SRI International

Mobile and Miniature Mass Spectrometers for Marine and Space Applications

Tim Short

Marine and Space Sensing

Space and Marine Technology Laboratory

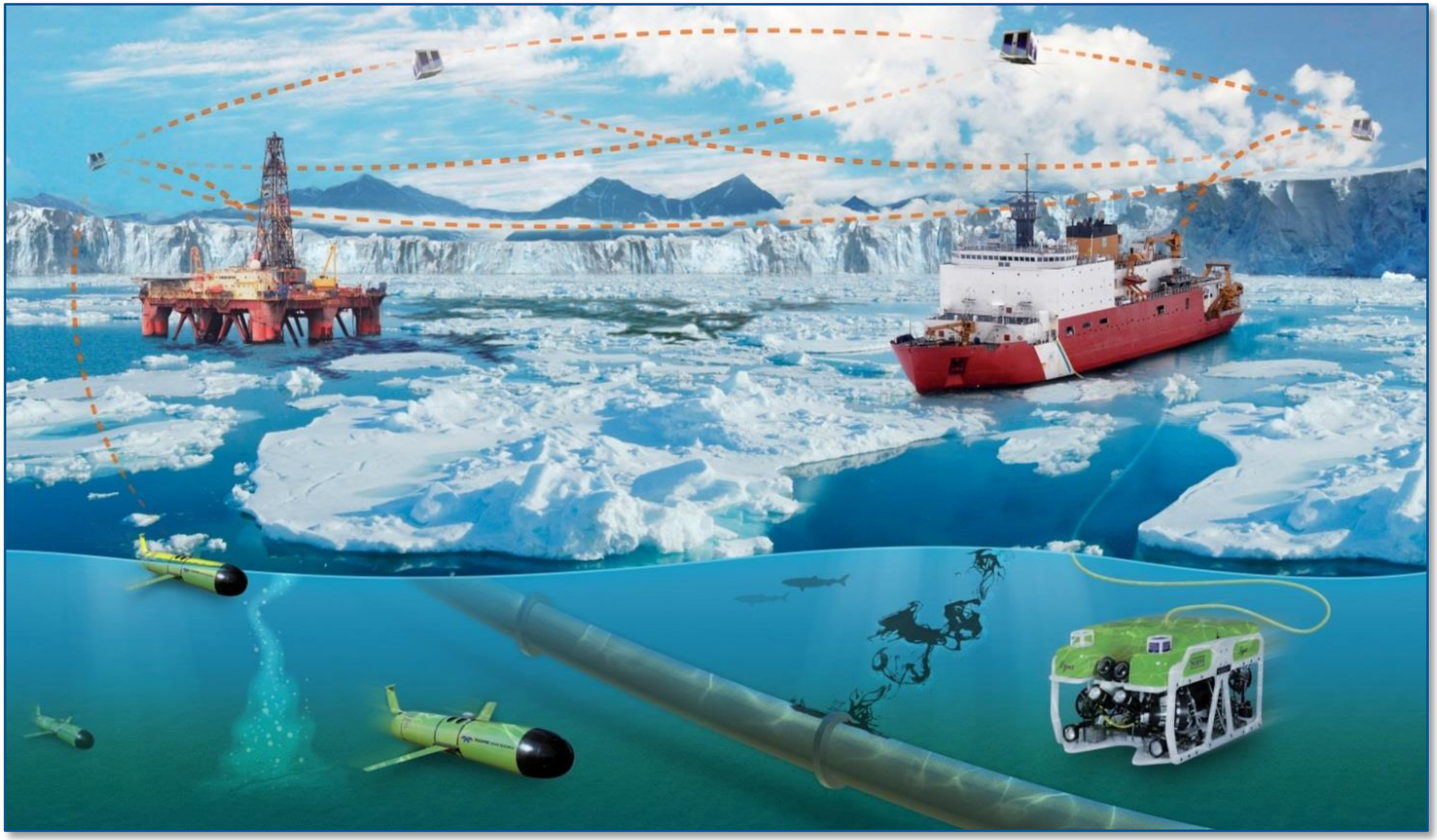
Scripps Institution of Oceanography

08 January 2015

Marine and Space Sensing Group

Tailored Sensing Solutions

Providing tailored sensing solutions to customers who require actionable information from harsh, remote, and access-limited environments



In Situ Capabilities Enabled by Novel SRI Instrumentation

- Mass spectrometry (MS)
  - *Continuous monitoring of dissolved gases and volatile organic compounds (VOCs)*
- Refractive index sensor
  - *Low-cost, distributed, continuous salinity and density measurements*
- Absorption and fluorescence spectrometry
  - *Continuous high-sensitivity measurements of nutrients, trace metals, and pH*
- Sediment porewater sampler
  - *Monitor biogeochemical processes in sediments to assess ecosystem health*
- Reagentless pH adjustment tool
  - *Autonomous adjustment of pH without use of corrosive reagents*
- Antifouling films
  - *Enable long-duration deployment of sensor systems*

Outline for Mobile and Miniature Mass Spectrometers

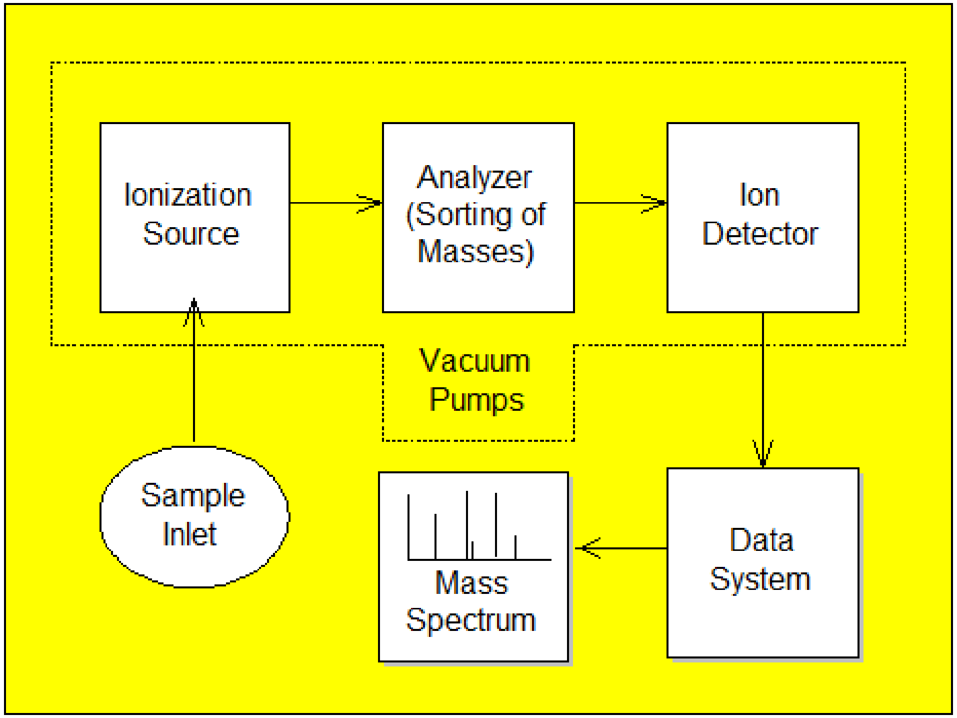
- Challenges for in situ mass spectrometry in extreme environments
  - Common for deep ocean and space
  - Specific for deep ocean or space

