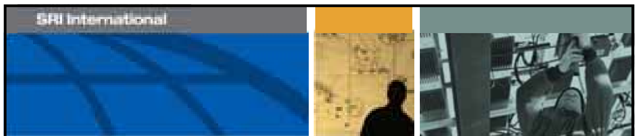


In Situ Membrane Introduction Mass Spectrometry for Subsea Characterization of Light Hydrocarbons

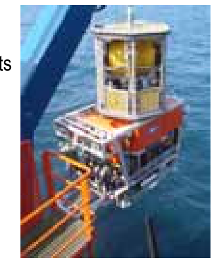
R. Timothy Short, Strawn K. Toler, Ryan J. Bell, Andres M. Cardenas-Valencia, Jwalant Dholakia, and Steve Untiedt

9th Workshop on Harsh Environment Mass Spectrometry

St. Pete Beach, FL
18 September 2013

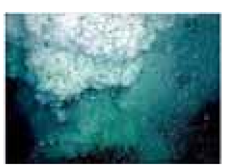
Outline

- Need for in-water chemical measurements of light hydrocarbons
- Membrane introduction mass spectrometry (MIMS)
  - Underwater MIMS systems
  - Detection of light hydrocarbons
- Examples of underwater MIMS deployments
  - 2D mapping in Santa Barbara Channel
    - Towed deployment with inverse modeling
    - Pumped surface water analysis
  - Deep water real-time hydrocarbon "sniffing"
  - Sea floor detection of methane at MC118
  - Osaka University Robot tests in Suruga Bay
  - Autonomous vehicle tests in Tampa Bay
- Summary



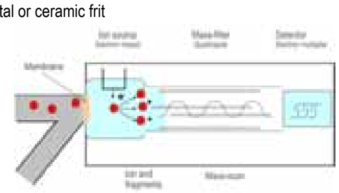
In-Water Chemical Surveys and Inspections

- Establish background levels of hazardous compounds
  - Underwater surveys on manned or unmanned vehicles near drilling platforms and pipelines
- Characterize natural hydrocarbon seep
  - Autonomous underwater vehicle (AUV) or remotely operated vehicle (ROV) surveys
- Detect elevated concentrations of leaking chemicals
  - Time series monitoring
  - Periodic surveys (AUV, ROV, or Towed)
- Inspect suspected leaks
  - ROV survey of location
  - Real-time feedback to find source



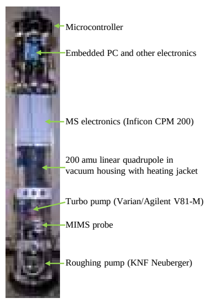
Membrane Introduction Mass Spectromery is Ideal

- MIMS can monitor multiple analytes simultaneously
- Introduction of analytes from the water column
  - Passive (except for sample pumping and heating, if desired)
  - Polydimethylsiloxane (PDMS) and Teflon are most common choices (hydrophobic)
  - Provides sensitive detection of dissolved gases and volatile organic compounds
- Need to mechanically support membrane (hydrostatic pressure)
  - Porous metal or ceramic frit



SRI MIMS Adapted for Deep Water In Situ Analysis

High pressure membrane interface

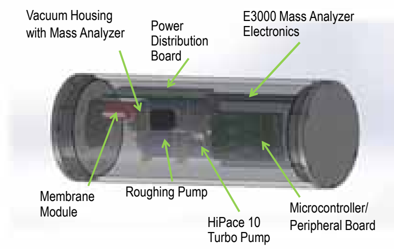


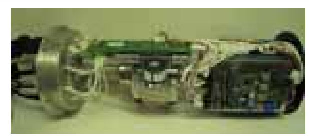
Older SRI MIMS system

New, Smaller SRI MIMS Instrument

Specifications

- Power: 60-80 Watts
- Voltage: 24 VDC
- Dimensions:
  - Length: 64 cm
  - Diameter: 24 cm
- Weight:
  - In air: 35 kg
  - In water: 5 kg neg.
- Depth rating: 2000 m





SRI MIMS is AUV Deployable (Bluefin BF-12)

