Development of a Mass Spectrometer for Deployment on Moorings and Cabled Observatories for Long-Term Unattended Observation of Low-Molecular Weight Chemicals in the Water Column

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LONG-TERM GOALS

The goals of this project are to address the need for advanced chemical sensing in the ocean environment through development of a new mass spectrometer for long-term unattended deployment. The mass spectrometer is based on Monitor Instruments' miniature cycloidal mass analyzer technology and oceanographic components developed by WHOI. Testing and trial deployments will be carried out by WHOI at its Deep Submergence Laboratory and Martha's Vineyard Coastal Observatory (MVCO). Monitor Instruments will carry out commercialization of this instrument, which will be known as TETHYS (TETHered Yearlong Spectrometer), Figure 1.

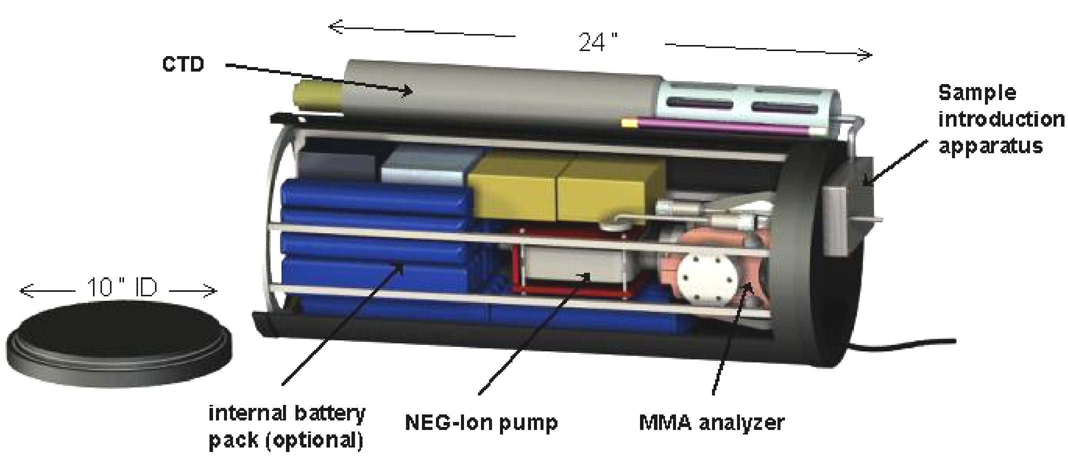

Figure 1: Preliminary CAD rendering of the TETHYS instrument, with optional internal battery pack.

OBJECTIVES

We are performing a multi-year development of the TETHYS instrument. TETHYS will be optimized for long-term measurement of low molecular weight dissolved biogenic, atmospheric, and noble gases as well as light hydrocarbon compounds from 2 to 100 AMU. This instrument will have minimum limits of detection on the order of parts-per-billion and be capable of shallow water to full ocean depth deployment. It will utilize techniques currently under development at WHOI to enable automated re-calibration in-situ and will also include measures for anti-fouling, an essential consideration for long-term deployment. TETHYS is being designed for production in significant quantity, through the use of low cost components that can be rapidly produced and is designed to operate without moving parts or high-frequency electronics. Without the need for mechanical pumping and high-frequency electronics, the instrument will better avoid mechanical wear and subsequent failure, and will not generate vibration or EM field fluctuations. These modes of noise are potential sources of interference to other instrumentation attached to a given mooring or cable node (i.e. hydrophones, seismometers, electromagnetic sub-bottom profilers, magnetometers). The instrument will also be capable of carrying an onboard battery for operation on moorings or in the case of power disruption to the node.

TETHYS is designed to be extremely durable, with service intervals on the scale of weeks to months, with modularity allowing for periodic maintenance and component upgrade. Its physical configuration will enable initial deployment and maintenance by scuba divers from the R/V Tioga at the MVCO. This configuration will also accommodate later deployment and maintenance with ROVs in deeper environments.

APPROACH AND WORK PLAN

The project team brings together a combination of expertise in mass spectrometry, marine chemistry, instrumentation design, and operations in laboratory and ocean testing environments.

