

Development and Deployment of In-Situ Mass Spectrometers

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Grant Number N000149810154

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

There were several diverse objectives during this phase of work, and significant progress has been made in a number of areas. At the beginning of this funding cycle, we had constructed, tested and deployed two underwater mass spectrometry systems, each of which employs a membrane interface to introduce analytes into the mass spectrometer. One membrane introduction mass spectrometry (MIMS) system uses a linear quadrupole mass filter for analysis, and the other system uses an ion trap mass spectrometer. Although these systems have many features in common (e.g., both are useful for detection of trace volatile organic compounds, VOCs), each has particular strengths and weaknesses that determine applicability for a particular problem or analysis. During this funding cycle, multiple field deployments of each instrument were planned, along with a number of instrumental modifications to improve the ease of use and performance of each system. In addition, development of alternative versions of underwater mass spectrometers with extended capabilities was to continue. In particular, we were to construct and test a new underwater linear quadrupole system with an extended mass range and increased sensitivity.

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. A long-term goal is to combine atmospheric pressure ionization, referred to as electrospray ionization (ESI), with mass spectrometry and tandem mass spectrometry (MS/MS) using an ion trap mass spectrometer. Sample pretreatment and analyte separation using microfluidic devices will be performed prior to electrospray ionization when necessary. This system will allow detection and identification of non-volatile compounds at trace levels, with a very high degree of certainty, in complex marine environments. In a multifaceted approach toward this goal, we are evaluating a variety of types of mass spectrometers with unique capabilities. We are also testing and using simpler sampling methods, such as membrane introduction of volatile organic species. Our approach includes miniaturization of components, wherever possible, by incorporation of micro-systems technology (MST) and use of micro-electromechanical systems (MEMS).

WORK COMPLETED

During the current funding cycle, our 100-amu linear quadrupole system has been used in multiple field deployments. A number of instrumental modifications have also been implemented to improve performance and ease of use for both the 100-amu linear quadrupole and the ion trap underwater systems. In addition, a new 200-amu underwater linear quadrupole system has been assembled and tested. Progress has been made, as well, extending our MS capabilities with alternative mass spectrometer configurations and interfaces. We have also extensively evaluated the performance of the existing systems in the laboratory and have undertaken systematic investigations of the effects of salinity, temperature and pressure on our systems' detection limits. Examples of our developments and deployments are described below

Linear quadrupole and ion trap mass spectrometers

As mentioned above, we have constructed and tested an underwater membrane introduction linear quadrupole mass filter system that has twice the mass range of the initial linear quadrupole system. The construction of this system was made possible by the recent availability of a compact 200-amu residual gas analyzer from Inficon (Syracuse, NY). Previous commercially available 200-amu units were substantially larger in size and not directly compatible with our underwater design. In addition to providing analytical access to compounds with molecular weights between 100 and 200 amu, as well as a more compact and lower power configuration than the underwater ion trap MIMS system, the new Inficon "closed" ion source design also dramatically improves the sensitivity of linear quadrupole analysis. The closed ion source design typically provides an order of magnitude increase in sensitivity and substantially improved detection limits for many compounds. The increased mass range of the 200-amu system allows low-level detection of compounds associated with fuels oils and other petroleum products. Laboratory measurements of naphthalene standards in seawater suggest that the in-situ analysis capabilities of the new 200-amu underwater system will be extremely important to the oil industry, for example in pipeline leak detection.

The membrane introduction/gas chromatograph (MI/GC) interface described in last year's proposal has been successfully tested in the laboratory ion trap system. A new microprocessor control board has been developed and integrated into the system for the many additional operations of the new interface. This MI/GC system will allow analyses of many semi-volatile compounds with improved specificity,

and at greater depths than are accessible with a simple membrane interface. The new interface system is presently being incorporated into the underwater ion trap MS system.

