Characterizing marine hydrocarbons with *in-situ* mass spectrometry

R. Camilli
Woods Hole Oceanographic Institution
Applied Ocean Physics & Engineering Department
Deep Submergence Laboratory, MS#7
Woods Hole, MA 02543 USA

A. Duryea
Monitor Instruments Company LLC
290 East Union Rd.
Cheswick, PA 15024 USA

Abstract-**Identification and tracking of hydrocarbons in the marine environment is challenging. State of the art systems typically rely on surface slicks to identify hydrocarbon contamination such as oil spills. Subsurface detection remains challenging. This paper describes the TETHYS *in-situ* mass spectrometer and results of real-world deployments. TETHYS is a small, self contained mass spectrometer capable of operation to 5000 meters depth. The TETHYS instrument can quantitatively identify a wide range of hydrocarbons at trace concentrations (minimum limits of detection typically 500 parts-per-trillion) in the subsurface environment. TETHYS has been successfully deployed on AUVs, ROVs, towfish, manned submersibles, and with divers for a variety of purposes, including deep ocean scientific exploration and mapping missions as well as commercial offshore oil and gas leak detection and cleanup.**

I. INTRODUCTION

Locating and identifying marine hydrocarbons is a problem of growing concern as production facilities increasingly move offshore and the use of heavy oil and related slurry products becomes more prevalent. Despite the technological improvements that have been made in identifying oil spills through surface slick detection, heavy oils with limited or no surface slick expression remain challenging. In recent years a number of spills (e.g., M/T Athos 1 and DBL-152) [1] have been difficult to remediate because of poor estimates of subsurface spill volume and the inability to track petroleum product migration due to advection and dispersion within the water column and on the seafloor. The inability to provide clear estimates of subsurface source location and spill movement persists because of inadequate sensing technology.

Oil spill surveillance relies almost exclusively on remote sensing such as infrared, ultraviolet, and radar imaging from satellites and planes [2, 3]. These approaches are only suitable for detecting surface slicks, and are unable to detect dissolved petroleum fractions at depth. Oil spill assessment based on surface slick as well as subsurface data is important when dense aqueous phase liquids or water-soluble fractions are present and when wave-induced mixing is a factor. For instance, approximately 77% of the 825,000 gallons of petroleum from the North Cape oil spill was dispersed into the water column [4]. Estimates of this spill's size, based upon oil-slick area, underestimated the magnitude of the disaster, thus contributing to an ill-prepared cleanup response.

Present state-of-the-art techniques for identifying subsurface contamination and their sources are generally slow, labor intensive, and expensive. Systems such as V-SORS (Vessel-Submerged Oil Recovery Systems) have proven effective in localizing the general areas of pooled and mobile spills, but are unable to determine precise locations. Furthermore, because V-SORS and other technologies (sorbent drops, and sediment cores) are used in contact with the seafloor, these systems pose significant risk to snagging on or otherwise damaging benthic marine life and structures (e.g., reefs, cables, pipelines). Single parameter chemical measurement techniques such as fluorometry and tin oxide sensors (i.e., METS methane sensor) can identify dissolved hydrocarbons in the water, but cannot effectively discriminate between petroleum hydrocarbons and biogenic compounds (i.e., biogenic aromatic hydrocarbons [5] or dissolved oxygen levels [6], respectively). Other non-contact survey techniques such as Remotely Operated Vehicle (ROV) video surveys are routinely used to identify leak source locations but pose the additional problems of only being operational in high visibility water, low sea states and generally being un-navigated, or if navigated, then requiring large, costly, dynamic positioned ships.

Conventional analytical chemical techniques such as gas chromatography or wet chemistry involves collecting and transporting samples to a laboratory for off-site analysis, resulting in sampling and measurement that is generally labor intensive and time-consuming. Additionally, error often arises because of chemical and physical changes occurring to the sample during transport such as degassing and biological or photochemical degradation.

Experimental technologies such as airborne laser fluorescence show promise in detecting aromatic hydrocarbons at water depths to a couple of meters. However the effectiveness of this technique rapidly deteriorates with increasing depth or water turbidity [7]. Other methodologies such as side-scan sonar have been periodically employed but proven unreliable in detecting spilled oil [1].

