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Subject: Final Report

Reference: Contract N00014-07-C-0720  
(SRI Project P18063)

Dear Dr. Swean:

SRI International is pleased to submit our Final Report entitled "Development and Deployment of In Situ Mass Spectrometers." This report has been prepared in accordance with the requirements of CDRL A002 of the referenced contract.

If this report is acceptable please sign and return the attached DD Form 250 to my attention.

Technical questions concerning this report should be addressed to Tim Short at (727) 553-3990; all other matters should be addressed to me at (650) 859-4424.

Sincerely,

A handwritten signature in black ink that reads "Margaret Baxter-Pearson". The signature is written in a cursive style with a large loop at the end of the last name.

Margaret Baxter-Pearson  
Division Manager of Contracts

Enclosures

Cc: DCMA Northern California – Letter Only

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## Development and Deployment of *In Situ* Mass Spectrometers

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Contract Number N00014-07-C-0720  
Final Report

### 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 project were diverse, including underwater mass spectrometer (MS) deployments focusing on quantitative measurements of dissolved gases, and improvements on existing 200-amu systems and peripherals. Plume mapping capabilities were to be extended by integrating the underwater MS with a remotely operated vehicle (ROV), and by exploring methods to mathematically improve the spatial and temporal resolution of membrane introduction MS measurements. Instrumental developments (e.g., a novel, modular, deep-water syringe sampling pump system) were to further extend the analytical capabilities of the systems. In-line acidification methods were to be explored to more thoroughly study aqueous carbon systems in the field. Alternative membrane materials, such as carbon nanotubes, were also to be evaluated. Major accomplishments in each of these areas of research and development are discussed below.

### APPROACH

It can be argued that among the techniques used in modern elemental and molecular analysis, none surpasses mass spectrometry in analytical access to elements, isotopes (stable and radioactive), and complex molecules (including natural and anthropogenic organics). 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. Evolving prototype designs constitute major steps toward undersea mass spectrometers capable of long-term autonomous operation. To focus the effort, initial work has been directed toward measurements of selected trace

and ultra-trace volatile organic and inorganic compounds in seawater using *in situ* membrane introduction mass spectrometry (MIMS).

The work performed by SRI International (SRI) for this contract is a continuation of work performed within the College of Marine Science (CMS) and Center for Ocean Technology (COT) at the University of South Florida (USF). To ensure continued collaboration with USF, a subcontract was budgeted to include Professor Robert H. Byrne (a former co-PI on the USF project) and supplementary engineering support from COT.

## WORK COMPLETED

### Positive Displacement Sampling Pump

It has been shown that variations in sample flow rate through a membrane introduction sampling interface can influence mass spectrometer signals, producing an apparent variation in analyte concentration in the sample (LaPack et al. 1990). This effect is due to changes in the diffusive boundary layer that forms in the sample at the membrane interface. Careful control of the sampling speed can help to mitigate this problem. However, to date we have been unsuccessful in finding a commercially available deep-water sampling pump that provides the necessary stability. As a consequence, we have designed and constructed a deep-water, positive-displacement syringe pumping system that provides significantly improved stability. The syringe pump system also allows for the introduction of reagents into the sample flow stream to induce chemical reactions that convert non-volatile and/or polar compounds into volatile non-polar species, which are then detectable with a MIMS system. One example of the utility of this capability is to add acid to a seawater sample stream to convert dissolved inorganic carbon (DIC) into carbon dioxide. Preliminary lab experiments that employed acidification to measure total DIC are described below. The new syringe pump system will allow for *in situ* implementation of the technique.



**Figure 1. Photograph of positive displacement syringe pump system that provides constant flow sampling and the capability to add reagents to the sampling stream.**

## **In-line Acidification**

To fully describe the carbon system in an aqueous environment, at least two of the following four parameters must be measured: (1) pH, (2)  $p\text{CO}_2$ , (3) DIC, and (4) total alkalinity. From two measurements, the remaining parameters can then be calculated. MIMS analyses allow determination of  $p\text{CO}_2$ , so determination of one of the other parameters allows complete characterization. We have tested a prototype sampling interface that couples in-line sample acidification with subsequent MIMS analyses for *in situ* determination of DIC. Initial laboratory results indicate that the underwater mass spectrometer can be used for *in situ* characterization of aqueous carbon systems by alternating between direct sample analysis ( $p\text{CO}_2$ ) and analysis of acidified samples (DIC). No other single instrument can currently perform this task.

