetic stirrer were immersed in a constant temperature water bath. A thermometer immersed in the water bath was used to monitor solution temperature. The opening of the flask was covered with a rubber cap through which two lengths of 1/8” diameter stainless steel tubing and one length of 1/16” stainless steel tubing were inserted. One of the 1/8” diameter tubes terminated just above the bottom of the flask and was fitted with a cylindrical stone gas bubbler to dispense bubbles of certified gas standards within the flask. The second 1/8” stainless steel tube was approximately 7 cm in length and served as a pressure relief to
prevent super-saturation of the standard solution. The 1/16” diameter tubing was connected to a two-way sampling valve which was connected to the MS system sample inlet. The second flask (Flask 2) contained approximately 1,500 mL of Hillsborough River water that was open to the atmosphere. One end of a 50 cm length of 1/16” diameter stainless steel tubing was inserted into the water in the flask, the other end was fitted to the same two-way sampling valve to which the first flask was connected. This configuration made it possible to instantaneously switch from one solution to the other while the mass spectrometer was actively scanning.

The mass spectrometer was calibrated one day prior to the deployment on the Hillsborough River. A solution of standardized dissolved gases was produced for each of the three certified gas standards. The first solution was produced from Tank 3, the second solution from Tank 1 and the final solution from Tank 2. At the beginning of the

<table>
<thead>
<tr>
<th>Tank #</th>
<th>Gas</th>
<th>Gas Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Argon (Ar)</td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>Carbon dioxide (CO₂)</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>Methane (CH₄)</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>Nitrogen (N₂)</td>
<td>74.96</td>
</tr>
<tr>
<td></td>
<td>Oxygen (O₂)</td>
<td>14.96</td>
</tr>
<tr>
<td>2</td>
<td>Argon (Ar)</td>
<td>5.07</td>
</tr>
<tr>
<td></td>
<td>Carbon dioxide (CO₂)</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>Methane (CH₄)</td>
<td>3.01</td>
</tr>
<tr>
<td></td>
<td>Nitrogen (N₂)</td>
<td>85.34</td>
</tr>
<tr>
<td></td>
<td>Oxygen (O₂)</td>
<td>5.95</td>
</tr>
<tr>
<td>3</td>
<td>Argon (Ar)</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>Carbon dioxide (CO₂)</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Methane (CH₄)</td>
<td>4.98</td>
</tr>
<tr>
<td></td>
<td>Nitrogen (N₂)</td>
<td>92.20</td>
</tr>
<tr>
<td></td>
<td>Oxygen (O₂)</td>
<td>2.00</td>
</tr>
</tbody>
</table>
calibration run, water from Flask 2 was pumped through the mass spectrometer sampling system while gas from Tank 3 was bubbled into Flask 1. The solution in Flask 1 was allowed to equilibrate for 30 minutes at which point the flow of gas into the flask was stopped. Immediately after the gas was turned off the two-way sampling valve was switched so that the equilibrated dissolved gas standard in Flask 1 was pumped through the mass spectrometer sampling system. Each standard solution was sampled until the mass spectrometer signal stabilized and remained stable for at least 10 minutes. This process was repeated for the other two dissolved gas standards. Figures 16-20 plot mass spectrometer ion intensity vs. scan number for all 5 gases during the three calibration runs.

The ion intensity values in Figures 16-20, span several hundred scans at each gas concentration. Five ion intensity values were used from each ‘plateau’ to produce a single ion intensity value associated with a specific gas concentration. The five values were chosen near the end of the equilibration run to ensure that the solution had reached equilibrium. For example: In Figure 16 intensity values for the plateau observed between scans 2449 and 2976 resulted from a solution equilibrated with a certified gas standard that was 74.96% nitrogen. Of the 527 ion intensity data points in this range, the five values between scans 2906 and 2911 were used to produce an average intensity value of $3.56(10)^{-8}$ amps. Ion intensity values for all remaining gases were related to gas concentrations in the same manner for each of the five gases being measured.
Figure 16. Mass spectrometer calibration plot for diatomic nitrogen (N$_2$) showing the ion intensity associated with three concentrations of nitrogen gas in Hillsborough River water. (Reported water temperatures are the temperatures at which each solution was equilibrated; atmospheric pressure assumed to be 101.325 kPa)

N$_2$ Calibration for the Hillsborough River (m/z 28)

Scan #

Intensity (Amps)