The original membrane interface used on the 100-amu linear quadrupole system was replaced with a modified version of the MI/GC interface. By removing the GC capillary (and need for helium stripper gas), this interface can be connected directly to the MS vacuum housing. The performance of this design is comparable to the previous MIMS design, and allows operation at much greater depths (when the peristaltic pump is replaced by a mechanical gear pump). This increased depth capability is a direct result of the “inverted” design of the new interface: the high-pressure water is on the *outside* of the PDMS membrane. This new design has been tested in the laboratory to 30 atm pressures (equivalent to 300 m depths) whereas the previous membrane interface was found to fail at three atm.

Electrospray ionization

Colleagues at Chem-Space Associates have modeled a variety of atmospheric source designs and ion transmission elements for high ion-source to mass-detector throughput. The creation of high-density transport ion optics will enhance the performance of any of the atmospheric pressure sources that we are considering for field devices. Models have been generated for Electrospray (ES) and atmospheric pressure chemical ionization (APCI) sources. Chem-Space is currently building test-beds to evaluate the model output. From this current development we will be in a position to recommend a specific design/need for our instrument that is based on a soft ionization source.

Small Linear Quadrupole Array

A Ferran Scientific (San Diego, CA) linear quadrupole array was installed into a small vacuum housing/membrane interface system in an attempt to create a truly hand-portable underwater dissolved gas MS analyzer. We replaced the turbo/drag and roughing pump system with a very small 3 liter/sec ion getter pump to evaluate the feasibility of using a very small vacuum pump for this application. Although the pump had sufficient capacity to maintain vacuum in a closed vacuum system (no membrane inlet), the gas load through the membrane interface proved to be too high for such a small pump. We are presently evaluating other commercial options (which are limited) for very small vacuum pumps with sufficient pumping capacity.

RESULTS

Water Quality Monitoring (100-amu linear quadrupole)

We have performed field measurements using the 100-amu linear quadrupole systems at Palm River (Hillsborough County, FL) and the Manatee County (FL) Water Treatment Facility. These deployments focussed on both dissolved gas measurements and determination of trace VOC levels. At the Water Treatment Facility we had access to various stages of the treatment process and were able to see clear differences in, e.g., chloroform concentrations. The measurements demonstrated the portable MIMS system capability for continuous process monitoring.

Chemical Plume Mapping (Ion Trap and 100 amu linear quadrupole)

We have analyzed in greater detail the dimethylsulfide chemical plume data obtained during the previous proposal period (ion trap MIMS deployment in July 2001). These analyses have improved our

ability to visualize and assimilate data into meaningful three-dimensional chemical concentration fields. Ion trap MS data for dimethylsulfide (DMS, m/z 62) concentrations were spatially coordinated by global positioning system (GPS) measurements. The coherence of data, when corrected for the response time of the MIMS system, demonstrated the capability of coordinating in-situ MS analysis with GPS location to provide depictions of evolving environmental VOC distributions.

In order to correlate field MS data with DMS signal intensities from discrete samples, DMS plume concentrations were modeled as a function of distance from the dispense boat. This model accounts for the fact that concentrations measured with the underwater MIMS systems are obtained as integrated signals in a flowing sample stream. With a very simple conical plume model we obtained reasonably good agreement (within a factor of 2) with discrete samples that were subsequently analyzed on the same instrument. Similar field experiments (two deployments) were performed in early 2002 using the underwater linear quadrupole (100-amu) system. In these experiments the system was placed on board a small Zodiac boat with the sample intake approximately 30 cm below the water surface. A DMS plume was created and the Zodiac was driven in a “lawn mower” pattern to map the plume. The plume was detected as far as 300 m from the dispense boat (the farthest distance attempted).

Yellowstone Lake Vent Analysis

A two-week field exercise (June 27 – July 6, 2002) at Yellowstone National Park was coordinated with David Lovalvo of Eastern Oceanics and a University of Wisconsin at Milwaukee group led by Val Klump (Director of the Great Lakes WATER Institute). The first week was spent integrating the various sensors and water collection system with the Eastern Oceanics remotely operated vehicle (ROV). In the second week we had six consecutive days of ROV deployments in Yellowstone Lake. Using in-situ MS, CTD measurements, and a video system on the Eastern Oceanics ROV, we were able to study (in real-time) the gas composition of a variety of hydrothermal vents in Yellowstone Lake. The results of these in-situ measurements, obtained at depths to 180 feet, are presently being analyzed and will be compared with gas chromatographic (GC) analyses of concurrently collected discrete samples.