## **Calibration Standards for Hydrogen Sulfide Measurements**

During field deployments of the *in situ* mass spectrometer, we have at times encountered anoxic environments (e.g., Saanich Inlet, B.C.; Yellowstone Lake, WY) in which we have detected dissolved hydrogen sulfide. To quantify these *in situ* measurements, we have investigated methods for preparing sulfide standards for calibration of the underwater MIMS instrument. Preparation of such standards is complicated by several factors, including the presence of oxidizing species (oxygen, metal oxides, etc.), formation of precipitates (metal sulfides, magnesium carbonate, etc.), emissions of hazardous gases (hydrogen sulfide), and loss of analyte due to volatility. A methodology must thus be devised to overcome each of the complications while retaining simplicity and field portability.

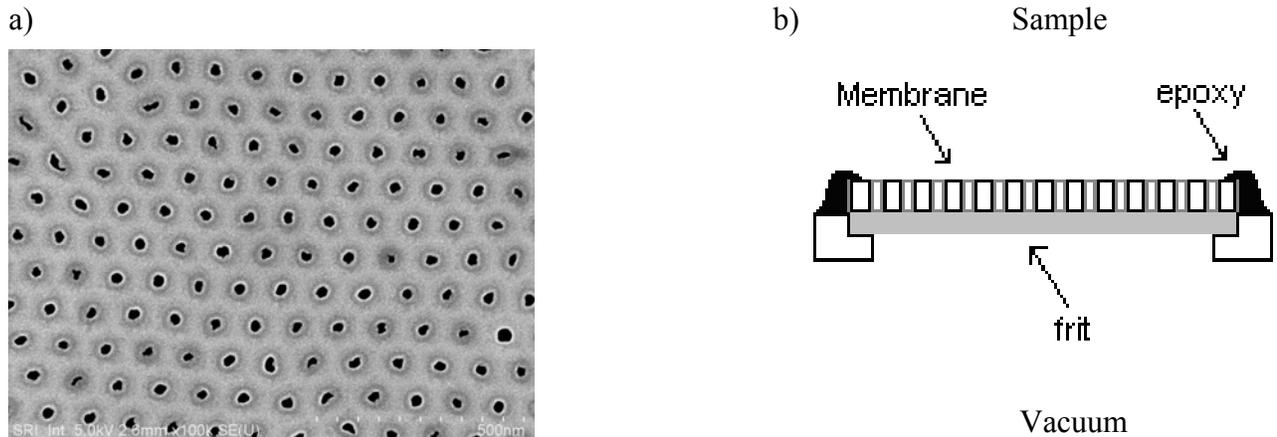
Our work has focused on the production of aqueous samples via the addition of sulfide salts. Sulfide standards were created through the gravimetric addition of washed and inert atmosphere-dried sodium sulfide nonahydrate. To protect the operator and preserve sulfide concentration, the evolution of hydrogen sulfide was prevented by maintaining a pH greater than 8.0. The addition of a basic chelating agent achieved the necessary pH while sequestering precipitating and/or oxidizing metals. To avoid the precipitation of Brucite, care was taken not to drive the pH of seawater solutions greater than about 9.0. Once prepared, the samples could be acidified in-line (in the same manner described above for the carbon system) for conversion of total sulfide to gaseous hydrogen sulfide for MIMS analysis.

## **Carbon Nanotube Membranes**

Although calibration for the effects of hydrostatic pressure on analyte transmission through compressible membranes (such as polydimethylsiloxane) allows quantitative measurements at depth, it would be advantageous to use a membrane that is much more resistant to compression under pressure. Use of such a membrane should improve the precision of depth-profiling measurements by significantly reducing errors introduced through the calibration procedure. Arrays of carbon nanotubes (CNTs) coupled with very thin polymeric membranes are good candidates for robust, highly selective sampling interfaces. For this reason, we have constructed a chemical vapor deposition apparatus for fabrication of carbon nanotube membranes. Membranes are formed at 900 °C by pyrolysis and deposition of carbon within the pores of an anodic aluminum oxide porous disk.

Preliminary analyses of gaseous samples using an uncoated CNT membrane coupled to a laboratory MIMS system indicated a selectivity that favors transmission of lower molecular weight molecules, such as methane. To use CNT membrane interfaces to analyze aqueous samples with the *in situ* MIMS system, they will need to be coated with a very thin polymer, such as Teflon, to reduce water vapor

influx in the mass spectrometer vacuum system. A hot filament chemical vapor deposition system has been designed for this purpose.



**Figure 2. Carbon nanotube membrane. a) Scanning electron micrograph of carbon nanotube membrane surface. b) Side view schematic of membrane mounting scheme for coupling to mass spectrometer vacuum system.**

### ROV Deployment of the In Situ Mass Spectrometer

The *in situ* MIMS system was integrated with a Sea Max Rk1 Remotely Operated Vehicle (ROV) for testing in Bayboro Harbor, St. Petersburg, FL. Power was supplied to the MIMS system, and high-bandwidth communication was established between the MIMS system and a shipboard laptop computer via the ROV tether. Several plumes of gases were created to test the ability of the ROV/MIMS system to find and identify chemicals in the plumes. A plume of carbon dioxide was created by immersing dry ice into the water, a plume of methane was created by feeding a gas line from a methane compressed gas cylinder into the water, and a plume of dimethylsulfide (DMS) was created by encasing a sample of DMS in a semi-permeable silicone tube and placing it in the harbor. Sonar and video systems on the ROV helped to locate the plumes by observing bubbles.