- Need for underwater MS – oil and gas
  - Underwater membrane introduction MS (MIMS)
  - Detection of light hydrocarbons
- Examples of underwater MIMS deployments
  - 2D hydrocarbon mapping in Santa Barbara Channel
  - Deep-water, real-time hydrocarbon "sniffing" in Gulf of Mexico
  - Osaka University robot tests in Suruga Bay
  - Autonomous gas plume detection in Tampa Bay

- Micro-MS Development for Space
  - Prototype for cometary missions
  - Design details and considerations
- Summary

Primary Challenge for Mobile Mass Spectrometry

- Mass analysis is performed in a vacuum system
  - Requires small, rugged, low-power vacuum pumps – battery powered
  - Analytes must be introduced into the vacuum system from the “real world”
  - Ions (charged atoms or molecules) must be formed for mass analysis



Basic components of a mass spectrometer

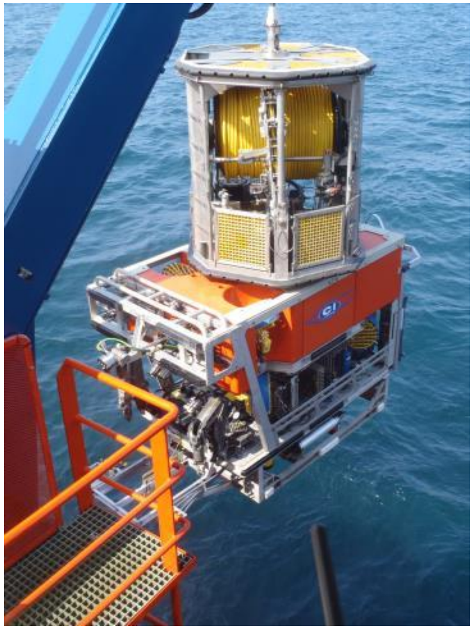
Needs and Challenges for MS in Extreme Environments

- Common needs for deployment in the deep ocean and space
  - Low size, weight, and power (SWaP)
  - Rugged construction (tolerant of vibration, impact, and temperature variations)
  - Capable of remote control or autonomous operation
  - Transmission of data to a "home base" located in a less extreme environment
- Specific needs for deployment in deep ocean environments
  - Introduction of analytes from high pressure to vacuum (~1 atmosphere / 10 meters)
  - Corrosive environment and instruments are subject to biofouling
  - Limited bandwidth communication through water unless hardwired
- Specific needs for deployment in deep space environments
  - Weight and power limitations are much more stringent
  - High acceleration during launch
  - Extreme temperature variations and ionizing radiation
  - Delayed communication from long distances of transmission

Marine Applications for the Oil and Gas Industry

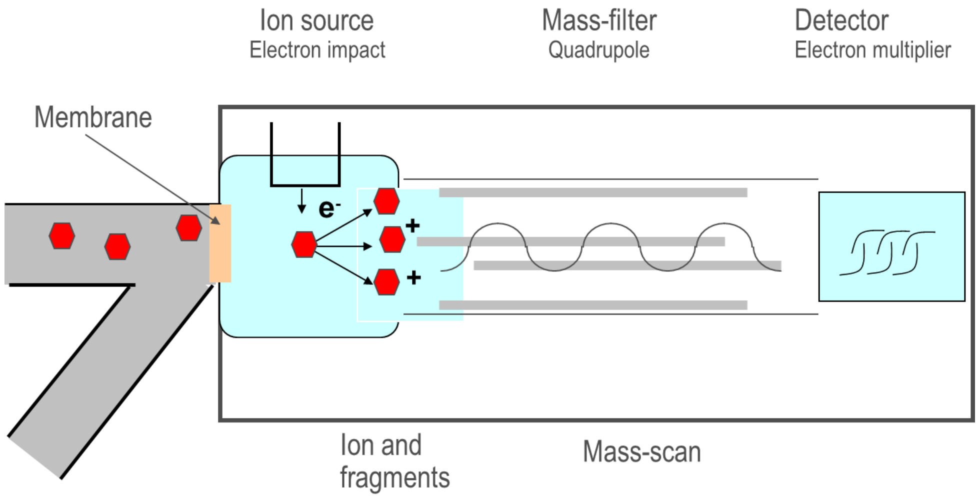
In-water Chemical Surveys for Oil and Gas Companies

- Establish background levels of hazardous compounds
  - Underwater surveys on manned or unmanned vehicles near drilling platforms and pipelines
- Characterize natural hydrocarbon seeps
  - Remotely operated vehicle (ROV)
  - Autonomous underwater vehicle (AUV)
- 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

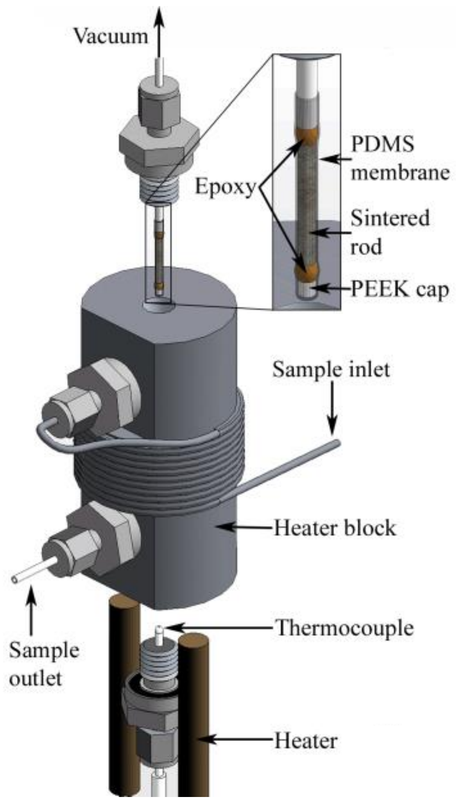


Membrane Introduction Mass Spectromery is Ideal

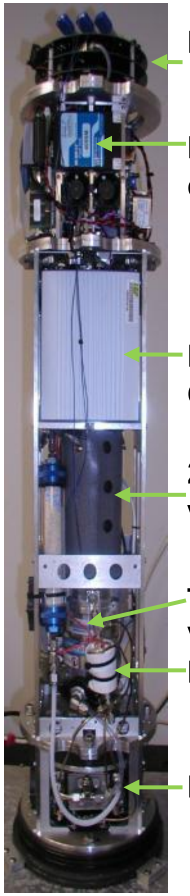
- MIMS can monitor multiple analytes simultaneously
- Introduction of analytes from the water column
  - Passive (except for sample pumping and heating, if desired)
  - Polydimethylsiloxane (PDMS) and Teflon are the most common choices (hydrophobic)
  - Sensitive detection of dissolved gases and volatile 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