Laboratory Calibration and Comparison

The performance characteristics of our various membrane introduction mass spectrometry systems have been examined using VOC standard solutions. In most, but not all, cases the ion trap MIMS system provided higher sensitivity than the 100-amu linear quadrupole. The 200-amu linear quadrupole system, however, typically provided a sensitivity comparable to the ion trap system. We believe this is primarily due to the superior design of the “closed” ion source on the 200-amu analyzer. In addition to these measurements, we have been studying the response of our membrane introduction mass spectrometry systems to environmental variables. This work includes, for example, investigations of temperature, pressure and salinity effects on dissolved carbon dioxide and methane measurements.

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 and MS/MS for detection and quantification a wide variety compounds in complex environments, underwater MS

sensors should have extremely broad application in environmental, chemical, biological and marine science.

TRANSITIONS

An exclusive licensing agreement for the membrane introduction/quadrupole mass filter version of the *in-situ* mass spectrometer has been negotiated with Applied Microsystems, Ltd.

RELATED PROJECTS

Another ONR funded project entitled “Fieldable Microsystems II” is an extension of the microfluidic work originally performed in this project.

PUBLICATIONS

“Field Chemical Profiling in Aqueous Systems Using Remotely Operated Mass Spectrometers”, R.T. Short, D.P. Fries, G.P.G. Kibelka, M.L. Kerr, J. Patten and L. Langebrake, Proceedings of the 28th Annual Meeting Federation of Analytical Chemistry & Spectroscopy Societies, Detroit MI (2001).

“Membrane Introduction Mass Spectrometry on Unmanned Underwater Vehicles”, G. P. G. Kibelka, R. T. Short, D. P. Fries, R. H. Byrne, Proceedings of the 28th Annual Meeting Federation of Analytical Chemistry & Spectroscopy Societies, Detroit MI (2001).

“Field Chemical Analysis Using Real-Time In-Water Mass Spectrometry”, R. T. Short, D. P. Fries, G. P. G. Kibelka, M. L. Kerr, S. K. Toler, P. G. Wenner and R. H. Byrne, Proceedings of Oceans 2001, Honolulu, HI (2001).

“Automated MS Environmental Screening: Toward Biomimetic Chemical Sensing Platforms“, D. P. Fries, R. T. Short, G. P. G. Kibelka, M. L. Kerr, J. Patten and L. Langebrake, Proceedings of the 17th Asilomar Conference on Mass Spectrometry: Real World Challenges and New Developments in Environmental Mass Spectrometric Measurements, Pacific Grove, CA (2001).

“Underwater Membrane-Introduction Mass Spectrometers for Use in Harsh Environments”, R. T. Short, G. P. G. Kibelka and D. P. Fries, Proceedings of the Sixteenth International Forum Process Analytical Chemistry, San Diego, CA (2002).

“Underwater Mass Spectrometry for Detection of VOCs and Dissolved Gases”, G. P. G. Kibelka, R. T. Short, D. P. Fries, J. E. Edkins, Proceedings of PittCon 2002, New Orleans, LA (2002).

“Mass Spectrometry in the Marine Environment: Attempting to Imitate Fish”, R. T. Short, Proceedings of the 15 Annual Secondary Ion Mass Spectrometry Workshop, Clearwater, FL (2002).

“Underwater Mass Spectrometers for Detection of VOCs and Dissolved Gases” G. P. G. Kibelka, R. T. Short and D. P. Fries, Proceedings of the Third Workshop on Harsh Environment Mass Spectrometry, Pasadena, CA (2002).

“Applications of Underwater Mass Spectrometers for Detection of Dissolved Gases and Trace Pollutants” Gottfried P. G. Kibelka, John Edkins and R. Timothy Short, Proceedings of the 50th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando, FL (2002).

PATENTS

Submitted Patent Title: Portable Underwater Mass Spectrometer filed Oct. 4, 2001. Claims priority to provisional application 60/237,811.