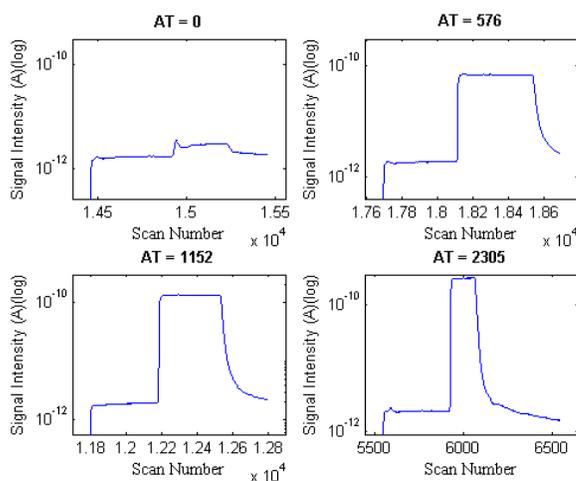
### Deconvolution Algorithms

Diffusion of analytes through the membrane interface is the major time-limiting factor for MIMS analyses. When a MIMS system moves through the water while sampling (e.g., on a ROV), membrane diffusion becomes the primary factor limiting spatial resolution of analyses and mapping. We have performed initial laboratory experiments and calculations to describe diffusion of analytes through the MIMS sample interface, to investigate methods to deconvolute the instrument response of the membrane interface and to obtain true concentration profiles in time and space.

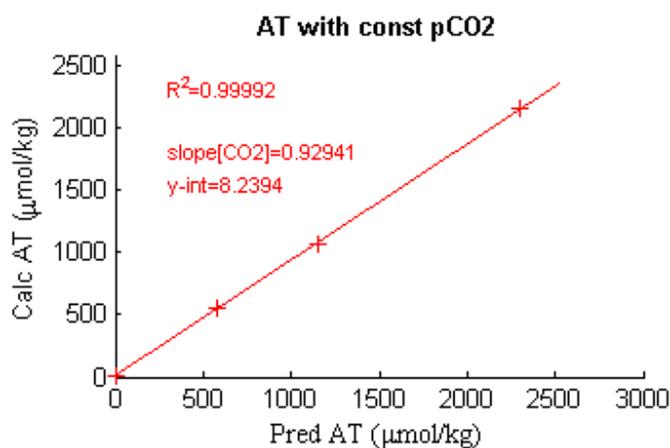
## RESULTS

### In-line Acidification

Several solutions of various total alkalinities (AT) were created and analyzed for  $p\text{CO}_2$  using the underwater MIMS system. Tartaric acid was then added to each sample using the in-line acidification system to obtain a  $\text{pH} \leq 4$ . Figure 3 displays the results from four samples. The leading edge of the step near the center of each plot is the point at which tartaric acid was introduced. Figure 4 is a plot of the alkalinity (AT) calculated from the DIC measurements using the mass spectral data displayed in Figure 1 vs. the alkalinity predicted by the sample preparation procedure. The linear relationship is excellent; however, the slope of less than 1 indicates a small systematic error.