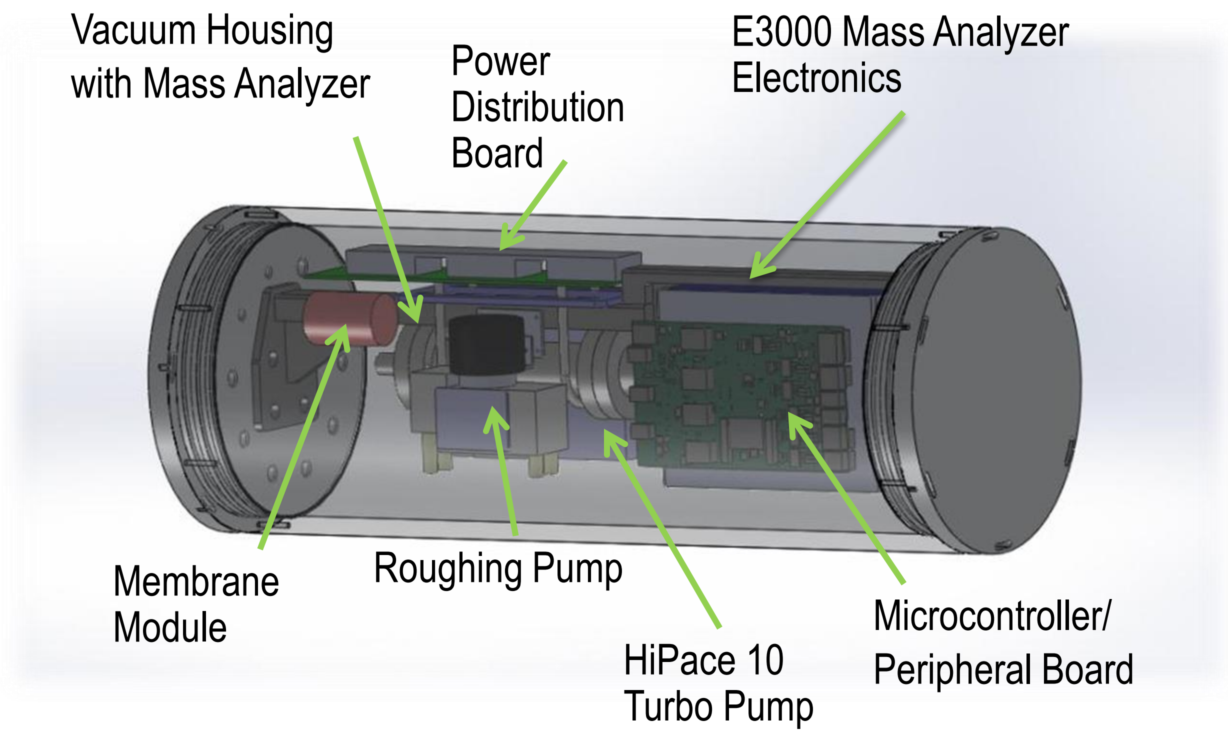
Older SRI MIMS system

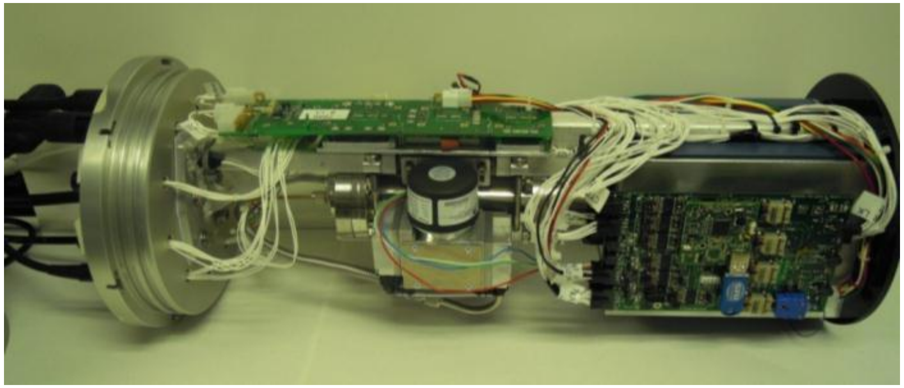
SRI Underwater MIMS Instrument

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

Licensed to Spyglass Technologies, Inc. in 2013



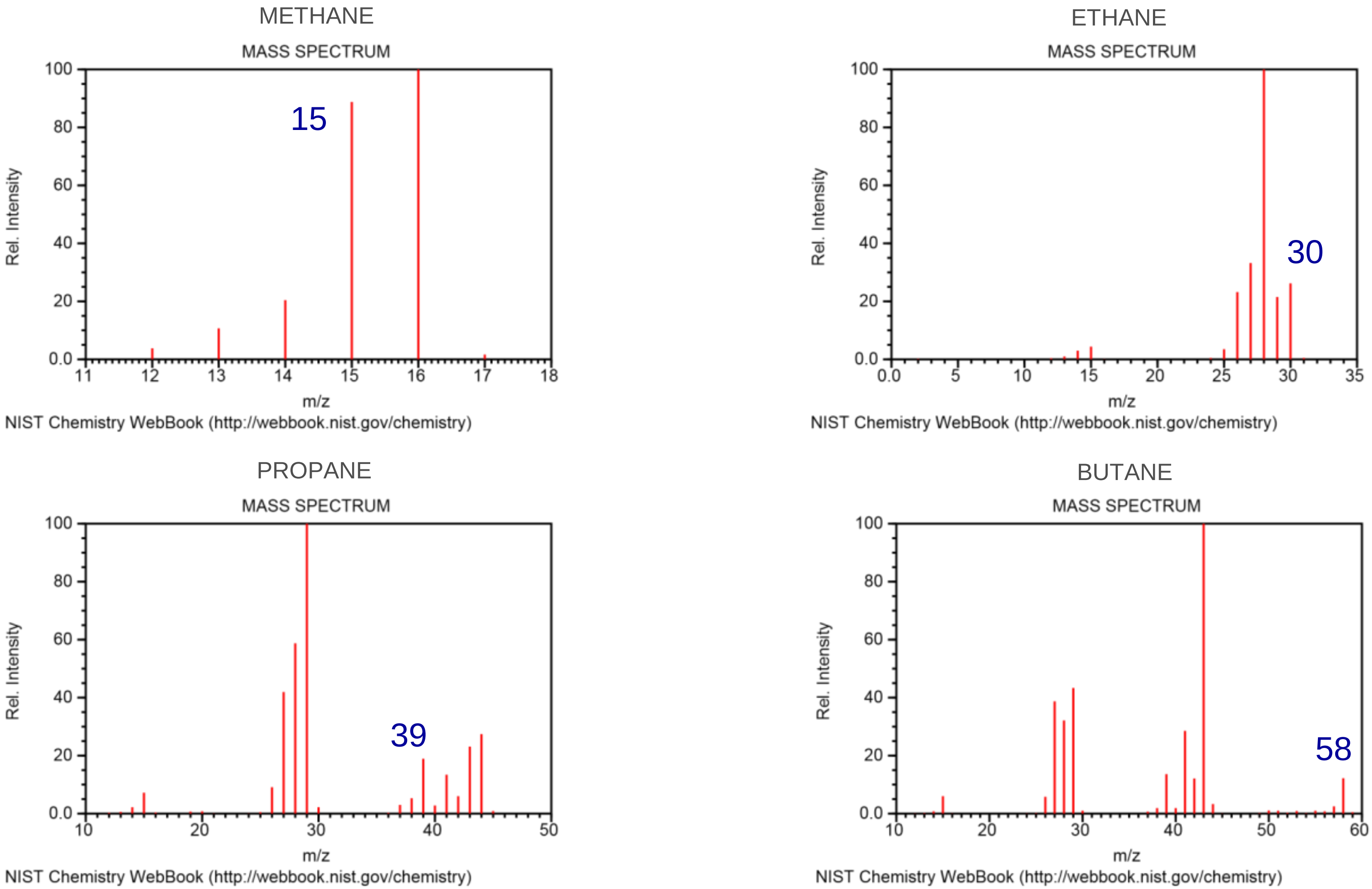


Typical MIMS Diagnostic Ions

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 45 m/z values can be monitored with a cycle time of ~5 seconds