0-933957-35-1 ©2007 MTS

II. *IN-SITU* MASS SPECTROMETRY

Mass spectrometry is a well understood analytical technique dating back to the late 19th century [8-10]. In 1942 Consolidated Engineering Corporation built the world's first commercially available mass spectrometer for the Atlantic Refining Corporation [11]. Present day mass spectrometric uses encompass a wide range of applications, including industrial process control, clinical diagnoses, isotope fractionation analyses, radioactive half-life determinations, and diverse types of environmental monitoring. As new applications have emerged, specialized instruments have been developed to better fit environmental constraints, ranging from terrestrial battlefields [12], to Jupiter's atmosphere [13]. In recent years efforts have been undertaken to develop mass spectrometers for underwater applications [14-18]. In principle, mass spectrometry is well suited for *in-situ* analysis of dissolved hydrocarbons in marine environments because of the unique capacity to quantitatively identify multiple dissolved chemicals at low concentrations without exhaust or consumable reagents while in the presence of mixtures.

III. TETHYS

TETHYS (TETHered Yearlong Spectrometer) is a 4th generation mass spectrometer developed through a joint research program between the Woods Hole Oceanographic Institution and Monitor Instruments Co. (Fig. 1). The TETHYS design is based on the Gemini mass spectrometer (the first system successfully deployed onboard a human occupied submersible) [19], the NEREUS mass spectrometer (developed for Autonomous Underwater Vehicle [AUV] operations) [15], and the Miniature Mass Analyzer developed by Monitor Instruments Co. through a NASA research program. TETHYS is optimized for endurance, depth, detection of low molecular weight chemicals, long-term accuracy, and overall reliability. It is a compact, self-contained system that is sufficiently low power and ruggedized for extended deployment on moorings and cabled observatory nodes as well as deployment on AUVs, towed platforms, ROVs, and human occupied submersibles.

Unlike many other instruments that use standard laboratory based technology (i.e., commercially available quadrupole analyzers and pumping systems), the TETHYS design utilizes components specifically developed for underwater application. At the heart of the instrument is a novel inverted cycloidal mass analyzer based on ion path equations originally set forth in 1938 by [20]. This design uses a fixed magnetic field superimposed upon an orthogonal electric field. This electrical field is supplied with low power DC, thereby reducing the need for complex circuitry and the potential for RF interference. The superimposed electric and magnetic fields make the cycloid a "perfect" mass analyzer; it provides both momentum and position focusing for ions produced from sample molecules in the source. This unique double focusing provides exceptional abundance sensitivity, stability, and mass resolution in an extremely compact design. The low power consumption of this analyzer enables remote operation with battery power. Minimum detection limits typically are on the order of parts-per-billion with the overall instrument response time of ~5 seconds (for concentration quantification at a 95% confidence interval) for light hydrocarbons [21]. This allows high spatial and temporal resolution mapping of dissolved hydrocarbon fractions on spatial scales as small as 1 meter.

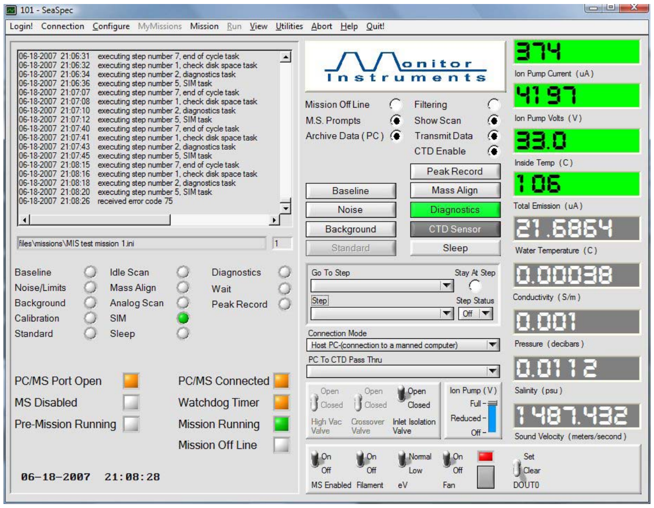
TETHYS data handling and control (including autonomous *in-situ* calibration) is accomplished with SeaSpec software (Fig. 2). Its communication system accepts NMEA position estimate strings and CTD data that are processed in real time and assimilated into TETHYS data. SeaSpec provides mission based functionality (controls can be scripted to carry out mission-specific or adaptive operations based on sensor data) in fully autonomous and supervisory control modes.

A standard communications protocol is available via 10Mb/s Ethernet or 38.4 Kb/s serial. This communications architecture is preferable for ROV, manned submersible, cable moored, and towfish applications. A low bandwidth serial protocol is also available for transmitting processed data and receiving parameterized mission control commands. This low bandwidth protocol is useful for AUV operations or

Fig. 1. Photo of the 5000 meter rated TETHYS mass spectrometer with shoe in foreground for rough scale reference.