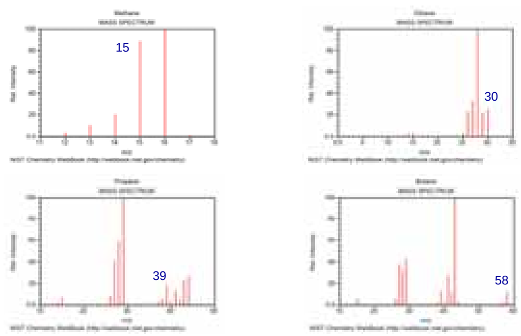
AUV is easily deployed

Typical MIMS Diagnostic Ions

M/Z VALUE	COMPOUND	ISOTOPIC FORM
15	Methane (CH_4)	$^{12}CH_3$ Fragment
28	Nitrogen (N_2)	$^{14}N^{14}N$
30	Ethane (C_2H_6)	Various
32	Oxygen (O_2)	$^{16}O^{16}O$
34	Oxygen (O_2) Hydrogen Sulfide (H_2S)	$^{16}O^{18}O$ $H_2{}^{32}S$
39	Propane (C_3H_8)	Various
40	Argon (Ar)	^{40}Ar
44	Carbon Dioxide (CO_2)	$^{12}C^{16}O^{16}O$
58	Butane (C_4H_{10})	Various
78	Benzene (C_6H_6)	Various
92	Toluene (C_7H_8)	Various
106	Xylene (C_8H_{10})	Various
128	Naphthalene ($C_{10}H_8$)	Various

- Full mass scans or selected ion monitoring
- A total of 40 m/z values can be monitored with a cycle time of ~7 seconds

The Best Diagnostic Ions are Often Not the Most Intense



NIST Electron Impact Mass Spectra of Hydrocarbons

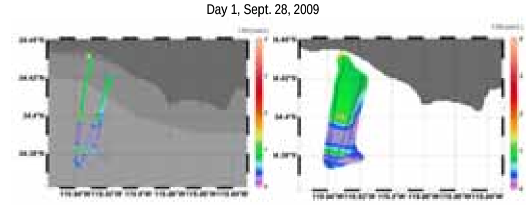
Methane Distributions in the Santa Barbara Channel Determined using In Situ MIMS Analyses (Sept. 2009)

- Surface tow surveys of dissolved gases and light hydrocarbons with MIMS in Santa Barbara (SB) Channel
- MIMS mounted on custom towfish along with conductivity, temperature, and depth (CTD) sensor and battery vessel
- Communicated with instrument through a tethered Ethernet connection

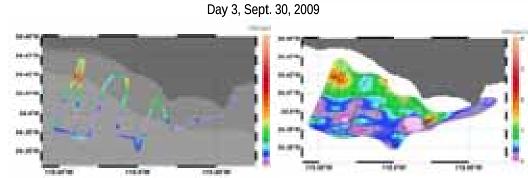
Ira Leifer (UCSB) and Michael Schlueter (AWI)

Transects and Interpolated Methane Data in SB Channel

Day 1, Sept. 28, 2009



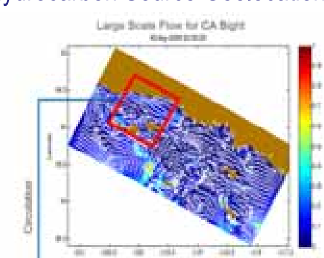
Day 3, Sept. 30, 2009



Inverse Modeling for Hydrocarbon Source Geolocation

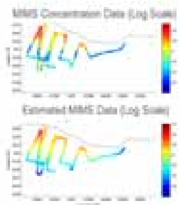
- Inputs
  - MIMS SB Channel methane concentration data
  - Ocean circulation (velocity and turbulence fields) for region of interest
- Output
  - Methane source field

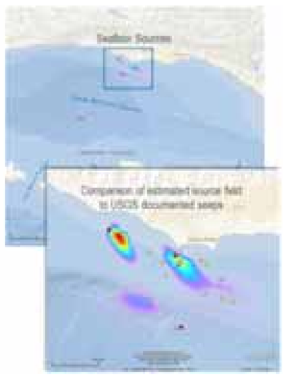
David Walker, Michelle Cardenas
Tom Almeida, Andres Cardenas



Inverse Model Results for Seep Location Estimates

- Estimated seafloor source field is consistent with documented seeps
- Quantitative comparisons are good except for infrequent high observed concentrations





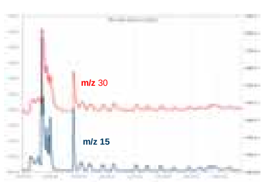
New SB Channel Data – Trilogy Seep (Nov. 2012)