The Best Diagnostic Ions are Often Not the Most Intense



NIST Electron Impact Mass Spectra of Light Hydrocarbons

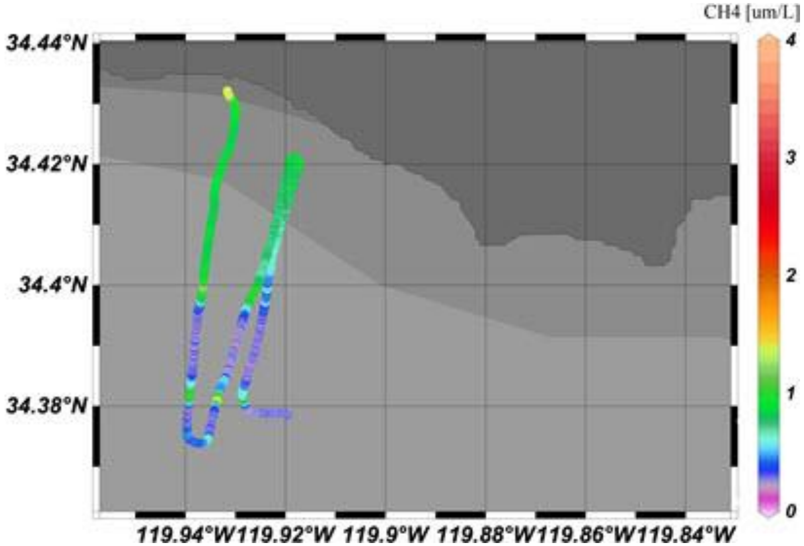
Methane Distributions in the Santa Barbara Channel Determined Using In Situ MIMS Analyses (Sept. 2009)

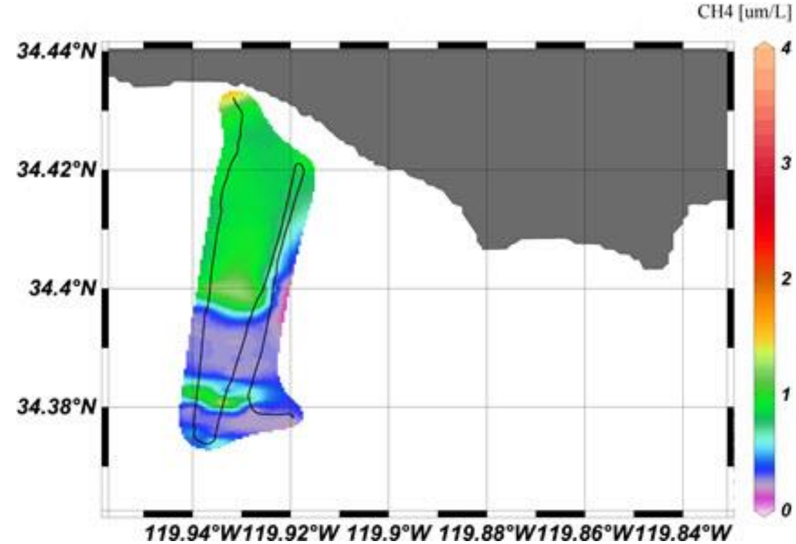
- Surface tow surveys of dissolved gases and light hydrocarbons with MIMS in Santa Barbara (SB) Channel
- MIMS mounted on custom towfish along with conductivity, temperature, and depth (CTD) sensor and battery vessel
- Communicated with instrument through a tethered Ethernet connection

Ira Leifer (UCSB) and Michael Schlueter (Alfred Wegener Institute, Germany)

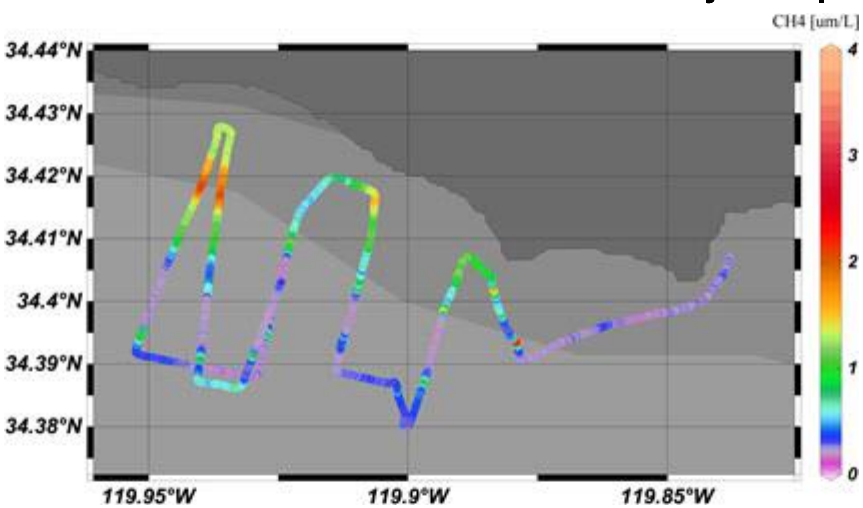
Transects and Interpolated Methane Data in SB Channel

