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

Richard Camilli
Woods Hole Oceanographic Institution, MS#7 Woods Hole, MA 02543
Phone: (508) 289-3796 FAX: (508) 457-2191 E-mail: rcamilli@whoi.edu

Award Number: (#0537173)
http://www.monitorinstruments.com

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. Monitor Instruments will carry out commercialization of this instrument, the TETHYS (TETHered Yearlong Spectrometer).

OBJECTIVES

The TETHYS design is being optimized for long-term measurement of low molecular weight dissolved biogenic, atmospheric, and noble gases as well as light hydrocarbon compounds from 2 to 150 AMU. The current prototype instrument has minimum limits of detection on the order of parts-per-billion and is now capable of shallow water to full ocean depth deployment.

APPROACH AND WORK PLAN

During this past year 2 of the program a working TETHYS prototype has been developed and is now in routine deployment onboard human occupied submersibles, ROVs, and towfish. Monitor Instruments has also taken the initiative and assumed the cost of constructing a second shallow water (1000 meter) prototype. This second prototype has greatly accelerated the development program by allowing simultaneous deployment and design modifications (i.e. one instrument being deployed while the other undergoes modifications and laboratory testing).

Overall direction and technical leadership is being provided by the Principal Investigator, Richard Camilli 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 2005, now focuses her efforts on education and outreach activities. Development of many hardware components 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. Jim Buchner (of Monitor Instruments) is leading the analytical chemistry program development. Tom Shaffer (of Monitor Instruments) is leading the electronic circuitry design for Monitor Instruments. Al Celo (of Monitor Instruments) is leading the software development. Bob Moskala (of Monitor Instruments) is leading the bench testing and operational trials. Joanne Goudreau (of WHOI) is leading the gas chromatographic ground truthing during scientific deployments.

In the coming months the TETHYS prototype will be deployed by WHOI at the MVCO, and a parallel effort will be underway to integrate the TETHYS unit onboard AUVs. Furthermore, the new 1000 meter unit will be used in a scientific expedition (funded by the US Fulbright program) to characterize reef ecology in the Pacific coast of Panama, north of the Panama Canal Zone. The results of these scheduled AUV, towfish, and moored deployments will be scientifically useful and also used to further refine the design of TETHYS, with the objective of commercial production.

Figure 1: TETHYS mass spectrometer (with shoe in foreground as size reference)

WORK COMPLETED

During this year, year two of a three year effort we have completed the following objectives: 1) completed the first TETHYS prototype 2) deployed the TETHYS prototype onboard a human occupied submersible, numerous ROVs, and towfish 3) collected scientifically meaningful data that has proven useful for various lines of scientific enquiry.

RESULTS

The first working TETHYS prototype was completed in August 2006. This instrument is designed for deepwater operation (to 5,000 meters). The TETHYS prototype is approximately 45 cm in length, 20 cm in diameter and operates on less than 20 Watts (figure 1). Beginning this summer, the TETHYS prototype has been successfully used on 6 scientific research expeditions –operating without fault every time. These scientific programs include:

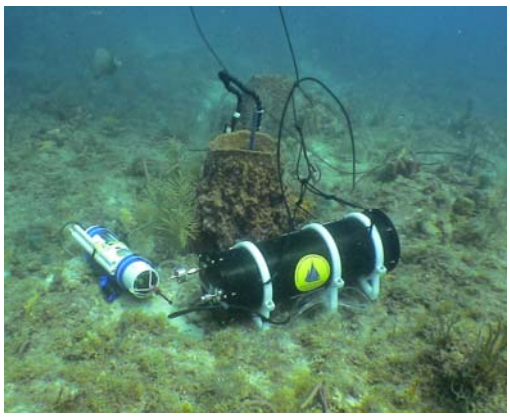

Figure 2: TETHYS-Gemini hybrid mass spectrometer deployed in moored configuration for investigation of pollution in coral reef habitats.

Figure 3: photo of TETHYS-Gemini prototype during deployment onboard the HCMR Thetis submersible at a depth of approximately 300 meters in the Santorini Caldera.