TABLE I
TETHYS OPERATIONAL CHARACTERISTICS

Mass range	1-200 AMU
Mass resolution	<0.1AMU
Power	25 Watts @ 24V
Maximum depth	5,000 meters
Endurance	~1 year
Response time	5 seconds
Sensitivity (LOD)	~1 ppb
External dimensions (with 5,000m housing)	23cm OD x 61cm
Weight in water (with 5,000m housing)	13 kg
Moving parts	none



```
06-18-2007  21:06:31   executing step number 7, end of cycle task
06-18-2007  21:06:32   executing step number 1, check disk space task
06-18-2007  21:06:34   executing step number 2, diagnostics task
06-18-2007  21:06:36   executing step number 5, SIM task
06-18-2007  21:07:07   executing step number 7, end of cycle task
06-18-2007  21:07:08   executing step number 1, check disk space task
06-18-2007  21:07:10   executing step number 2, diagnostics task
06-18-2007  21:07:12   executing step number 5, SIM task
06-18-2007  21:07:40   executing step number 7, end of cycle task
06-18-2007  21:07:41   executing step number 1, check disk space task
06-18-2007  21:07:43   executing step number 2, diagnostics task
06-18-2007  21:07:45   executing step number 5, SIM task
06-18-2007  21:08:15   executing step number 7, end of cycle task
06-18-2007  21:08:16   executing step number 1, check disk space task
06-18-2007  21:08:18   executing step number 2, diagnostics task
06-18-2007  21:08:20   executing step number 5, SIM task
06-18-2007  21:08:26   received error code 75
```

files\missions\MIS test mission 1.ini 1

Mission Off Line ○ Filtering ○
M.S. Prompts ● Show Scan ●
Archive Data (PC) ● Transmit Data ●
CTD Enable ●

Go To Step
Stay At Step ○
Step
Step Status: Off

Connection Mode: Host PC-(connection to a manned computer)
PC To CTD Pass Thru

PC/MS Port Open 🟧
MS Disabled ☐
Pre-Mission Running ☐
PC/MS Connected 🟧
Watchdog Timer 🟧
Mission Running 🟩
Mission Off Line ☐

06-18-2007 21:08:28

374	Ion Pump Current (uA)
4197	Ion Pump Volts (V)
33.0	Inside Temp (C)
106	Total Emission (uA)
21.6864	Water Temperature (C)
0.00038	Conductivity (S/m)
0.001	Pressure (decibars)
0.0112	Salinity (psu)
1487.432	Sound Velocity (meters/second)

Fig. 2. Screen shot of SeaSpec software control panel

deployments utilizing acoustic communications (i.e., where intermittent connectivity is likely). Both the standard and low bandwidth serial connections can be coupled to cellular modem or Iridium satellite networks, enabling command and control centers to access information in real-time.

IV. DEPLOYMENT RESULTS

TETHYS underwent sea trials in July 2006; since then units have been deployed on approximately two dozen scientific expeditions and in routine use for offshore oil platform and pipeline leak detection/cleanup operations. We present the results of some characteristic hydrocarbon surveys using ROV, towfish, and manned submersible platforms.

Wide area survey is typically accomplished using the TETHYS instrument in a towfish configuration. For near surface survey between 2 and 5 meters depth the towfish is typically towed at a speed of 2.5 m/s, but can be towed at speeds in excess of 5 m/s with additional ballast weight. Because TETHYS possesses no moving parts it is unaffected by mechanical vibration (e.g., line strumming) inherent to towed operations. Fig. 3 provides an example map generated from a broad-area survey of a natural seafloor hydrocarbon source off the coast of California. This survey was completed in approximately one hour using a small 12 meter trawler that surveyed the ~1.3 km^2 area in grid transects with trackline spacing of approximately 90 meters at a velocity of 3 m/s.

During this survey the TETHYS instrument collected approximately 1,000 measurements from a depth of approximately 5 meters (50 meters above the seafloor) at five second intervals, yielding a 15 meter linear spatial resolution. Geo-referencing is accomplished through a transom mounted DGPS position recording at 1Hz. These position estimates are fed to the SeaSpec software operating from a topside laptop computer. Towcable X-Y position offset is compensated through a simple accounting of cable layback length. Depth is calculated by the integrated CTD and assimilated in real time by the TETHYS instrument. Results from this survey clearly indicate the presence of multiple seafloor hydrocarbon sources in a linear East-West feature. These source features correlate extremely well with a known geologic fault at the seafloor suggesting hydrocarbon migration through the fault from a sub-seafloor reservoir. TETHYS data also indicates hydrocarbon composition variations along the feature, suggesting multiple active conduits and sources.

