

Phase Two 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, 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 objectives for this phase-two effort were several-fold. The primary goal was to deploy a small membrane-introduction mass spectrometer (MS) on the Ocean Explorer (OEX) AUV for (underwater) *in-situ* detection of volatile organic compounds and dissolved gases. For initial deployment we were to evaluate and choose between either a time-of-flight (TOF) or linear quadrupole mass spectrometer--we had determined that reconfiguration of the more analytically powerful ion trap mass spectrometer was a formidable task best tackled during phase three of this project. In parallel with this effort we also planned to modify the membrane-introduction ion trap mass spectrometer for shipboard operations on a research vessel in order to provide the capability for *real-time* detection and quantification of compounds such as dimethylsulfide. These operations were deemed important as intermediate steps prior to AUV deployment of the ion trap MS. Continuing development of methods and apparatus for analytical access to non-volatile species (i.e., electrospray ion-introduction) is also an important aspect of this work.

APPROACH

Our approach to underwater mass spectrometry development has been modular and stepwise, initially involving simpler designs, while simultaneously testing other subsystems for more ambitious configurations. Our ultimate configuration 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

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analyte separation using microfluidic devices will be performed prior to electrospray ionization when necessary. This system would allow detection and identification of 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 relatively simple sampling methods (such as membrane introduction of volatile organic species) and simpler forms of mass spectrometry, such as small linear quadrupole mass filtration and time-of-flight mass spectrometry (neither of which has the capability to easily 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).

WORK COMPLETED

AUV deployment of a mass spectrometer

Evaluation of both a quadrupole mass filter and a time-of-flight mass spectrometer for suitability as a first deployable MS sensor led to the conclusion that a quadrupole mass filter was the logical choice. The quadrupole MS is smaller in size, has lower power requirements and readily available commercial software that is directly compatible with membrane introduction mass spectrometry (MIMS) analysis. The time-of-flight MS has features desirable for future analyses, but is not as readily packaged as an underwater MS.

Following tests of a demonstration model, we chose the Transpector quadrupole mass filter of Leybold Inficon as the central component of our first underwater MS system. We had also tested a very compact gas analysis quadrupole-array made by Ferran Scientific; this analyzer does not use an electron multiplier detector and consequently has detection limits approximately three orders of magnitude higher than the Transpector. We have performed ion optical modeling to assist Ferran Scientific in adding an electron multiplier detector to their system. We plan to incorporate their Micropole quadrupole array into an AUV MS system in the future once they have comparable detection limits to the Transpector.

When coupled with a membrane introduction probe, the Transpector mass analyzer has low (approximately 1 ppb) detection limits for many VOCs which are of major concern to regulatory agencies such as the EPA. The quadrupole mass filter provides full mass scans for the entire 1-100 amu range, or can monitor selected masses as a function of time. The latter mode provides higher signal-to-noise capability for those selected masses and will be typically used for membrane introduction analyses.

One of the foremost challenges to the development of underwater *in-situ* mass spectral analysis centers on the fact that mass spectrometry is performed in vacuum, typically 10^{-5} Torr or less. Vacuum maintenance inside a mass spectrometer requires continuous pumping due to gas loads from sample introduction and outgassing from the walls of the vacuum housing. Most vacuum pumps ultimately compress the pumped gases and exhaust to the atmosphere, a mode of operation that becomes problematic underwater, particularly at extreme depths.

We have tested a viable vacuum system (with 24 VDC power requirements) for underwater operation over periods up to at least 8 hours. High vacuum (10^{-5} Torr or better) in the mass spectrometer housing is provided by a Varian V70LP Turbo/molecular drag pump backed by two KNF Neuberger, Inc. dry diaphragm pumps in series. Our underwater vacuum pumping scheme involves housing the diaphragm backing pumps inside a separate pressure vessel and venting the exhaust directly into a closed pressure

vessel. Gas throughput calculations indicate that continuous pumping of a previously evacuated system into a receiving vessel that starts at atmospheric pressure will increase the pressure of the receiving vessel by only a few percent in an 8-hour period. This period can be extended by pre-evacuation of the receiving vessel to around 100 Torr, which we have demonstrated experimentally.