<table>
<thead>
<tr>
<th>Scan #</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>5.00E-09</td>
<td>5.00E-09</td>
</tr>
<tr>
<td>1.00E-08</td>
<td>1.00E-08</td>
</tr>
<tr>
<td>1.50E-08</td>
<td>1.50E-08</td>
</tr>
<tr>
<td>2.00E-08</td>
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<td>4.00E-08</td>
</tr>
<tr>
<td>4.50E-08</td>
<td>4.50E-08</td>
</tr>
</tbody>
</table>

92.2000% N$_2$
Water Temp: 74.96°C

74.96% N$_2$
Water Temp: 85.345°C

85.345% N$_2$
Water Temp: 24.5°C

2.000% O$_2$
Water Temp: 24.8°C

14.96% O$_2$
Water Temp: 24.5°C

5.949% O$_2$
Water Temp: 24.5°C

Figure 17. Mass spectrometer calibration plot for diatomic oxygen (O$_2$) showing the ion intensity associated with three concentrations of nitrogen gas in Hillsborough River water. (Reported water temperatures are the temperatures at which each solution was equilibrated; atmospheric pressure assumed to be 101.325 kPa)

Scan #

Intensity (Amps)

<table>
<thead>
<tr>
<th>Scan #</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>5.00E-09</td>
<td>5.00E-09</td>
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<tr>
<td>1.00E-08</td>
<td>1.00E-08</td>
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<td>3.50E-08</td>
<td>3.50E-08</td>
</tr>
<tr>
<td>4.00E-08</td>
<td>4.00E-08</td>
</tr>
<tr>
<td>4.50E-08</td>
<td>4.50E-08</td>
</tr>
</tbody>
</table>

2.000% O$_2$
Water Temp: 24.8°C

14.96% O$_2$
Water Temp: 24.5°C

5.949% O$_2$
Water Temp: 24.5°C
Figure 18. Mass spectrometer calibration plot for methane (CH$_4$) showing the ion intensity associated with three concentrations of methane gas in Hillsborough River water. (Reported water temperatures are the temperatures at which each solution was equilibrated; atmospheric pressure assumed to be 101.325 kPa).

Figure 19. Mass spectrometer calibration plot for methane (CO$_2$) showing the ion intensity associated with three concentrations of methane gas in Hillsborough River water. (Reported water temperatures are the temperatures at which each solution was equilibrated; atmospheric pressure assumed to be 101.325 kPa)
Figure 20. Mass spectrometer calibration plot for argon (Ar) showing the ion intensity associated with three concentrations of methane gas in Hillsborough River water. 
(Reported water temperatures are the temperatures at which each solution was equilibrated; atmospheric pressure assumed to be 101.325 kPa)

Next, equations fitted to the solubility data from several sources (Garcia & Gordon, 1992, Hamme, 2004, Weiss, 1974, Wiesenburg & Guinasso, 1979) were used to calculate the Bunsen solubility coefficient for each gas at its respective equilibration temperature (for the purpose of these calculations salinity was assumed to be zero and pressure was assumed to be 101.325 kPa). Dissolved gas concentrations could then be calculated with the Bunsen coefficients by using Henry’s law:

\[ C_i = s_ip_i \]  

(1)

Where \( s_i \) is the Bunsen solubility coefficient, \( p_i \) is the partial pressure of the gas being measured and \( C_i \) is the dissolved gas concentration in µmol/kg. This was done for each
of the gases in the three certified gas standards. In this way dissolved gas concentrations, in units of µmoles/kilogram, were correlated to mass spectrometer ion intensity values. These data were then plotted (Figure 23) to produce 3-point calibration curves for each of the five gases to be measured during the Hillsborough River deployment. These calibration curves were then used to convert the mass spectrometer ion intensity data, collected during the deployment, to dissolved gas concentrations.

Interferences arising from molecular fragmentation occurring in the mass spectrometer ion source results in three of the calibration plots in Figure 23 (oxygen at $m/z$ 32 and 34 and nitrogen at $m/z$ 28) having a positive y-axis intercept. During electron impact ionization a percentage of H$_2$O and CO$_2$ molecules entering the ion source through the membrane inlet are fragmented. Two ions formed in this process, O$_2^+$ and CO$^+$, add to the ion intensity signal measured for $m/z$ 32, 34 and $m/z$ 28 respectively. This increase in the ion intensity signal for all oxygen and nitrogen calibration standards resulted in a positive offset of the calibration curve. It was assumed that the rate of fragmentation and subsequent increase in the m/z 28, 32 and 34 signals remained constant and was not accounted for in the final calibration.
Figure 21. Calibration plots correlating mass spectrometer ion intensity data with dissolved gas concentrations. A calibration curve for oxygen, at $m/z$ 34, is included in this figure to verify the oxygen plot at $m/z$ 32.
Hillsborough River Deployment