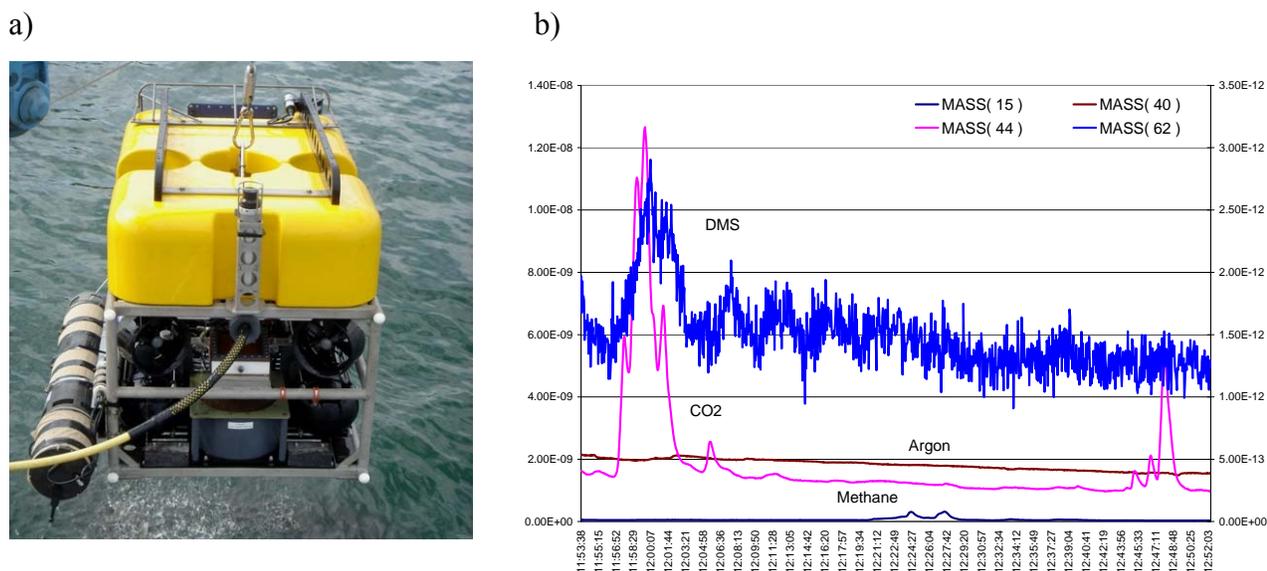
**Figure 3. MIMS analyses of acidified samples with different total alkalinity (AT). In each case, the log of the mass spectrometer signal intensity for  $m/z$  44 is plotted as a function of scan number. Each scan had a duration of 1 sec.**



**Figure 4. Plot of relationship between calculated alkalinity (determined by  $p\text{CO}_2$  and mass spectral DIC measurements) and predicted alkalinity (from sample preparation procedures).**

## ROV Deployment of the In Situ Mass Spectrometer

The general locations of the plumes of carbon dioxide, methane, and DMS were found using real-time sonar and video systems on-board the Sea Max Rk1 ROV by locating bubbles emanating from the sources. Once close to the plume, the robotic arm of the ROV (to which the MIMS system sample intake tube was attached) moved the sampling tube to the vicinity of the plumes. During this time, the MIMS data were viewed in real-time on board the deployment boat. Figure 5 shows the ROV/MIMS system being deployed and MIMS data demonstrating the ability to distinguish the individual plumes. The carbon dioxide ( $m/z$  44), DMS ( $m/z$  62), and methane ( $m/z$  15) plumes were all detected as indicated by the rise in intensity of the mass spectrometer signal at certain times. Argon ( $m/z$  40) was also monitored to determine the drift in instrument background, since argon concentrations were not expected to change during the deployment.



**Figure 5 . In situ MIMS deployment on ROV. a) Photograph of ROV/MIMS system being lowered into Bayboro Harbor. b) MIMS data from the deployment that demonstrate chemical identification of plumes (x-axis is “time of day” and y-axis is “intensity” in amps from the mass spectrometer electron multiplier detector).**

## IMPACT/APPLICATIONS

We believe that *in situ* mass spectrometers will become the most powerful deployable chemical sensors in the marine environment. Due to the versatility of mass spectrometry for detection and quantification of a wide variety of compounds in complex environments, underwater MS sensors should have extremely broad application in environmental, chemical, biological and marine science.

## RELATED PROJECTS

This work is an extension of work performed under Grant Number N00014-03-1-0479 to the USF titled “Development and Deployment of *In Situ* Mass Spectrometers”.

Underwater mass spectrometer systems under continuous development in this project have been used in NSF Award No. 0536345 to USF titled “Collaborative Research: Benthic Observatory and Technology Test Bed on the Midshelf - Understanding Processes”. SRI International has a subcontract to this award.

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M. H. LaPack, J. C. Tou, C. G. Enke, Membrane mass spectrometry for the direct trace analysis of volatile organic compounds in air and water, *Anal. Chem.* 62 (1990) 1265-1271.

## **PUBLICATIONS**

Calibration of a deep-water *in situ* membrane introduction mass spectrometer with respect to hydrostatic pressure, R. J. Bell, R. T. Short, F. H. W. van Amerom, and R. H. Byrne, *Env. Sci. & Technol.* 41 (2007) 8123-8128.

Underwater mass spectrometry: Developments and calibration, R. J. Bell, S. K. Toler, P. G. Wenner, R. T. Short, and R. H. Byrne, Proceedings of the 6<sup>th</sup> Workshop on Harsh-Environment Mass Spectrometer, Cocoa Beach, FL (2007).

Measurements of horizontal and vertical gradients of dissolved gas concentrations using a calibrated underwater membrane inlet mass spectrometer, R. J. Bell, S. K. Toler, R. T. Short, and R. H. Byrne, 56<sup>th</sup> American Society of Mass Spectrometry Conference, Denver, CO (2008).

## **PATENTS**

Modular deep water syringe sample pump and probe. US patent application number 61/096694, filed 12 September 2008.