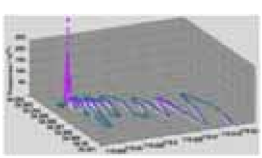
- Towfish with side scan sonar, fluorometer, and pump to direct water to shipboard MIMS
- Towfish navigated through seep area and performed vertical profiles to ~20 m
- *Real-time MIMS analysis showed presence of methane, ethane, propane, and butane*
- Plots show ion intensity (A) vs. time (hr:min)

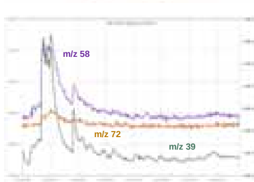
with Bubbleology Research International and Terrasond

Tent Seep MIMS Light Hydrocarbon Data

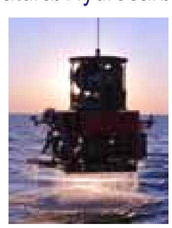
- Crossed through Tent Seep and then "criss-crossed" downstream of seep
- Used MIMS signal to reverse boat direction
- *Detected methane, ethane, propane, butane and pentane*



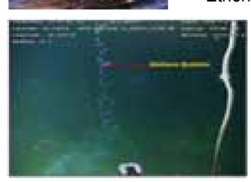


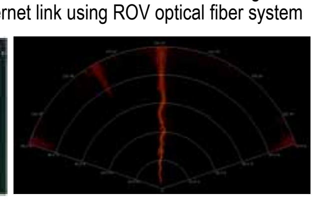


Natural Hydrocarbon Seep Characterization (2011)

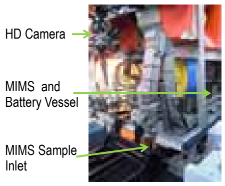


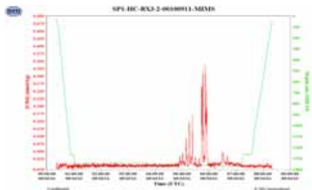
- ROV surveys of hydrocarbon seeps with MIMS in the Gulf of Mexico to depths >1900 m
- MIMS mounted on a Schilling ROV along with acoustic instrumentation, HD video camera, and other instruments (CTD and dissolved oxygen (DO) sensor)
- Communication with instrument through an Ethernet link using ROV optical fiber system



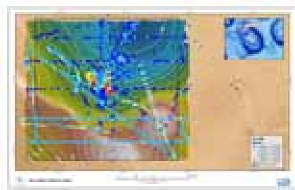


MIMS Used to Map Hydrocarbon Distributions



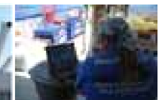


MIMS data synchronized with ROV navigation system to create 2-D and 3-D maps of methane and other light hydrocarbon concentrations near seeps



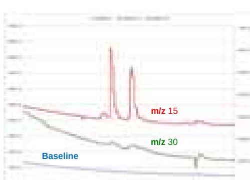
Lander Deployment at MC118 with SRI MIMS (July 2013)

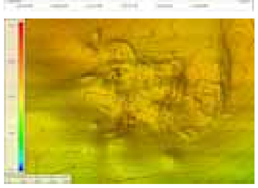
- *R/V* Pelican cruise with Gulf of Mexico Hydrates Research Consortium to characterize gas chemistry and biological communities near hydrocarbon seeps at MC118
- Integrated MIMS with University of Georgia (UGA) Lander, HD video, 30-filter microbe collection system, CTD and DO sensors
- *Detected methane near the sea floor at 880 m depth*
- Real-time HD video of sea floor for seep visualization



Geo-referenced MIMS Methane Data at MC118

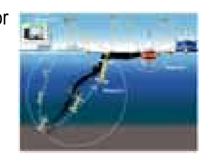
- Lander drifted past suspected seep several times (HD video showed bubbles on previous dive)
- An ultra-short baseline (USBL) navigation system recorded 3D position of the Lander
- HD video did not show bubbles during this dive
- *Both methane and ethane were detected at two locations*
- MIMS data will be plotted on geo-referenced bathymetric map to show location of seeps

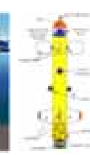




Osaka University Robot Deployment (March 2013)