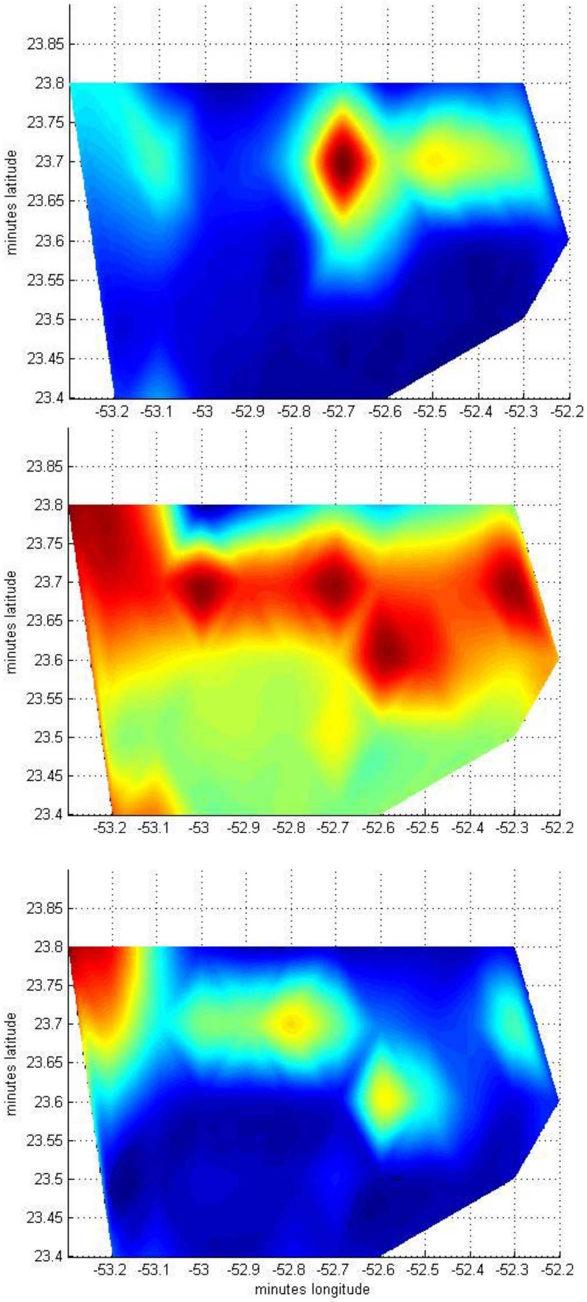


Fig. 3. Geo-referenced TETHYS maps of hydrocarbons (methane top, ethane center, propane bottom) dissolved in the water column. Red indicates high, yellow medium, and blue low concentrations.

Smaller area surveys have also been completed with TETHYS mass spectrometers operating as payload onboard ROVs and human occupied submersibles. The relatively low velocity of these platforms (typically less than 1 m/s) allows for higher spatial resolution mapping of hydrocarbon sources at very close proximity to the seafloor or manmade structures. This approach has been successfully used for post hurricane Katrina/Rita cleanup efforts in the Gulf of Mexico to locate sub-sea broken pipelines and leaking oil platform structures. For this work a smaller and lighter 1,000 meter rated TETHYS instrument is usually integrated onto a work-class ROV (Fig. 4) to perform high-density grid surveys (i.e., trackline spacing at 10 meters or less). The ROV integration process is normally completed within 30 minutes, including all mechanical and electronics required for real-time chemical data streaming to the ship's ROV control room. Once integration is completed the TETHYS instrument can operate non-stop for the duration of the effort. The real-time data processing and visualization available from the SeaSpec software provides a valuable navigation tool for the ROV pilot to rapidly localize hydrocarbon sources in low visibility environments. As a result, survey operations are typically completed with leak sources positively identified within a few days.