- Prior to completion of the TETHYS instrument, TETHYS components were incorporated into the Gemini mass spectrometer. The TETHYS-Gemini hybrid was deployed in a moored configuration by SCUBA divers in a coral reef to investigate pollution and ecological response of coral reef areas (figure 2). This is the first time that an isotopic study was successfully performed in-situ and shows great potential in determining eutrophication effects in coral reefs and other sensitive habitats. The data from this preliminary study was gathered in less than an hour, demonstrating clear superiority (i.e. speed and quality of data) over traditional off site analysis.
- The TETHYS-Gemini hybrid was also integrated into the HCMR Thetis human occupied submersible and used to investigate hydrothermal venting and volcanism in the Hellenic Back Arc of the Aegean Sea (figure 2). The instrument was used during these dives to locate and

characterize hydrothermal vents in real-time, allowing the science observer to direct sampling. This was the first time that a mass spectrometer was successfully deployed as a payload instrument on a human occupied submersible.

- Real-time in-situ exploration for gas hydrates in the Gulf of Mexico aboard the Johnson SeaLink manned submersible. During this program the TETHYS unit was attached to the submersible's air ballast tanks, amidships along the portside (figure 4). Like the Thetis deployment, supervisory control and data visualization/storage was carried out using a laptop computer operating in the forward crew module via a comms link to the TETHYS instrument. The scientific goal of these mass spectrometer deployments was to characterize methane hydrates and dissolved hydrocarbons in-situ. The TETHYS dives allowed mapping and quantitative estimates of hydrocarbon composition and distributions (Figure 5), as well as biogenic and atmospheric gases at depths to 1,000 meters (the maximum operational depth of the submersible).

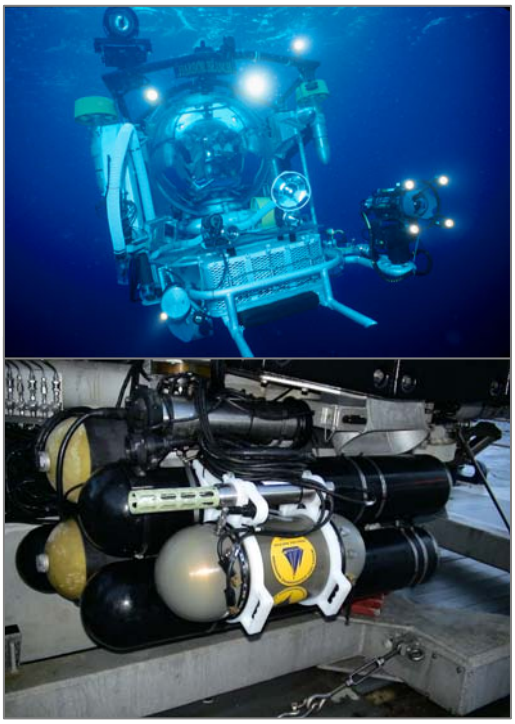

Figure 4: above, photo of Johnson Sea Link submersible; below, TETHYS mounted to Johnson Sea Link submersible external ballast tanks.