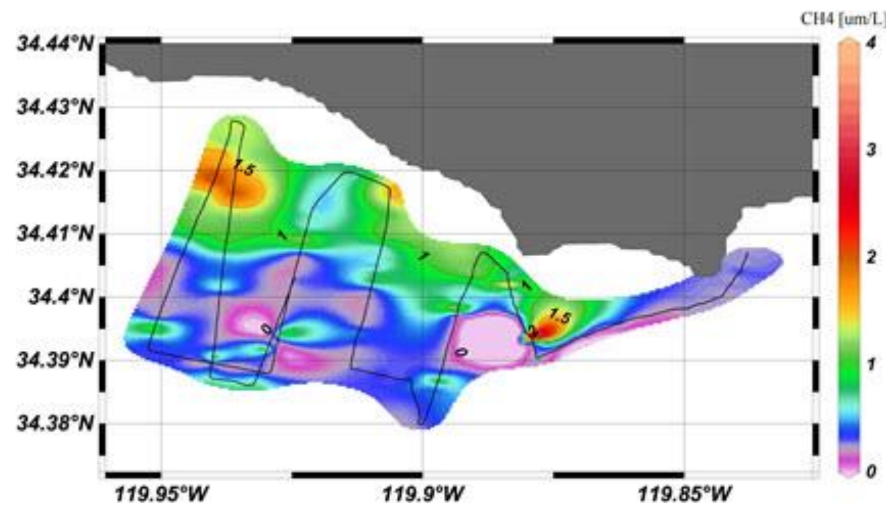
Day 1: Sept. 28, 2009





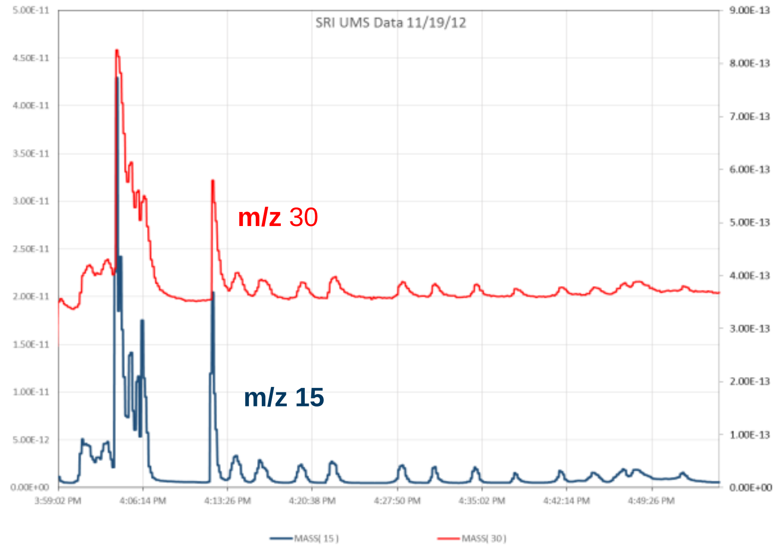
Day 3: Sept. 30, 2009

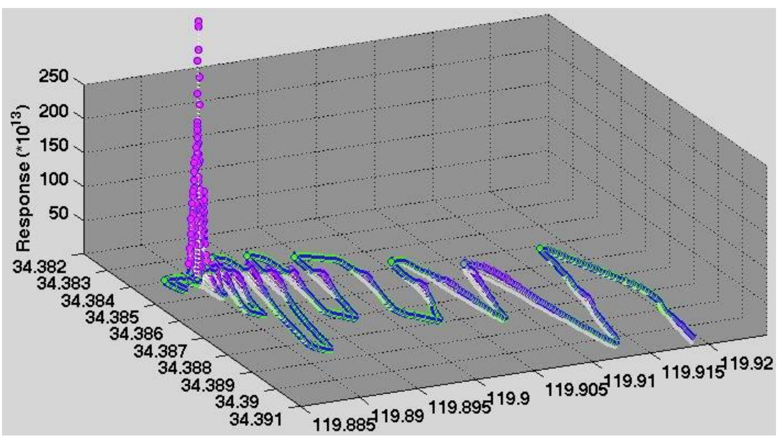


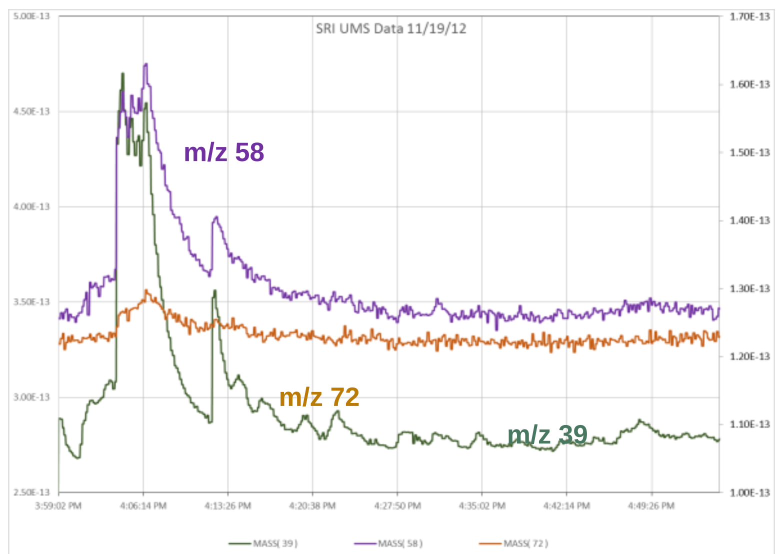


Tent Seep MIMS Light Hydrocarbon Data (Nov. 2012)

- Crossed through tent seep and then “crisscrossed” downstream of seep
- Used MIMS signal to reverse boat direction
- *Detected methane, ethane, propane, butane, and pentane*



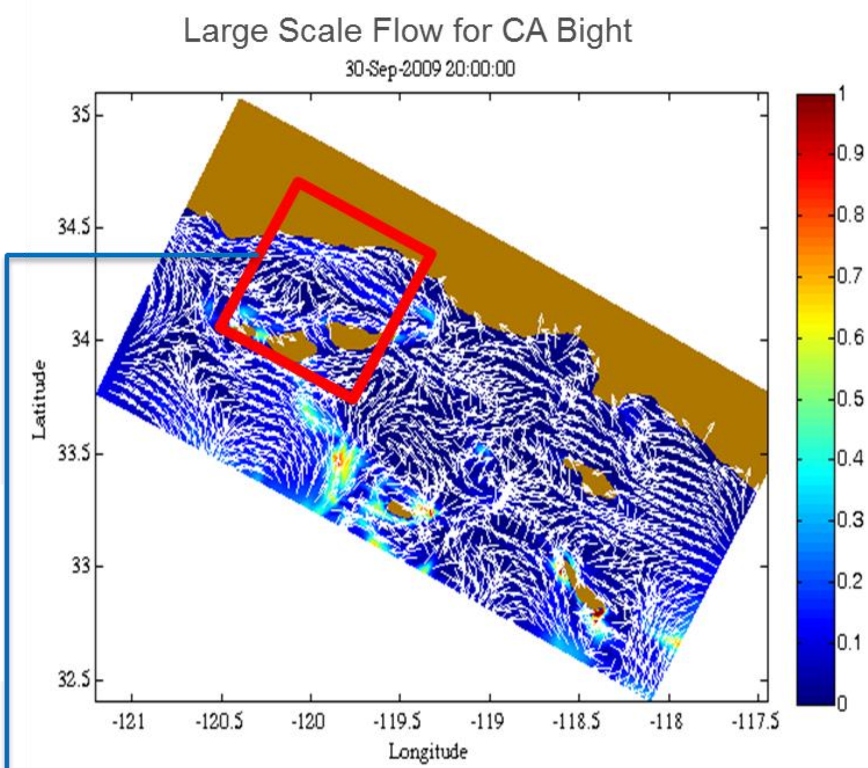




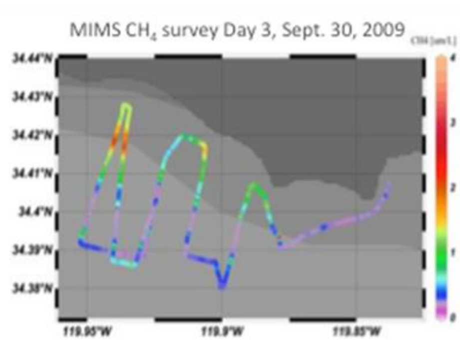
Inverse Modeling for Hydrocarbon Source Geolocation

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

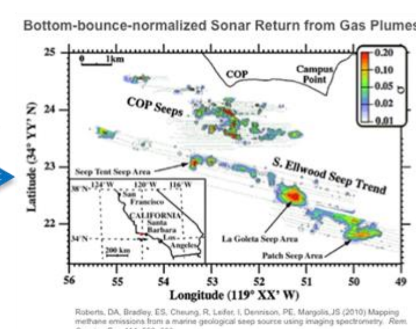
David Walker, Michelle Cardenas, Tom Almeida, & Andres Cardenas