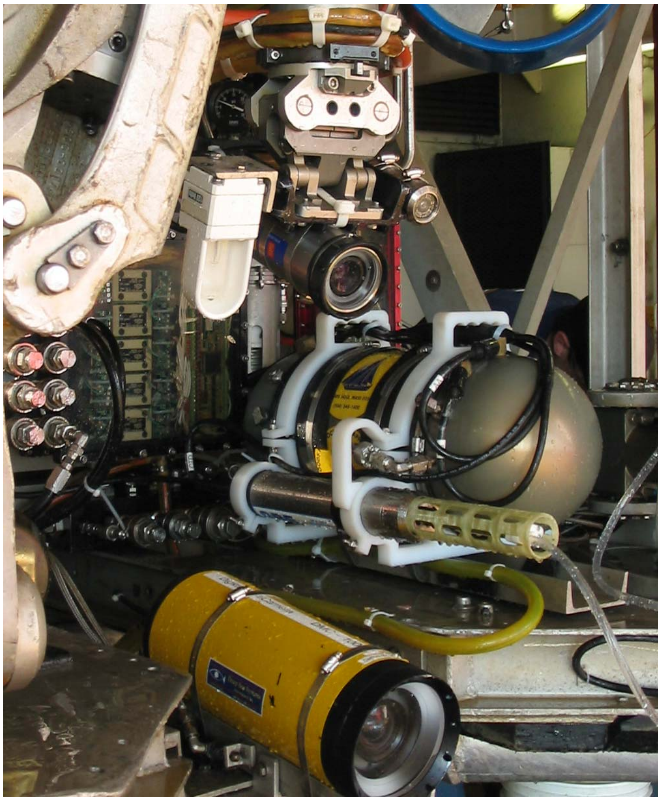


Fig. 4. Photo of TETHYS mass spectrometer (1,000 meter rated unit) integrated onto the forward payload area of an Oceaneering Maxxim ROV during 2006 post-Katrina offshore oil & gas survey and cleanup work in the Gulf of Mexico.

In addition to ROV deployments TETHYS mass spectrometers have also been deployed on human occupied submersibles, including 2006 dive operations onboard Johnson-Sea-Link and 2007 operations onboard the National Deep Submergence Vehicle Alvin (Fig. 5). Operations on both submersibles were conducted as part of scientific investigations of seafloor hydrocarbon seeps. Although human safety considerations for these operations necessitated higher factors of safety than ROV requirements, real-time data were also available to the submersible's pilot and scientist observers via a serial communications link to a laptop computer in the crew cabin. This allowed the crew to rapidly locate and characterize seafloor hydrocarbon seeps *in-situ*. Fig. 6 illustrates a comparative analysis of data from two differing gas hydrate samples. The first sample was recorded during a DSV Alvin dive at a seafloor mud volcano (sometimes referred to as a pingo structure) at approximately 810 meters depth off the coast of Southern California. The second sample is from the Johnson-Sea-Link at a seafloor pockmark feature in the Gulf of Mexico's Mississippi Canyon 118 block (approximately 890 meters depth). The spectral signature of each suggests that the Southern California hydrate is a methane hydrate of biogenic origin (lacking ion peaks from higher hydrocarbons), while the Gulf of Mexico hydrate is a gas hydrate of thermogenic origin (possessing ion peaks from methane as well as those of higher petroleum hydrocarbons).

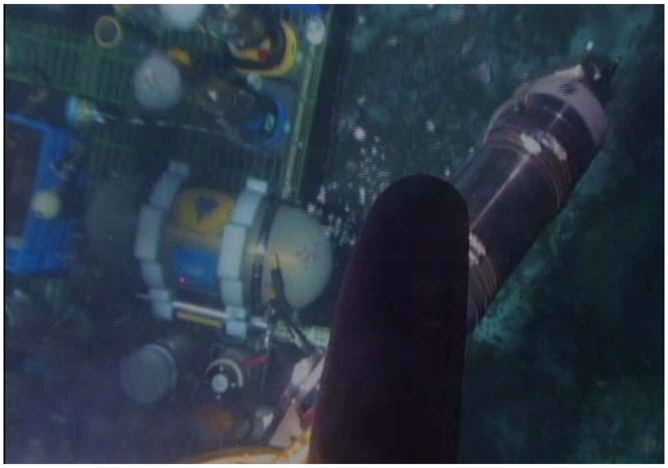


Fig. 5. Photo of TETHYS mass spectrometer (5,000 meter rated unit) operating during DSV Alvin dive mission off the coast of Southern California. The TETHYS instrument is mounted to the starboard side of the forward science basket. Small bubbles of free gas can be seen between TETHYS and the starboard manipulator arm.