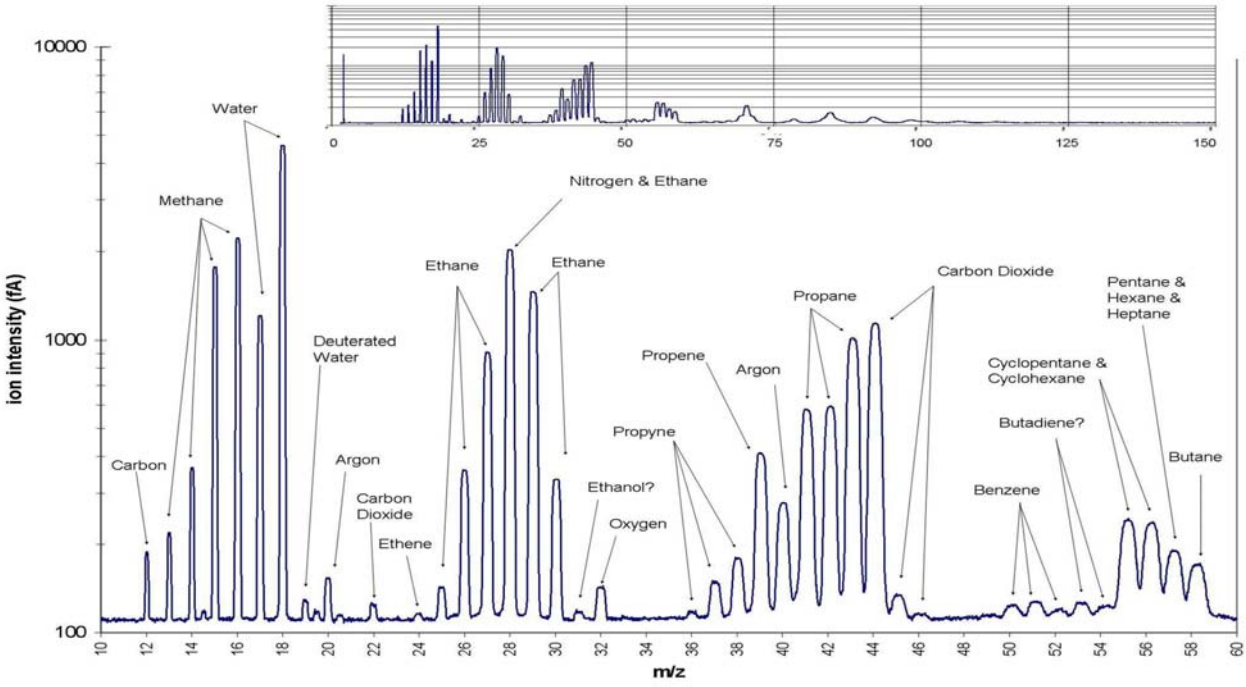

Figure 5: TETHYS spectrum of volatilized components from methane hydrate sample. Spectral peaks indicate a homologous series of alkanes (methane through pentane), along with other higher hydrocarbons.

- Mapping of coastal seep activity with TETHYS in a towfish configuration. Large spatial area surveys (of up to 20 km length) were carried out with the TETHYS unit operating onboard a high-speed towfish (Figure 6), capable of operating at 5 m/sec, in shallow coastal areas in the Atlantic and Pacific basins. The data collected during these operations has proven useful for identifying groundwater outflow and methane cold seep venting (Figure 7).
- Investigation of subaerial landslides and fault structures near the Gaviota slide. These areas were suspected to be caused by fluid expulsion from seafloor sediments. The TETHYS unit was integrated onto the Scripps control vehicle (Figure 8) and surveyed slope areas from approximately 500 meters to 100 meters depth. TETHYS data from these deployments indicate that the fault structures are not actively venting gas enriched fluids, but that upslope areas near these sites may be active.
- Post-Katrina environmental cleanup in the Gulf of Mexico. The TETHYS instrument was successfully integrated onto a work class ROV and used to identify hydrocarbon leaks from oil and gas structures destroyed in hurricanes Katrina and Rita. TETHYS data was instrumental in identifying the locations of leak sources. Following localization TETHYS was used to fingerprint the composition of the leak, enabling positive identification of the source.

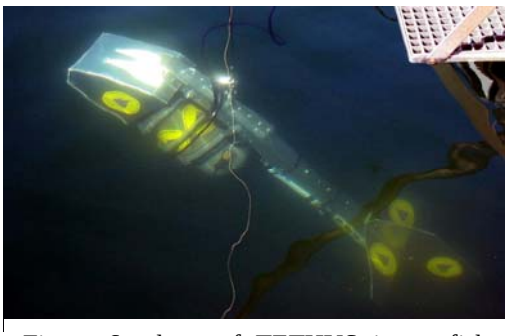

Figure 6: photo of TETHYS in towfish configuration. This system is capable of operating at speeds up to 10kts (5 m/s) and depths to 20 meters.