Circulation

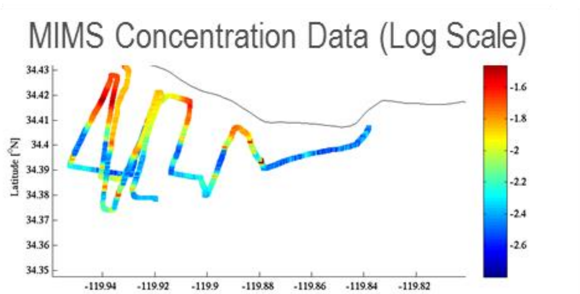


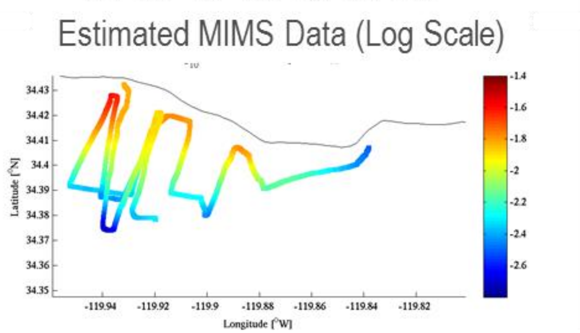
Observations → Inverse Model Algorithm → Estimate of Source Field

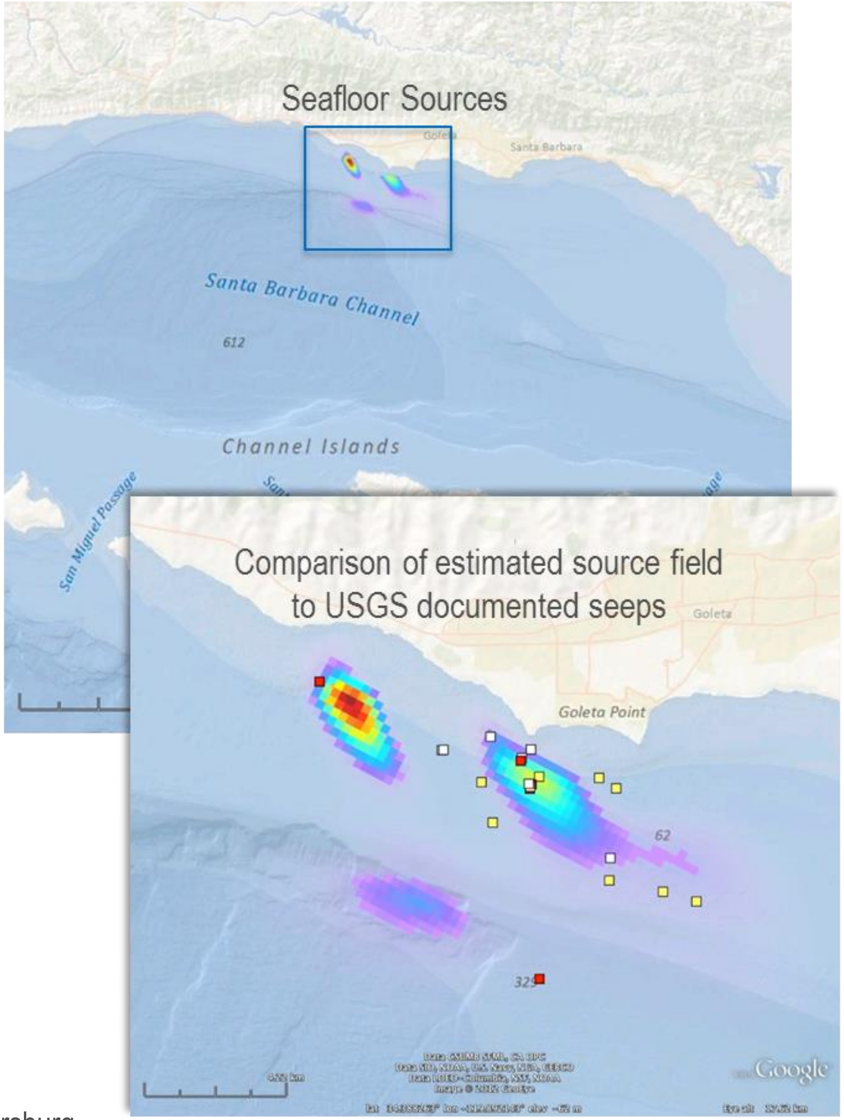


Inverse Model Results for Seep Location Estimates

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

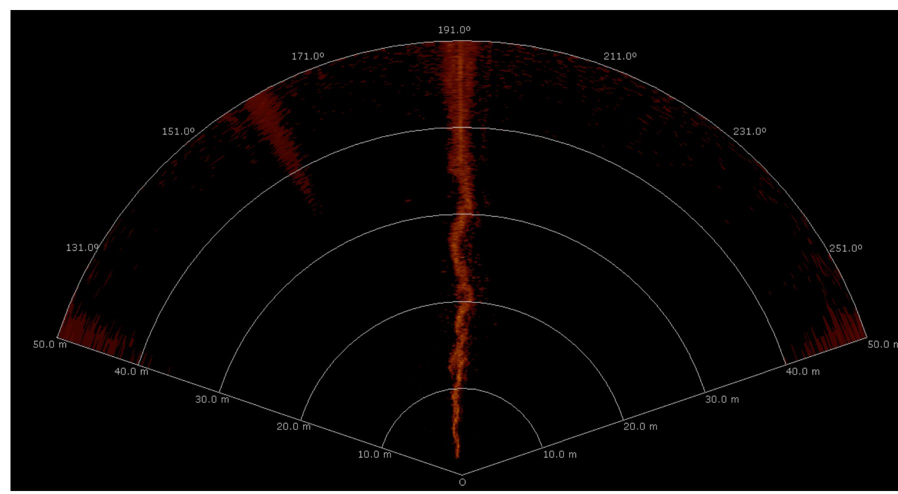






Natural Hydrocarbon Seep Characterization (2011)

