

Phase One Construction of an In-Situ Mass Spectrometer

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LONG-TERM GOALS

Long term goals for this project include deployment of mass spectrometers on network class autonomous underwater vehicles (AUVs) for *in-situ* detection, plus quantification and mapping of both volatile and non-volatile species in the water column. Ultimately we envision adaptation of our instruments as self-directed, true panoramic chemical sensors capable of, e.g., tracing dispersion of chemicals from point sources and investigating the evolution of reactive chemical species.

OBJECTIVES

The objective for this phase-one effort was to demonstrate, in the laboratory, the feasibility of using mass spectrometry as an underwater chemical sensor on an AUV. This effort was to include: a demonstration of the viability of mass spectrometry to detect compounds/elements of interest at concentrations found in the marine environment; construction of an interface for transporting analytes from solution phase to the vacuum of the mass spectrometer; evaluation of packaging requirements for deploying a mass spectrometer as an AUV payload; and development of a scheme for maintaining vacuum inside the mass spectrometer while underwater.

APPROACH

Our ultimate analytical protocol of choice involves atmospheric pressure ionization, referred to as electrospray ionization (ESI), followed by mass spectrometry and tandem mass spectrometry (MS/MS) using a quadrupole ion trap mass spectrometer. Sample pretreatment and analyte separation using microfluidic devices will be performed prior to electrospray ionization when necessary. This system would allow us to detect and identify non-volatile compounds at trace levels with a very high degree of certainty in complicated marine environments. As an intermediate step towards this goal, we are also evaluating and using simpler sampling methods (such as membrane introduction of volatile organic species) and simpler forms of mass spectrometry such as linear quadrupole mass filtration and time-of-flight mass spectrometry (neither of which has the capability to perform MS/MS). Our approach includes miniaturization of components, wherever possible, by incorporation of micro-systems technology (MST) and use of micro-electromechanical systems (MEMS).

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WORK COMPLETED

Quadrupole Ion Trap Mass Spectrometer

After evaluation of commercially available ion trap mass spectrometers, a Varian Saturn 2000 ion trap mass spectrometer was purchased. The Saturn 2000 was selected for three reasons: its physical size and configuration are most compatible with future repackaging within an AUV; it provides the capability to perform both electron impact ionization and chemical ionization inside the ion trap; and its advanced design, allowing tandem mass spectrometry (MS/MS) and selected ion storage (SIS), provides more flexibility than other systems. The Saturn 2000 mass spectrometer circuitry has been investigated to determine which control signals and features can be incorporated in alternative sample introduction techniques, such as ESI.

The footprint of the Saturn 2000 ion trap mass spectrometer is relatively small; however, the instrument is not immediately compatible with packaging in an AUV pressure vessel. The three largest components of the system are: the bench-top computer required for data acquisition and control; the oil-based mechanical vacuum pump that serves as an intermediate stage between the high-vacuum turbomolecular pump and atmosphere; and the main power board for the mass spectrometer. To approach AUV compatibility we have purchased the appropriate IEEE 488 interface in a PCMCIA format to allow instrument control from a notebook PC and transition to an embedded PC. We have replaced the standard turbomolecular pump with a two-stage turbo/molecular drag pump, providing a better compression ratio and allowing use of a much smaller dry diaphragm pump as the second stage. We are also replacing the large power distribution board with a much smaller board compatible with AUV battery power. Preliminary drawings for Saturn 2000 repackaging for AUV deployment are shown in figure 1.

Membrane Introduction Source

Although the Phase I proposal emphasized trace metal detection using ESI, we also alluded to the importance of organic vapor and dissolved gas detection as a future direction. For a number of reasons we have accelerated our efforts in this area. A selective method (membrane introduction) for transporting many of these compounds from solution to the gas phase exists, and presents little additional gas load on the mass spectrometer vacuum system compared with ESI. Subsequent to membrane introduction, volatile species can be readily ionized using electron impact or chemical ionization. We have chosen to explore membrane introduction mass spectrometry (MIMS) in parallel with the ESI development, because it gives us access to a wider variety of chemical substances and it represents the simplest means of sampling the water column with an *in-situ* mass spectrometer as a *first* deployable system.