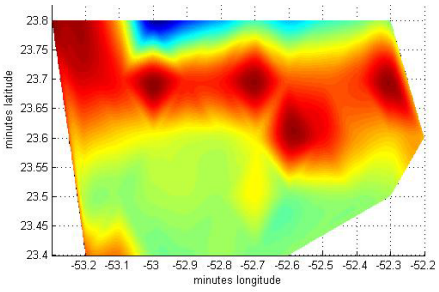

Figure 7: map of propane distribution in the water column above a seafloor fault showing active hydrocarbon cold seeps over an area of approximately 2 km^2. Red indicates higher, green indicates medium, and blue indicates low concentrations.

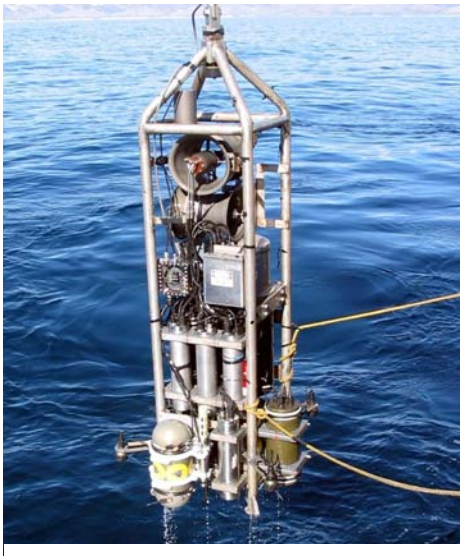

Figure 8: photo of post-dive recovery of the Scripps control vehicle with TETHYS as payload (mounted on the lower left). These dive missions utilized TETHYS to characterize water column chemistry at faults near the Gaviota slide in the Santa Barbara Basin.

IMPACT AND APPLICATIONS

National Security

The broad spectrum sensitivity and low limits of detection (typically on the order of 1 part per billion) show great potential for National Security or Homeland Defense in detecting explosives and toxic chemicals.

Economic Development

The TETHYS prototype has already demonstrated its utility as a survey. The information provided by TETHYS has also been useful for characterizing natural hydrocarbon seeps. This information is useful for oil and gas exploration and assessment of mineral lease rights (i.e. for determining minimum starting bids) by the Minerals Management Service.

Quality of Life

TETHYS has been successfully used as a tool to aid in the cleanup of oil and gas leaks emanating from offshore structures damaged in hurricanes Katrina and Rita. The instrument has also proven useful for identifying groundwater discharge into costal areas and for characterizing coastal pollution. All of these capabilities are useful for quality of life issues involving public and ecosystem health, coastal resource management.

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.

RELATED PROJECTS

The TETHYS prototype and technologies have been used in the following expeditions:

- NOAA Office of Ocean Exploration PHAEDRA Expedition June-July 2006
- NOAA National Undersea Research Program coastal reef survey August 2006
- Univ. of Mississippi Gulf of Mexico Hydrates Consortium cruise Sept 2006
- Scripps R/V Revelle Santa Barbara Basin geotechnical cruise November 2006
- WHOI Coastal Ocean Institute study of groundwater discharge survey Dec 2006

In addition, the following research programs are currently using the TETHYS instrument for related scientific research:

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 TETHYS instrument is now being extensively used for 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 TETHYS mass spectrometer. Integration work has commenced for TETHYS operation aboard the AUVs.

PUBLICATIONS

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

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

R. Camilli, D. Sakellariou, B. Foley, et al. "Real-time characterization of submarine hydrothermal vents with an in-situ mass spectrometer operating aboard a human occupied submersible". AGU fall Meeting, San Francisco CA, Dec 2006.

R. Camilli, J. Whelan, C. Martens, et al. "Coordinated mapping and characterization of ocean floor methane sources with manned submersibles, AUVs and modular observatory arrays". AGU fall Meeting, San Francisco CA, Dec 2006.