The Hillsborough River, flowing 54 miles from its source in the Green Swamp to Hillsborough Bay, is an important recreational and drinking water resource (Pillsbury, 2004). The lower 12 miles of the river passes through a heavily urbanized and industrialized area including the City of Tampa (Figure 22). This portion of the river is also subject to restricted flow due to construction of a dam that created the 6.1 billion liter Hillsborough Reservoir. Additionally, the lower Hillsborough is impacted by a high volume of groundwater flow in the form of freshwater springs and seeps.

The MS system was deployed on the lower Hillsborough River aboard a guided surface vehicle (see Bayboro Harbor and Lake Maggiore section of this chapter for the GSV description) in February of 2007. The GSV navigated a 2,640 meter stretch of the river (Figure 22) while the MS system sampled the surface water of the river and collected mass spectrometer data for the dissolved gases listed in Table 5. The GSV was also outfitted with a GPS, a conductivity, temperature and depth (CTD) probe and a dissolved oxygen (DO) probe. The deployment produced four data sets (gas concentrations, temperature, DO, latitude and longitude) that were subsequently combined, by use of a Matlab® script, to produce geo-referenced maps of the dissolved gas concentrations along the GSV track. Intermittent loss of GPS signal during the deployment resulted in gaps in the concentration maps shown in Figures 23-25. The mass spectrometer sampled continuously during the deployment, at a rate of 0.7 seconds/sample, resulting in the collection of mass spectrometer data over the entire 2,640 meter section of the river.
Dissolved oxygen (DO) concentrations are reported in Figure 23. A steady increase in DO concentration was observed over the first half of the deployment track. A sharper increase in DO concentration occurred in the vicinity of the U.S. 275 overpass and remained elevated in the area of the river adjacent to an active spring vent located on the property of Sulfur Springs. Elevated DO concentrations in this portion of the river were not anticipated as spring water, typically, has low DO concentrations. A large aeration basin on the Sulfur Springs site (Figure 23, Inset), used to increase spring water DO
concentrations before it enters the Hillsborough River, was the source of the elevated DO concentrations. Just east of the Sulfur Springs influence the DO signal begins to decrease until the last ~300 meters of the track where the DO signal begins a stepwise increase.
Comparison of this portion of the DO data with the corresponding portion of CO₂ data (Figure 26) shows that the two signals co-vary over this section of the river. As with the Lake Maggiore data, this O₂-CO₂ signal covariation is indicative of biochemical transformations associated with photosynthesis/respiration.

Figure 24. Dissolved carbon dioxide concentrations in a section of the lower Hillsborough River as recorded by the MS system during a 2,640 meter transect in February 2007.
Dissolved carbon dioxide concentrations (Figure 24) remained relatively constant over the first ~1,760 meters of the track. East of Sulfur Springs the CO₂ signal begins to increase until the section of the river where the O₂-CO₂ signals were observed to co-vary. The United States Geological Survey conducted an investigation of groundwater inputs to the lower Hillsborough by measuring radon (Rn) concentrations\(^{(59)}\), a natural groundwater tracer. The investigation showed steadily increasing Rn concentrations, indicative of increased groundwater input, along the section of the river where elevated CO₂ concentrations were observed. Groundwater can be supersaturated relative to CO₂ and often leads to supersaturation of CO₂ in streams and rivers (Jones & Mulholland, 1998). It is possible that increased groundwater flow could be contributing to elevated CO₂ concentrations in certain sections of the river.

Dissolved methane concentrations (Figure 25) remained relatively constant over the first ~1,200 meters of the track. In the area of Sulfur Springs, the CH₄ concentration fluctuates briefly before beginning a steady increase over the final 1,000 meters of the track. Increasing methane concentrations along this section of the river could be attributable to methanogenic bacteria in the river’s organic sediments as well as increased groundwater inputs.

In order to validate MS system performance during this deployment mass spectrometer DO data were compared to the YSI DO sensor data. The data plotted in Figure 26 show excellent agreement but the mass spectrometer DO concentrations were consistently lower than those recorded by the YSI DO sensor.