- 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

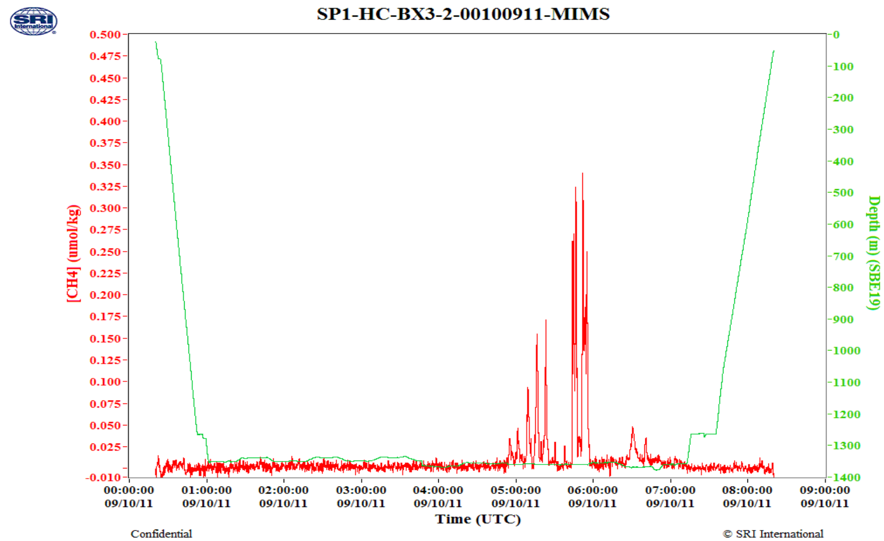


MIMS Used to Map Hydrocarbon Distributions

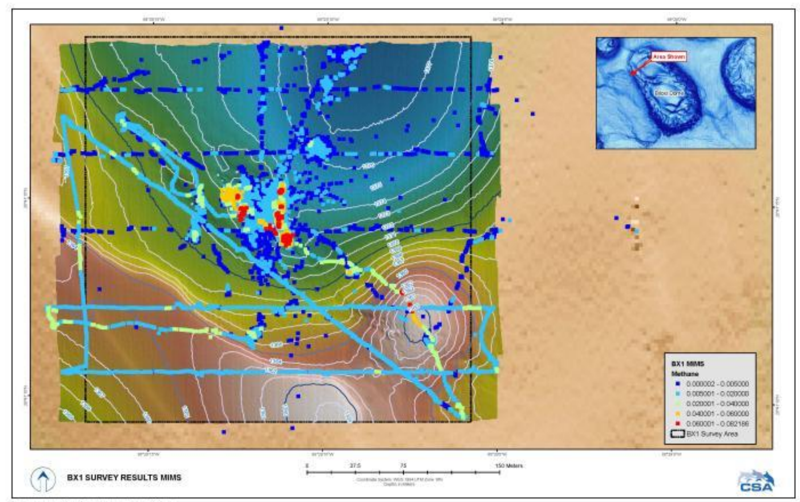
HD Camera

MIMS and
Battery Vessel

MIMS Sample
Inlet

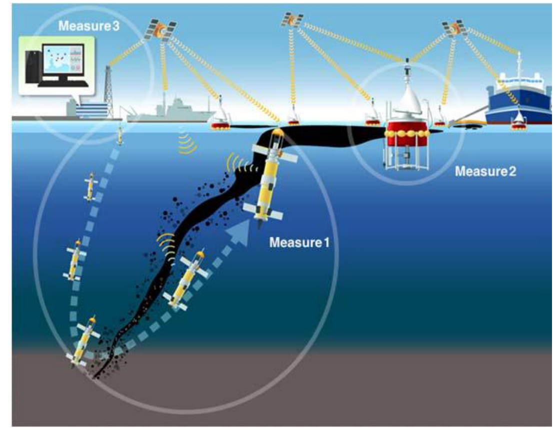


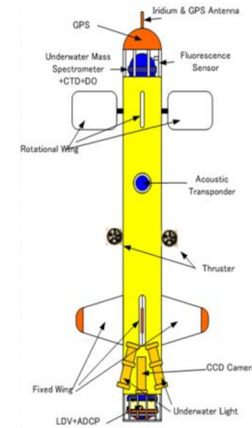
MIMS data synchronized with ROV navigation system to create 2D and 3D maps of methane and other light hydrocarbon concentrations near seeps

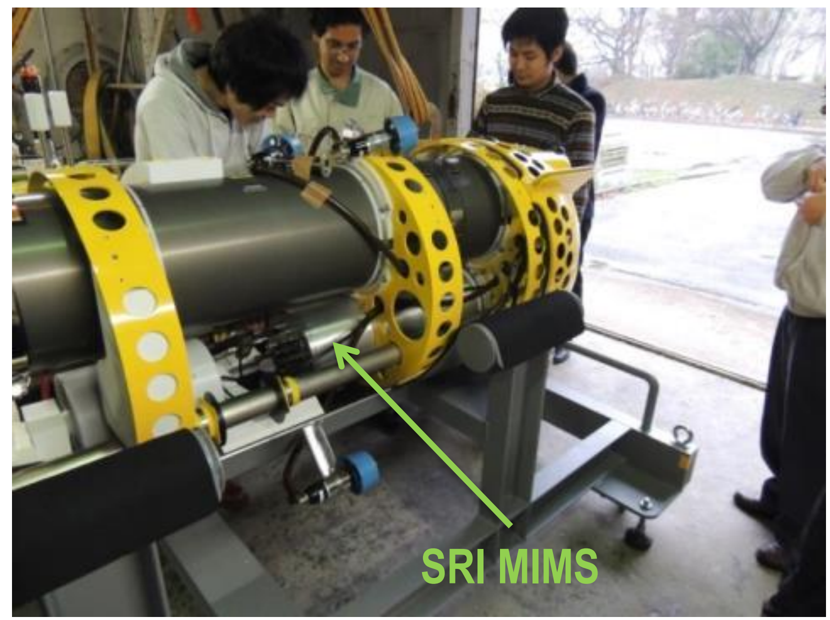


Osaka University Robot Deployment (March 2013)

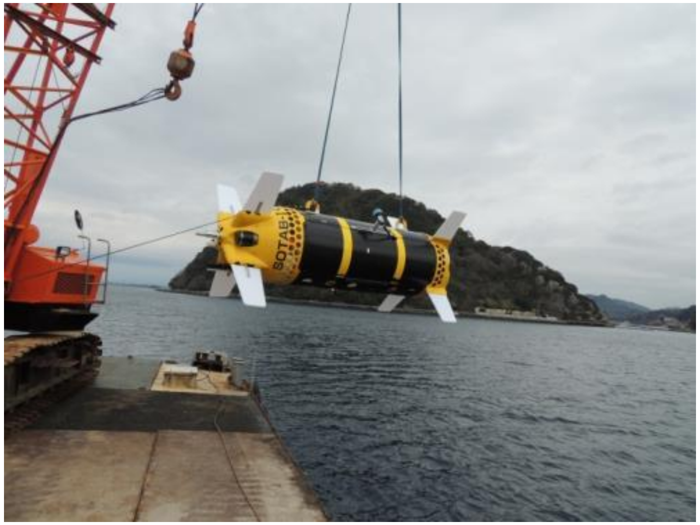
- Osaka University underwater robot for autonomous tracking and monitoring of spilled plumes of oil and gas (SOTAB-1)
  Prof. Naomi Kato
- Multi-sensor system (MIMS, CTD, DO, fluorometer, camera) with real-time acoustic communication
- MIMS data will be used to guide robot to track plumes of hydrocarbons
- First at-sea trials in Suruga Bay and Gulf of Mexico revealed a few communication problems
- Next sea trial planned in August 2015 off the coast of Joetsu in Sea of Japan