The engineering development necessary to realize a mass spectrometer optimized for operation from a mooring or cabled observatory is summarized by four activities over the three years of effort:

1. Develop a prototype mass spectrometer – TETHYS – for long-term deep ocean operation on moorings and cabled observatory nodes. **(Year 1)**
2. Trial deployment of the TETHYS prototype at the Woods Hole Oceanographic Institution’s MVCO. **(Year 2)**
3. Refine processes for automating in-situ calibration/re-calibration, analyze the performance of the instrument. **(Year 2)**
4. Optimize the TETHYS design for production. Construct second-generation prototype for commercial production. **(Year 3)**

During this first half of the Year 1 effort we have focused on development and fabrication of the initial TETHYS instrument prototype parts. The instrument utilizes a proprietary non-evaporable getter ion pump and mass analyzer developed by Monitor, called the Miniature Mass Analyzer (MMA). Components, such as the MMA, NEG-Ion pump, inlet system, and electronics are being designed to optimize performance for sensitivity, deployment depth, required response time, water temperature, power, and communications requirements.

Overall direction and technical leadership is being provided by the Co-Principal Investigators, Drs. Richard Camilli and Jean Whelan of Woods Hole Oceanographic Institution. Dr. Camilli is in charge of engineering development and deployment. Dr. Whelan, who has transitioned to an emeritus position since her retirement in October, now assists Dr. Camilli with instrument calibration and data interpretation. Development of analyzer hardware is being carried out by Monitor Instruments. Mr. Anthony Duryea, president of Monitor Instruments, is in charge of all aspects of Monitor Instruments involvement in the TETHYS development program, and Jim Buchner, also of Monitor Instruments, in charge of technical aspects of analyzer development. In year 2 of the program a working TETHYS prototype will be deployed by WHOI at the MVCO. During year 3 of the effort, Monitor will use the results of the MVCO deployments to further refine the design of TETHYS, with the objective of commercial production.

WORK COMPLETED

Although the NOPP project only began in July 2005, we have already made a number of significant advances. During the past five months we have successfully developed a miniaturized inlet system that is approximately 20% of the weight and size of the initial design (Figure 2) . This inlet permits a response time of less than 10 seconds for most gases (Figure 3). This inlet system has since been integrated with a MMA analyzer and successfully generated the first sets of benchtop spectra. Work has recently been initiated to optimize the analyzer and pumping system designs for maximum efficiency and minimal overall size. At present, a second generation prototype design is undergoing refinements which are expected to result in a significant size and weight reduction beyond the generation one prototype design. These improvements may permit the TETHYS design to also operate aboard small displacement AUVs.

In addition to the year 1 engineering design work, we have significantly leveraged ongoing research with the Gemini mass spectrometer to investigate inlet apparatus characteristics. This includes cruises in the Atlantic and Pacific and has allowed us to initiate Year 2 tasks focusing on temperature and pressure effects at depth (Figure 5).

Figure 2: second generation prototype of TETHYS inlet, weighing approximately ½ kg in air, measuring approximately 10 cm in diameter.