A semipermeable (polydimethylsiloxane or PDMS) membrane within the introduction probe is in the form of a small (~1 mm diameter) capillary approximately 1 cm long. A quantitative flow injection system is attached to the probe in such a way that precise volumes of water samples can be directed through the PDMS capillary. MIMS has been demonstrated to have parts-per-trillion detection limits for many compounds, and in some cases parts-per-quadrillion. We have evaluated our system for a standard suite of volatile organic compounds (VOCs) of concern to the Environmental Protection Agency (EPA). We are currently able to detect approximately 500 pg of benzene in deionized water with this setup, and have demonstrated a 100 ppt detection limit for toluene. We have also

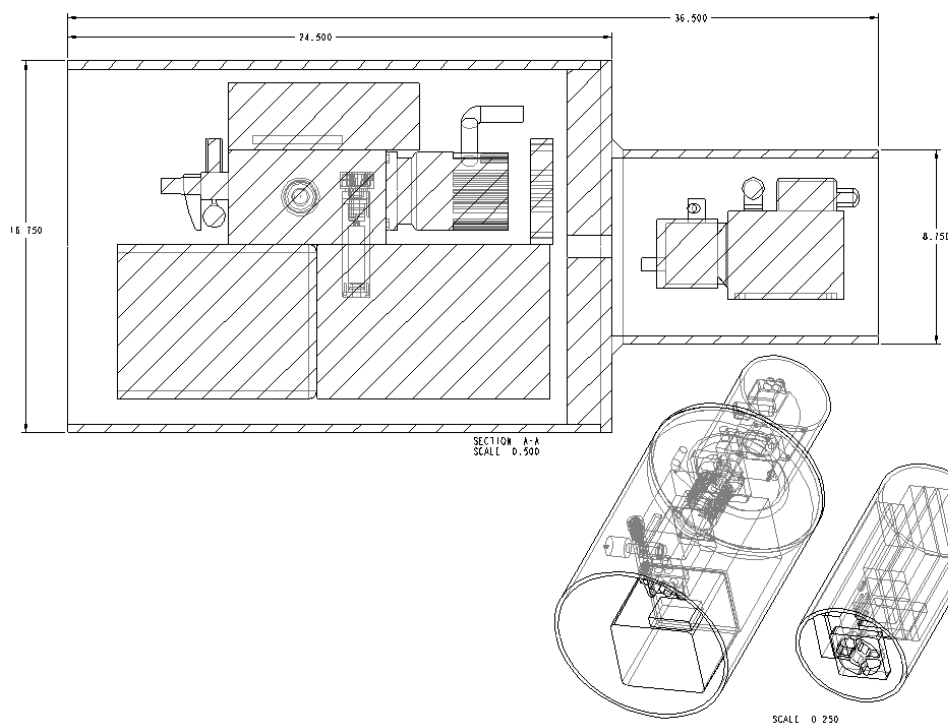


Figure 1. Ion trap configuration for AUV deployment.

investigated use of MIMS for detection of other compounds of marine interest. Our results for dimethyl sulfide (DMS) are described below in the results section.

Electrospray Ionization (ESI)

Development of an electrospray ion source has progressed on two fronts: applications methodology; and interface design for the Saturn 2000 ion trap mass spectrometer. Applications development was facilitated using a much larger console-type ion trap mass spectrometer (Chemistry Dept., USF) with an ESI source (Bruker). The work demonstrated 10 pg detection of various polyphenols extracted from natural products. The corrosive nature of seawater on ESI sources and the quenching effect of salts on electrospray have necessitated evaluation of electrospray needle compositions and sample pretreatment strategies prior to introducing such samples into an MS. From these studies we have decided to test an immersion electrode in a fused silica capillary, and are evaluating three sample prep strategies: (1) solid phase extraction; (2) microdialysis; and (3) microfluidic extraction. We have also demonstrated the ability to electrospray liquids from high pressure (500 - 1500 psi), as will be necessary in an AUV environment.

Vacuum system

Initial tests with exhaust from vacuum pumps have demonstrated that, once an appropriate vacuum is achieved in the ion trap vacuum housing, the throughput of the pumping system is quite low. In fact, our tests indicate that simply directing the exhaust of the second stage diaphragm pump into a closed vessel at atmospheric pressure will allow AUV operations for approximately two to four (2-4) hours. As an alternative, we have also demonstrated that an inline reciprocating piston pump (from Pumpworks, Inc.) can maintain low vacuum ($\sim 1/3$ atmospheric pressure) at an inlet port while

exhausting against 150 psi water pressure at the outlet. These tests indicate that even long-term *in-situ* vacuum maintenance is feasible.

Microfluidics

Fabrication efforts for microfluidic pre-separation and preparation devices have resulted in two designs for initial evaluation of microfluidic control and capillary electrophoresis (CE). Mask configurations for the microchannels were designed in-house and sent to Adtek, Inc. for fabrication. Masks were then sent to the USF Electrical Engineering department for photolithography and etching of the microfluidic devices. Scanning electron microscopy (SEM) confirmed channel widths on the order of 100 μm and depths around 10 μm . A subsequent batch of chips have bonded cover slips, thereby forming closed-channel networks. Microfluidic manipulation testing will be performed over the final months of the Phase I proposal period.