- Osaka University underwater robot for autonomous tracking and monitoring of spilled plumes of oil and gas (SOTAB-1) *Prof. Naomi Kato*
- Multi-sensor system (MIMS, CTD, DO, fluorometer, camera) with real-time acoustic communication
- MIMS data will be used to guide robot to track plumes of hydrocarbons
- First at sea-trials in Suruga Bay had multiple communication problems
- *Next deployment in Gulf of Mexico in December 2013 near MC252*



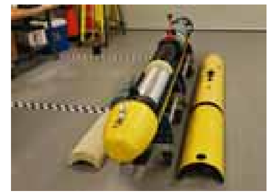
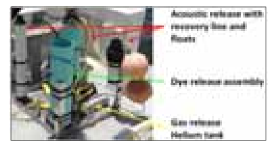


Robot Deployment in Suruga Bay, Japan

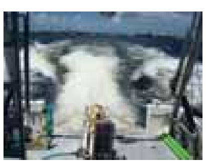


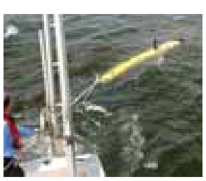

AUV Deployment of MIMS in Tampa Bay (Aug. 2013)

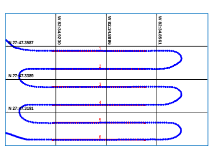
- Integrated UMS, CT sensor with SRI Bluefin BF-12 AUV to demonstrate performance of AUV with UMS and new equipment in Tampa Bay
- Successful deployment of UMS for "lawn mower" pattern survey
- *Next deployment plan is to add a fast optical sensor and deploy along with an artificial plume generator with fluorescence dye and helium gas as proxies for components of a natural seep*

AUV Deployment with UMS in Tampa Bay

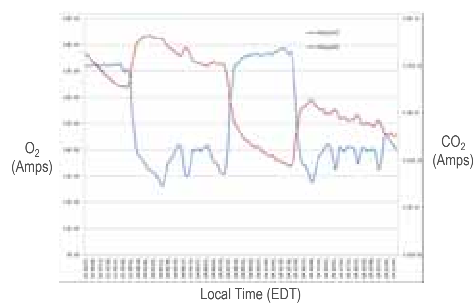




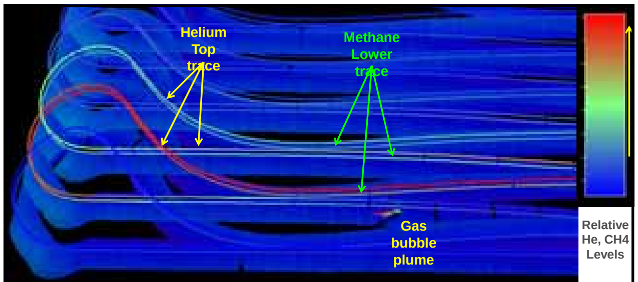


- AUV depth control within 6 cm 1σ (leg 2)
- Command depth 3.0 m, mean 2.93 m
- 10 m line spacing tested (20 m line spacing shown)

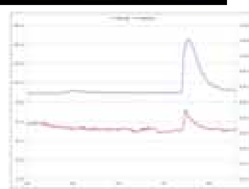
Tampa Bay AUV Dive MIMS Time Series Data



MIMS data showed inverse relationship of O_2 and CO_2 concentrations typical of biological activity in the water (O_2 mass 32 – blue, CO_2 mass 44 – red)



- Pure helium and 2.5% methane in air leaked into water column from plume generator
- Two surveys with AUV (different depths)
- BlueView multibeam MB1350 detected bubble stream and MIMS detected helium and methane



Summary

- In-water chemical measurements are needed and can be used to detect and characterize subsea hydrocarbon leaks and seeps
- Underwater MIMS systems can fill this need by providing concentration information for methane, ethane, propane, butane, and pentane (in near real-time for some platforms)
- Applications are diverse
  - Establish background levels of light hydrocarbons
  - High-resolution 2D and 3D maps of dissolved gas and light hydrocarbon concentrations near seeps and potential leak areas
  - AUV deployments for wide area surveys
  - ROV deployments for inspection and characterization of leaks and seeps
  - Time series monitoring (detect leaks or monitor ecosystem health)
- MIMS data can be used to guide survey patterns

Acknowledgements

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- Eric Roach (EGS Americas)
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- Funding received from Osaka University (ERC 12-021 Rev 5)
- R/V Pelican ship time provided by the Gulf of Mexico Hydrates Research Consortium (University of Mississippi)

Thank You!

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