A more serious problem with operation of the vacuum pumps in a closed pressure vessel is overheating. Our first tests operating the diaphragm pump system inside a sealed pressure vessel indicated that some components of the pumps reached temperatures in excess of 75° C, and that some deterioration of the diaphragm material occurs. To solve the overheating problem, we have added thick aluminum heat-sink plates to the endcap on which the diaphragm pumps are mounted. After this modification, the maximum temperature of all components was less than 45° C, and was closer to 40° C when the pressure vessel was submerged in water. This vacuum system should be fully capable of providing vacuum for the mass spectrometer during AUV deployments, which typically are limited to 4 hours or less. For long-term deployments, such as moored systems, the backing pump pressure vessel will need to be periodically evacuated underwater. We have already tested pumps that would allow decompression of the pressure vessel underwater at depths of 100 meters (i.e., pressures up to 150 psi).

Our design separates and packages components in three different pressure vessels. This modular approach allows components of *in-situ* mass spectrometers to be configured flexibly. For example, the flow injection system can be adapted to any MS, and the diaphragm roughing pump housing will not require any changes when connected to other MS vacuum systems. Each of the pressure vessels has a maximum diameter of 0.19 m in order to be readily compatible with physical constraints of smaller AUV platforms. The pressure vessels have been designed and fabrication is nearly complete. We are on schedule for system AUV deployments before the end of 1999.

Ion trap mass spectrometer

Due to a high sensitivity and a capability to perform multiple stages of mass spectrometry, we are pursuing deployment of the ion trap MS as an AUV sensor. The major component of the Varian Saturn 2000 ion trap MS that is not currently compatible with the OEX AUV is the large power distribution board. We have contracted a local company to redesign and manufacture a replacement set of smaller boards that will allow the ion trap MS to be powered from a DC source, such as the batteries on an AUV. Delivery of the new boards is expected in late 1999.

We are using the ion trap MIMS system to develop general analytical methods and also to identify compounds, other than those strictly of concern to regulatory agencies. In particular, we have analyzed seawater samples from the Gulf of Mexico that show clear temporal and spatial variations in dimethylsulfide (DMS) concentrations at the sub-ppb level. DMS is a product of blue-green algae and is an important component of the global sulfur cycle.

In order to study the variation of DMS concentration in more detail, and to demonstrate the rapid screening capability of the ion trap MIMS system, we have participated on several ECOHAB cruises in the Gulf of Mexico on the R/V Suncoaster. The Saturn 2000 ion trap MIMS setup has been mounted on a transportable platform, and the desktop control/data acquisition computer has been replaced with a laptop/docking station computer system to facilitate shipboard operations. Our analyses involve water sample collection for later analysis as well as real-time shipboard measurements.

Electrospray ionization

Membrane introduction interfaces only allow volatile compounds and dissolved gases to enter the vacuum system of the mass spectrometer. We are also developing interfaces that will allow analysis of non-volatile species. Electrospray ionization (ESI) has been targeted as the most promising method of transporting non-volatile molecules from the solution phase into the vacuum of the mass spectrometer. We are continuing our adaptation of ESI for analysis of seawater. The highly saline nature of seawater complicates the ESI process, making in-line salt removal, or extraction of analytes from seawater a necessary component of the ESI system. Using solid phase extraction (SPE) columns, we have demonstrated the feasibility of extracting analytes from seawater samples and enriching these analytes in solvents compatible with ESI.

RESULTS

Our measurements of DMS concentrations in the Gulf of Mexico have shown distinct differences in shipboard measurements and measurements of refrigerated seawater samples analyzed some days later in the laboratory. In most cases, the DMS levels in the refrigerated bottles are two to three times *higher* than the prompt measurements. These results emphasize the critical need for real-time *in-situ* mass spectrometry.

IMPACT/APPLICATIONS

We believe that *in-situ* mass spectrometers have the potential to be the most powerful deployable sensors 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 non-volatile compounds) MS sensors should have extremely broad application in environmental, chemical, biological and marine sciences.

TRANSITIONS

Our work on *in-situ* MS sensors construction and design 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

Another ONR funded project entitles “Application Specific Chemical Information Microprocessor” is an extension of the microfluidic work performed in this project.

PUBLICATIONS

R. T. Short, D. P. Fries, S. K. Toler and R. H. Byrne: Development of an *in-situ* mass spectrometer, Proceedings of Oceanology International 99 Pacific Rim, Singapore (1999).

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