The discrepancy in the two data sets was attributed to fine-scale changes (alteration of membrane geometry, change in sample flow rate, change in sample temperature, etc
Figure 25. Dissolved methane concentrations in a section of the lower Hillsborough River as recorded by the MSS system during a 2,640 meter transect in February 2007. in the MS system that could have affected mass spectrometer analyte measurements.
In order to compensate for these effects an argon correction factor was derived.

\[
\left( \frac{[\text{Ar}]_{s,c}}{[\text{Ar}]_m} \right) [O_2]_m = [O_2]_{\text{corr}} \quad (2)
\]

Where \([\text{Ar}]_{s,c}\) is the calculated argon saturation concentration along the deployment track, \([\text{Ar}]_m\) is the argon concentration measured by the mass spectrometer, \([O_2]_m\) is the oxygen concentration measured by the mass spectrometer and \([O_2]_{\text{corr}}\) is the corrected oxygen concentration. A Matlab® script was written for calculation of the argon corrected oxygen data. Mass spectrometer argon corrected oxygen data plotted against the YSI DO sensor oxygen data were in excellent agreement. All data plotted in Figures 23, 24 and 25 were argon corrected in this way.

Figure 26. Oxygen data as recorded by the MS system and the YSI DO sensor during the Hillsborough River deployment of February 2007. The green trace represents mass spectrometer data that have been argon corrected.
Conclusions

The work presented in this thesis provides evidence that a mass spectrometer can be deployed in aquatic environments and collect unique and meaningful data. Much work remains to be done to realize the full potential of this new technology. Improvement in the accuracy and precision of in-situ mass spectrometer data is crucial if the instrument is to provide data that can be employed in interpreting the fine-scale, biogeochemically important fluctuations in the dissolved gas concentrations of natural systems.

Measurement of dissolved gases has long been an integral part of understanding the biogeochemical cycling of marine and freshwater systems. These measurements are of immense importance in today’s global environment as scientist’s attempt to understand the impact of anthropogenic inputs of greenhouse gases to the earth’s atmosphere and the ocean’s role in that process. Traditional methods for the collection of dissolved gas samples are labor and time intensive as well as being prone to sample loss. Typically, single grab samples are collected and analyzed leading to poor spatial and temporal data densities, leaving conditions in most of the water column, which is not sampled, to be interpolated.

The USF UMS system, utilizing a membrane inlet, is well suited to address many of the shortcomings of traditional dissolved gas sampling methods. Continuous sampling, with high through-put of sample, and rapid scan rates provide real-time, temporally dense data sets. Deployment of the USF UMS system on a variety of platforms, such as a GSV and ship’s crane, has resulted in the collection of dissolved gas data over large areas and at great depths. The UMS system has the unique capability of simultaneously monitoring
multiple analytes, eliminating the need to deploy several analyte specific instruments.

The power of this method was evident in the measuring of covarying oxygen and carbon dioxide signals, diagnostic of biochemical processes, in both Lake Maggiore and the Hillsborough River, with concomitant collection of GPS data. These data were then plotted, with high precision, on georeferenced maps providing the exact geographic location where the biochemical processes occurred. Absent either the oxygen or carbon dioxide signal the significance of these data might not have been recognized.

It is anticipated that UMS systems will become an integral component of ocean observing networks. Network infrastructure, in most cases, will provide power and data transmission such that UMS will collect data over extended periods of time. UMS, outfitted with membrane inlets, have been deployed to depth at MC118, located in the Gulf of Mexico, at depths of ~900 meters, off the coast of Mississippi, to detect methane seeps associated with methane hydrates. Advances in micro-fabrication techniques have led to the miniaturization of mass spectrometer sensors, which require less power. Manufacture of smaller vacuum components (diaphragm backing pumps, turbo/molecular pumps) will further reduce the footprint and power requirements of entire mass spectrometer systems. This miniaturization of mass spectrometer systems makes possible the manufacture of other mass spectrometer geometries that can be packaged as in-situ instruments. Efforts are underway at the University of South Florida to develop an in-situ magnetic sector mass spectrometer with a Mattauch-Herzog geometry that will have the capability of measuring carbon, nitrogen and oxygen isotopes in aquatic environments.
On-site, real-time analysis of large organic molecules by in-situ MALDI-TOF mass spectrometers could lead to better understanding of the biochemistry of coastal and estuarine waters. Similarly, in-situ ICP-MS could provide further insight into the cycling and complexation of trace metals in aquatic environments. In-situ hyphenated methods such as GC-MS and HPLC-MS also hold great potential to produce data that will further our understanding of aquatic environments. In time, in-situ mass spectrometry will be as robust and versatile an analytical method as its lab-borne predecessor.
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