This spectral analysis technique can also be applied for positive identification of subsurface petroleum leaks. The resolution, sensitivity, and range of the TETHYS design permits real-time *in-situ* 'fingerprinting' of petroleum based on hydrocarbon composition as well as isotopic distribution. In highly productive areas such as the Gulf of Mexico a significant number of pipelines and wellheads, carrying various petroleum products, can be found within very short distances. Search spaces can be rapidly constrained by cross referencing spectral data with local structures producing/carrying petroleum products in this area. Fig. 7 illustrates the spectral signature of *in-situ* measurements taken onboard the DSV Alvin near a naturally occurring seafloor heavy crude oil leak in the Pacific Ocean in comparison to *in-situ* measurements taken from a work class ROV near an oil platform wellhead leak in the Gulf of Mexico. The spectral signatures of each possess unique hydrocarbon ion peak distributions and intensities.

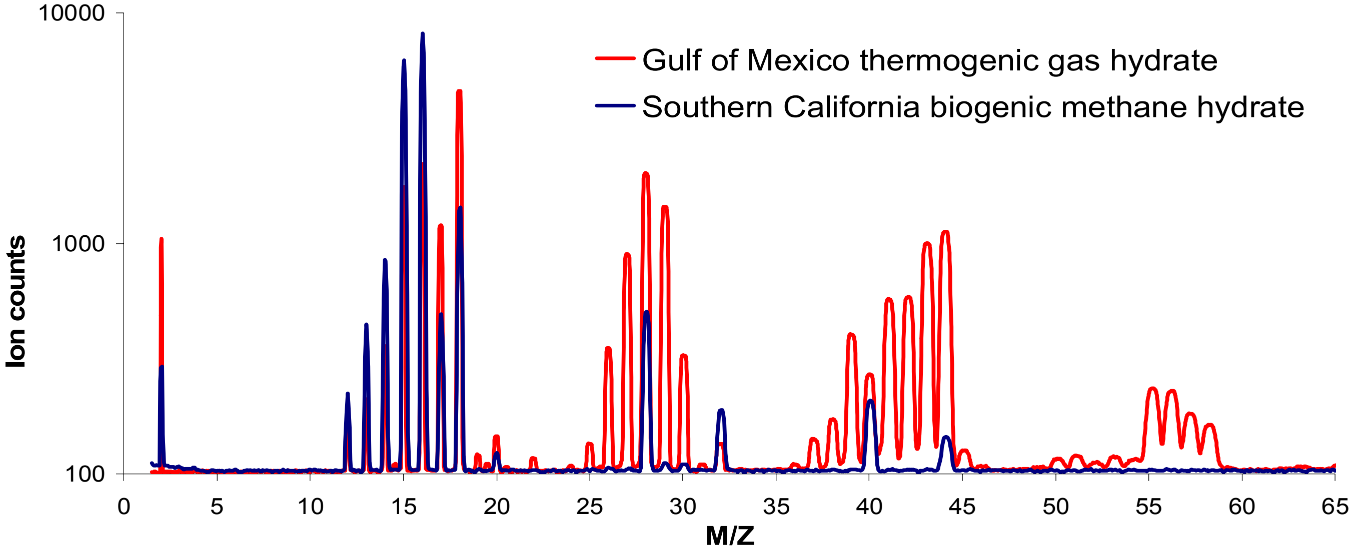


Fig. 6: Comparison of TETHYS mass spectra gas hydrate data from the Gulf of Mexico and along the continental margin of Southern California. Spectral peaks from the Gulf of Mexico data suggest a homologous series of alkanes (methane through pentane) along with other higher hydrocarbons, indicating that the hydrate is thermogenic in origin. In contrast, the spectral data from Pacific hydrates indicate the presence of methane, but no higher hydrocarbons, suggesting that these hydrates are biogenically derived.