Alternative Mass Spectrometers

Although the ion trap mass spectrometer is admittedly the most powerful mass spectrometer for its size, the complexity of the software, firmware and associated electronics necessitates an incremental design and test strategy towards AUV deployment. As an intermediate step, we are investigating use of alternative deployable MS sensors. Candidates include the quadrupole mass filter (QMF) and the time-of-flight (TOF) mass spectrometer. The limitation of both of these types of instruments is that they are not able to perform tandem mass spectrometry, a highly desirable feature for *in-situ* analyses. The simplicity of the software and electronics for QMF and TOF instruments makes them especially valuable for initial AUV deployment.

Using the membrane introduction system with a small (40 cm flight tube) commercially available TOF mass spectrometer we were able to detect <10 ppb of benzene. We believe that by use of a faster data acquisition system, we can extend our detection limits to a level competitive with the Saturn 2000 ion trap system (< 1 ppb). We are in the process of purchasing a TOF system for further development.

We have also integrated the membrane introduction technique with a miniature linear quadrupole array (Ferran Scientific). The complete system, including vacuum pumps, uses only 24 VDC power and is small enough to easily fit in a pressure vessel compatible with a 1 m long AUV. We have demonstrated a detection limit for dimethyl sulfide of < 1ppm at this time. We are presently exploring insertion of a high gain detector to lower the detection limits of the system.

RESULTS

We have been able to detect and quantify dimethyl sulfide (DMS) at natural concentrations (< 1 ppb) found in the Gulf of Mexico off the coast of Florida. DMS is an important compound in the global sulfur cycle and is an ideal candidate for *in-situ* detection using membrane introduction mass spectrometry. Figure 2 shows the intensity of DMS ion signals (m/z 62) for seven sequential flow injections. The first five peaks are from five different seawater samples taken in the Gulf of Mexico, and the last two are 1 ppb and 0.5 ppb DMS in seawater, respectively.

Dimethyl Sulfide detected by Membrane Introduction Mass Spectrometry

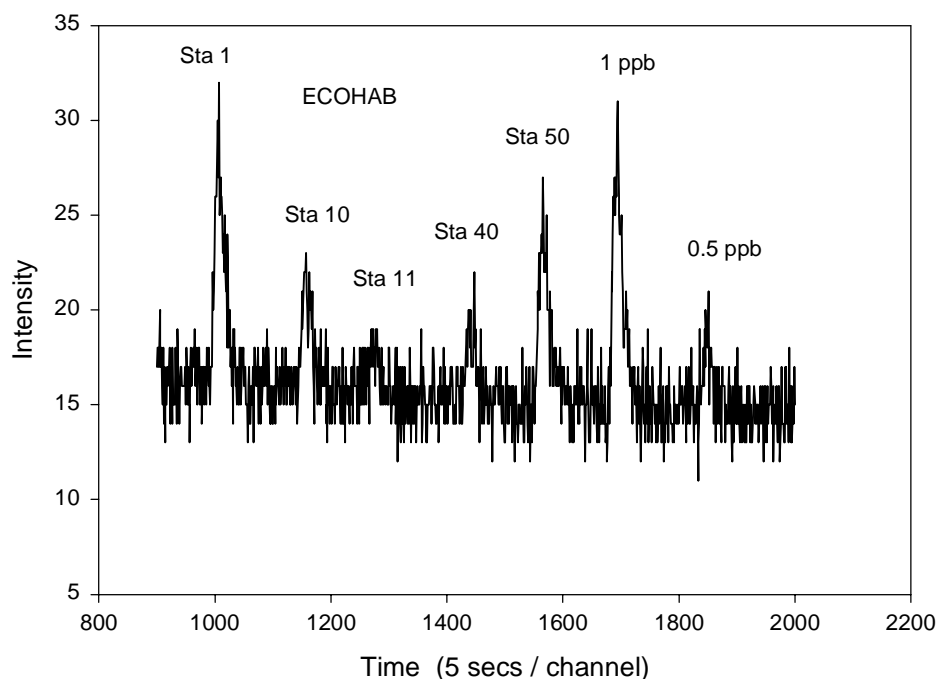


Figure 2. Flow injection MIMS analysis of DMS in seawater.

IMPACT/IMPLICATIONS

We believe the *in-situ* mass spectrometer has the potential to be the most powerful deployable sensor in the marine environment. Due to the versatility of mass spectrometry and MS/MS for detection and quantification of most elements in the periodic table, as well as a wide variety of volatile and nonvolatile compounds, the MS sensor should have extremely broad application in the environmental, chemical, biological and marine sciences.

TRANSITIONS

Our work on *in-situ* MS sensor design and construction is apparently unique. Upon completion of this work we expect that this technology will be much sought-after for both scientific and industrial applications.

RELATED PROJECTS

A recently funded (ONR) project entitled “Application Specific Chemical Information Microprocessor” is an extension of the microfluidic work performed in this project.