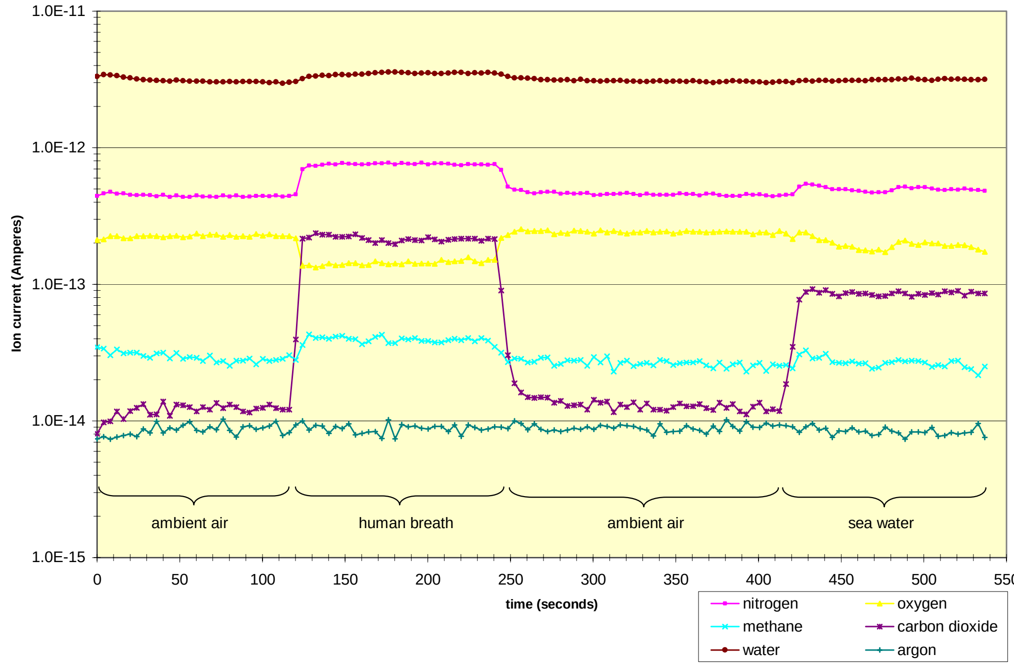

Figure 3: temporal response characteristics of the TETHYS inlet to pumped input of ambient air, followed by human breath, ambient air, then seawater. Data indicate a response time to steady state of 8 seconds or less for most dissolved gases.

Figure 5: Trial deployment of TETHYS inlet operating with Gemini mass spectrometer (in black pressure housing below the Nisken bottle rosette) during research cruise aboard the R/V Thompson.

RESULTS

Preliminary results from benchtop testing of the TETHYS analyzer indicate that the instrument possesses the necessary low m/z range mass resolution to be able to resolve ion peaks without overlap (Figure 6). This excellent mass resolution, particularly in the low mass region of interest, <50 AMU, is critical for making quantitative estimates for analyte gas concentrations such as methane and hydrogen. The inlet time response of less than 10 seconds will provide robust data sets and allow for monitoring transient environmental events. Preliminary results from inlet apparatus deployment with the Gemini mass spectrometer indicate that temperature and pressure effects are tractable based on measured analyte gas ion currents. Temperature and pressure calibrations will enable more accurate estimates of long term trends and vertical spatial variability of dissolved gas concentrations in the water column.

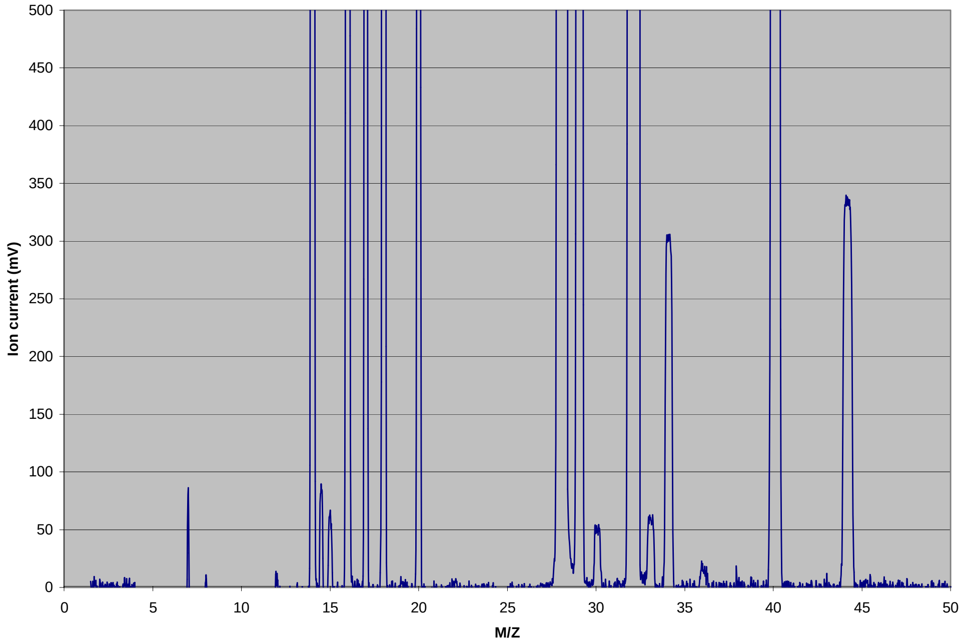

Figure 6: An example spectrum generated by the TETHYS analyzer. Peaks are clearly separated, exhibiting no overlap in the m/z region <25 amu. Nitrogen, oxygen, and argon isotopes are clearly visible at m/z = 29,30,33,34, and 36.