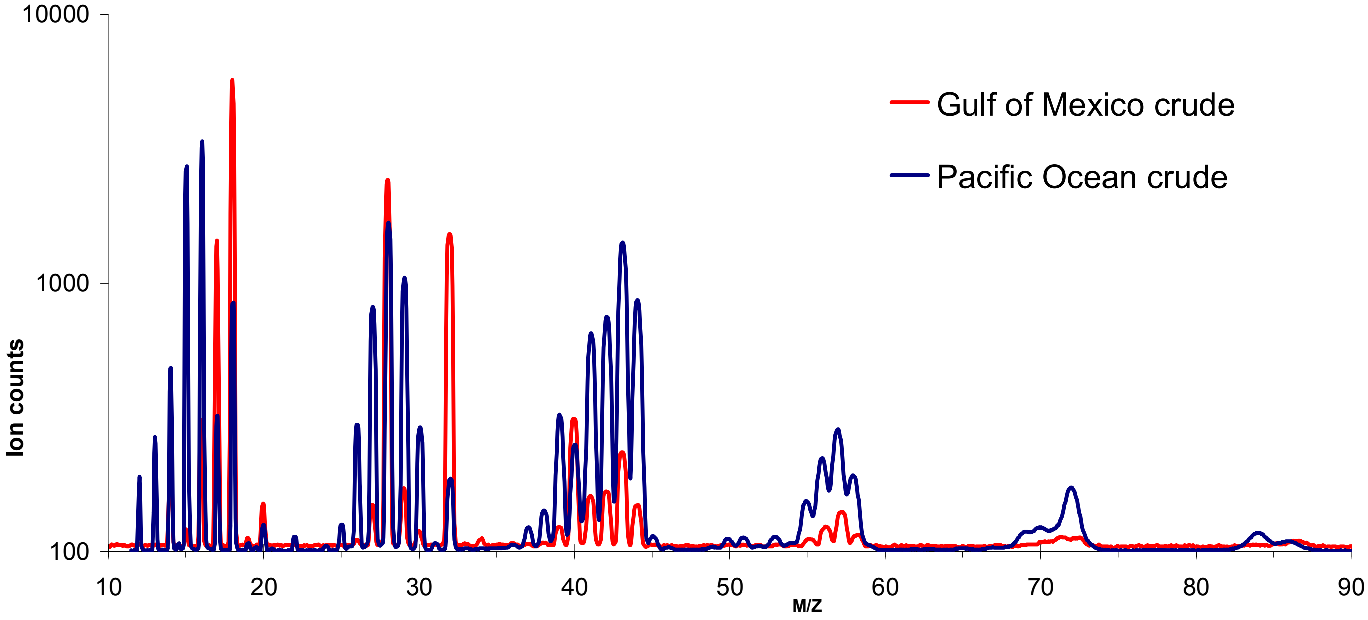


Fig. 7: Comparison of TETHYS mass spectral data from the Pacific Ocean and the Gulf of Mexico. These samples possess differing petroleum signatures, allowing each to be 'fingerprinted' for cross referencing with known petroleum libraries.

V. CONCLUSIONS

In-situ chemical sensing presents the challenges of characterizing large spatial volumes and highly dynamic environmental states when *a priori* knowledge is limited. However, TETHYS is a mass spectrometer specifically developed for *in-situ* marine operation. Its unique design permits rapid deployment onboard a wide variety of underwater vehicles and can operate for extended periods in severe environments (e.g., high vibration, extreme depth, wide temperature ranges). The real-time data interpretation and visualization provided by SeaSpec software enables quantitative identification and mapping of trace hydrocarbon concentrations in the water column. Furthermore, its ability to assimilate external sensor data (i.e., temperature, depth, salinity, position) enables state-based decision processes such as *in-situ* calibration, and chemotactic navigation. These advanced capabilities have been repeatedly utilized as part of offshore oil & gas cleanup efforts as well as scientific investigations of deep sea hydrocarbon sources.

In summary, the TETHYS mass spectrometer provides a new sensing modality to efficiently characterize hydrocarbons in subsurface marine environments. The technology and methods described in this paper are also directly applicable to other lines of inquiry such as hydrothermal vent research, environmental pollution monitoring (both point and non-point source), and ecological study of marine environments.

VI. ACKNOWLEDGMENTS

The authors would like to express their appreciation to the following organizations for their research support. The National Ocean Partnership Program (OCE #0537173) for supporting the development of TETHYS; the National Science Foundation for supporting multi-sensor integration research (OCE #0428737) and providing R/V Atlantis DSV Alvin cruise support (OCE #0447395); NOAA's Undersea Research Program and the National Institute for Undersea Science and Technology for R/V Seward Johnson Johnson-Sea-Link cruise support (#SC06-08-016). Finally, the authors would like to thank Drs. Dave Valentine and Jordan Clark of the University of California Santa Barbara for their collaborative support, as well as the crew of the DSV Alvin for operations assistance.

VII. REFERENCES

[1] J. Michel, "Assessment and Recovery of Submerged Oil," prepared for Research and Development Center, U.S. Coast Guard June 9 2006.

[2] M. Fingas and C. Brown, "Remote sensing of oil spills," *Sea Technology*, vol. 38, pp. 37-&, 1997.

[3] M. Fingas and C. Brown, "A review of the status of advanced technologies for the detection of oil in and with ice," *Spill Science & Technology Bulletin*, vol. 6, pp. 295-302, 2000.

[4] W. Lehr, J. Galt, G. Watabayashi, and J. Sermershein, "Tracking the North Cape Oil Spill," presented at Proceedings of the 19th Arctic and Marine Oilspill Program, Calgary, 1996.

[5] C. E. Brown, M. F. Fingas, R. L. Gamble, and G. E. Myslicki, "The Remote Detection of Submerged Oil," in *3rd R&D Forum on High-density Oil Spill Response*. Brest, France, 2002.

[6] T. Fukasawa, S. Honzumi, M. Morita, T. Oketani, and M. Masson, "Dissolved Methane Sensor for Methane Leakage Monitoring in Methane Hydrate Production," in *MTS/IEEE OCEANS*. Boston, 2006.

[7] J. W. Fant and K. A. Hansen, "U.S. Coast Guard Laser Fluorosensor Testing," presented at Proceedings of the Twenty-ninth Arctic and Marine Oilspill Program (AMOP) Technical Seminar, 2006.

[8] J. J. Thomson, "Cathode Rays," *The London, Edinburgh, and Dublin Philosophical Magazine*, vol. 44, pp. 293, 1897.

[9] J. J. Thomson, "Multiply-charged Atoms," *The London, Edinburgh, and Dublin Philosophical Magazine*, vol. 24, pp. 668-672, 1912.

[10] J. J. Thomson, *Rays of positive electricity and their application to chemical analyses*. London: Longmans, Green and Co., 1913.

[11] R. W. Kiser, *Introduction to Mass Spectrometry and its Applications*. Englewood Cliffs, Nj: Prentice-Hall, 1965.

[12] J. A. Syage, B. J. Nies, M. D. Evans, and K. A. Hanold, "Field-portable, high-speed GC/TOFMS," *Journal of the American Society for Mass Spectrometry*, vol. 12, pp. 648-655, 2001.

[13] H. B. Niemann, S. K. Atreya, G. R. Carignan, T. M. Donahue, J. A. Haberman, D. N. Harpold, R. E. Hartle, D. M. Hunten, W. T. Kasprzak, P. R. Mahaffy, T. C. Owen, and S. H. Way, "The composition of the Jovian atmosphere as determined by the Galileo probe mass spectrometer," *Journal of Geophysical Research-Planets*, vol. 103, pp. 22831-22845, 1998.

[14] G. McMurty and S. Smith, "Mass SURFER field mass spectrometer system for deep ocean and planetary lander applications," in *Third Workshop on Harsh-Environment Mass Spectrometry*. Pasadena, Ca, 2002.

[15] R. Camilli and H. F. Hemond, "NEREUS/Kemonaut a mobile autonomous underwater mass spectrometer," *Trends in Analytical Chemistry*, vol. 23, pp. 307-313, 2004.

[16] H. Hemond and R. Camilli, "NEREUS: engineering concept for an underwater mass spectrometer," *Trac-Trends in Analytical Chemistry*, vol. 21, pp. 526-533, 2002.

[17] G. Kibelka, T. Short, D. Fries, and J. Edkins, "Underwater Mass Spectrometry for Detection of VOCs and Dissolved Gases," Center for Ocean Technology, Applied Microsystems Ltd., unpublished.

[18] R. T. Short, D. P. Fries, M. L. Kerr, C. E. Lembke, S. K. Toler, P. G. Wenner, and R. H. Byrne, "Underwater mass spectrometers for in situ chemical analysis of the hydrosphere," *Journal of the American Society for Mass Spectrometry*, vol. 12, pp. 676-682, 2001.

[19] R. Camilli, D. Sakellariou, B. Foley, C. Anagnostou, A. Mallios, B. Bingham, R. Eustice, J. Goudreau, and K. Katsaros, "Investigation of Hydrothermal Vents in the Aegean Sea using an Integrated Mass Spectrometer and Acoustic Navigation System onboard a Human Occupied Submersible," in *38th Congress Commission Internationale pour l'Exploration Scientifique de la Mer Mediterranee*. Istanbul, Turkey, 2007.

[20] W. Bleakney and J. A. Hipple, "A New Mass Spectrometer with Improved Focusing Properties," *Physical Review*, vol. 53, pp. 521-528, 1938.

[21] R. Camilli, T. Duryea, J. Buchner, and J. Whelan, "TETHYS: an in-situ mass spectrometer for cabled observatories," in *4th International Workshop on Scientific Use of Submarine Cables and Related Technologies*. Dublin Castle, Dublin Ireland, 2006.