IMPACT AND APPLICATIONS

Mass spectrometers enable rapid identification and quantification of a wide range of chemical constituents present in the water column, greatly expanding observational capabilities of existing chemical oceanographic analyses.

National Security

TETHYS will be useful for a wide range of scientific, industrial, environmental, and military purposes such as monitoring of shipping lanes, hazardous chemical mitigation (e.g. oil spills, toxic chemicals).

Economic Development

WHOI and Monitor instruments have developed a collaborative research agreement for commercializing the TETHYS instrument.

Quality of Life

In-situ analyses of dissolved gases such as methane, hydrogen sulfide, nitrogen, carbon dioxide, and oxygen by TETHYS will be particularly useful for monitoring inland and shallow coastal waters affected by human activity (e.g. biogenic gases associated with red tides and eutrophication caused by waste discharge that may affect public and ecosystem health).

Science Education and Communication

Several cabled observatory networks, including the proposed Neptune array can potentially integrate this instrument into their architectures to rapidly collect data across wide spatial domains, providing synoptic coverage of large-scale transient chemical phenomena. In addition TETHYS is useful for chemical exploration of dynamic regions within the deep ocean such as hydrothermal vent and cold seep activity (i.e. detecting and monitoring hydrogen sulfide, oxygen, hydrogen, helium, carbon dioxide, and methane), as well as investigation of ocean-mediated green house and environmental gas dynamics.

TRANSITIONS

Science Education and Communication (Delete this section if there are none)

During the past 5 months Drs. Camilli and Whelan have given numerous seminars on in-situ chemical sensing and geochemistry, including overviews of the TETHYS project. These seminars include invited lectures at the University of Southern California, University of California Santa Barbara, and Cheyney University.

RELATED PROJECTS

NSF SST: Camilli and Whelan, along with Co-PIs Dr. Hanumant Sing of WHOI and Prof. Brian Bingham of Olin College, are currently developing new methods for integrating mass spectrometer data in real time aboard an AUV. The goal of this project is to develop a means by which an AUV can utilize the chemical data in real time to refine search strategies and dynamically re-task its mission planning. The data richness of mass spectrometry make the TETHYS instrument an ideal candidate for integration into this sensor networking development program.

ITR Multiple AUV for Hydrothermal Vent Localization and Mapping: PI H. Singh This work looks at the networking, acoustic communications and navigation, and adaptive search methodologies for locating, and mapping hydrothermal vents along sections of the Southern Mid-Atlantic Ridge using multiple AUVs. This may include telemetering TETHYS data from a fixed node to a mobile platform such as an AUV. ITR communications protocols will be made compatible for TETHYS instruments, allowing for this type integrated operation.

ASTEP Arctic program: PIs R. Reves-Sohn and H. Singh This project aims at building AUVs and a Towed Camera and Sampling Sled capable of deployment in the Arctic for studying hydrothermal vents at the Gakkel Ridge. Two vehicles are currently under development, Jaguar and Puma. Puma is envisaged to serve as a mid-water column scout vehicle for chemically locating hydrothermal vents. Jaguar will operate as a bottom mapping vehicle building microbathymetric maps, optical photomosaics and conducting autonomous sampling operations. Both AUVs are designed to accommodate a chemical sensor payload, including a mass spectrometer. Camilli’s responsibilities in this project include sensor payload design and various aspects of overall vehicle design. Jaguar and Puma are currently slated for their first arctic mission in Oct 2006. Tentative plans are being made to deploy a TETHYS prototype aboard the Jaguar vehicle during these operations.

PUBLICATIONS

R. Camilli, A. Duryea, J. Buchner, and J K Whelan, "TETHYS: an in-situ mass spectrometer for Cabled Observatories" accepted to the *Fourth International Workshop on Scientific Use of Submarine Cables and Related Technologies*. Dublin, Ireland February 2006.

R. Camilli, T. Duryea, M. Wilson, "Underwater Vacuum Technology", *Vacuum Technology & Coating Magazine* pp.34-39, December 2005