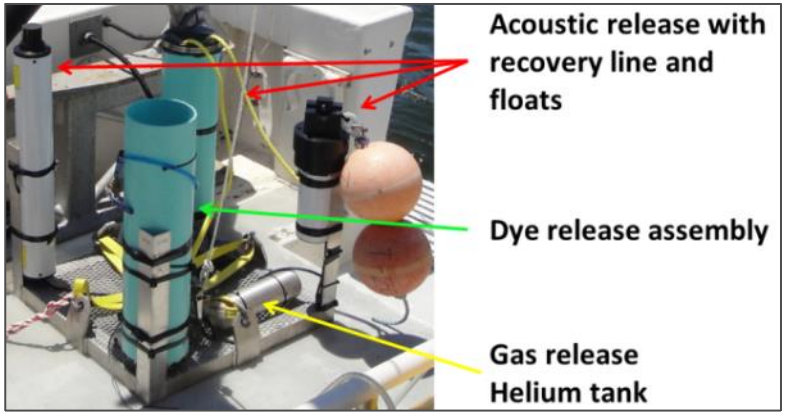


Robot Deployment in Suruga Bay, Japan

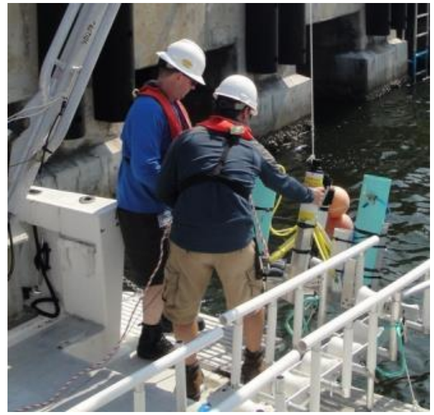


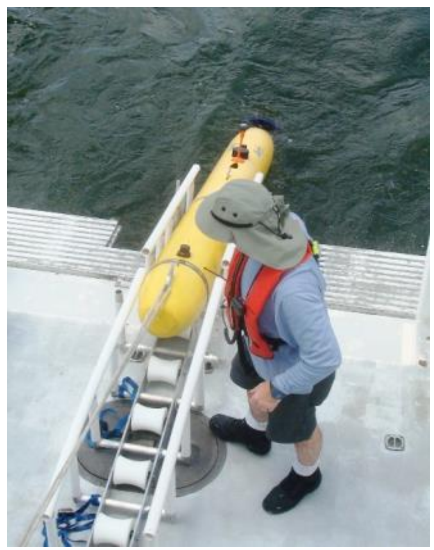
AUV Deployment of MIMS in Tampa Bay (Aug. 2013)

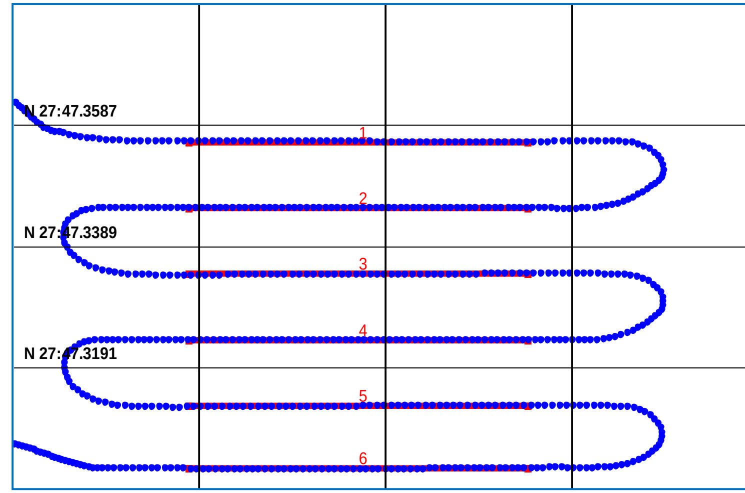
- Integrated MIMS, CT sensor, fluorometer, and 3D sonar system into SRI's Bluefin BF-12 AUV
- Demonstrates performance with MIMS and sensor suite in Tampa Bay
- Successful deployment of MIMS for "lawnmower" pattern survey
- AUV-based sensor suite deployed along with an artificial plume generator
- Fluorescence dye and helium gas as proxies for components of a natural seep



AUV Deployment “Lawnmower” Pattern Tested



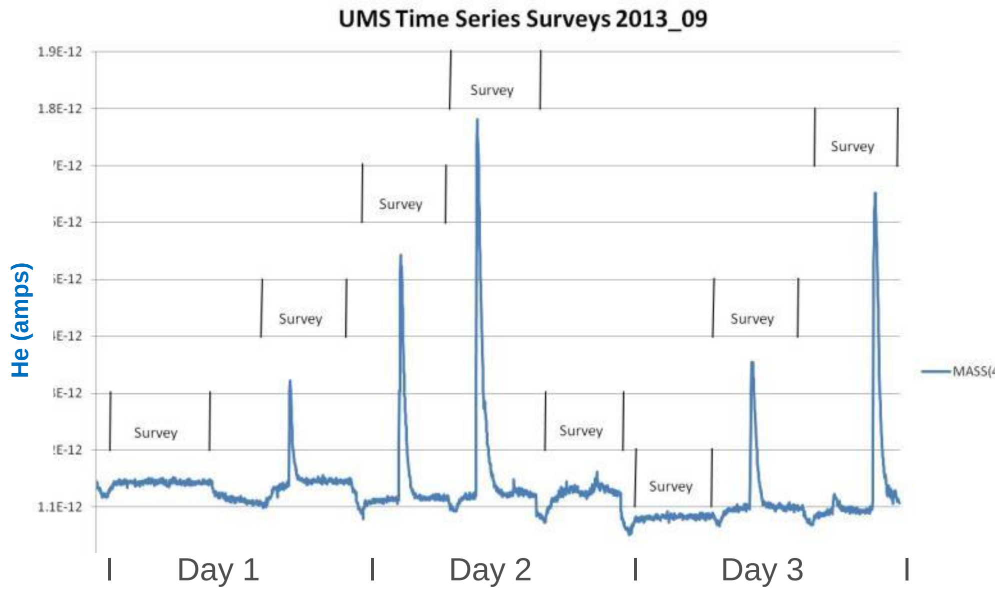


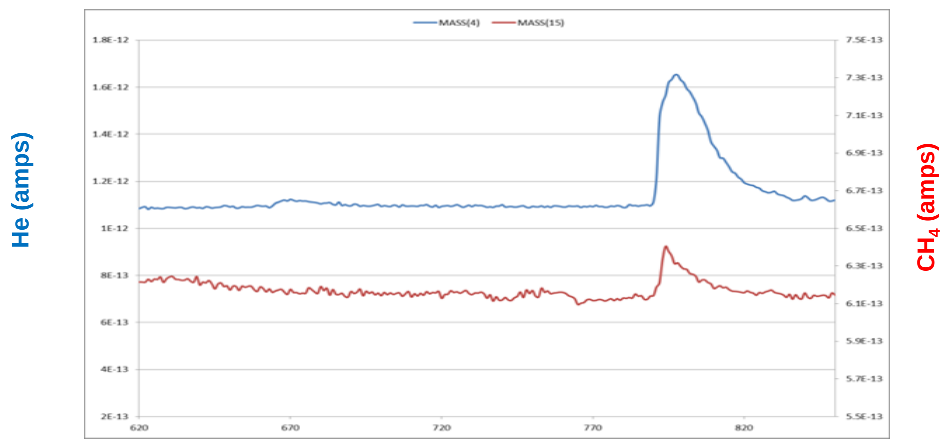


- AUV depth control within 6 cm 1σ (leg 2)
- Command depth 3.0 m, mean 2.93 m
- 10 m line spacing tested (20 m line spacing shown)

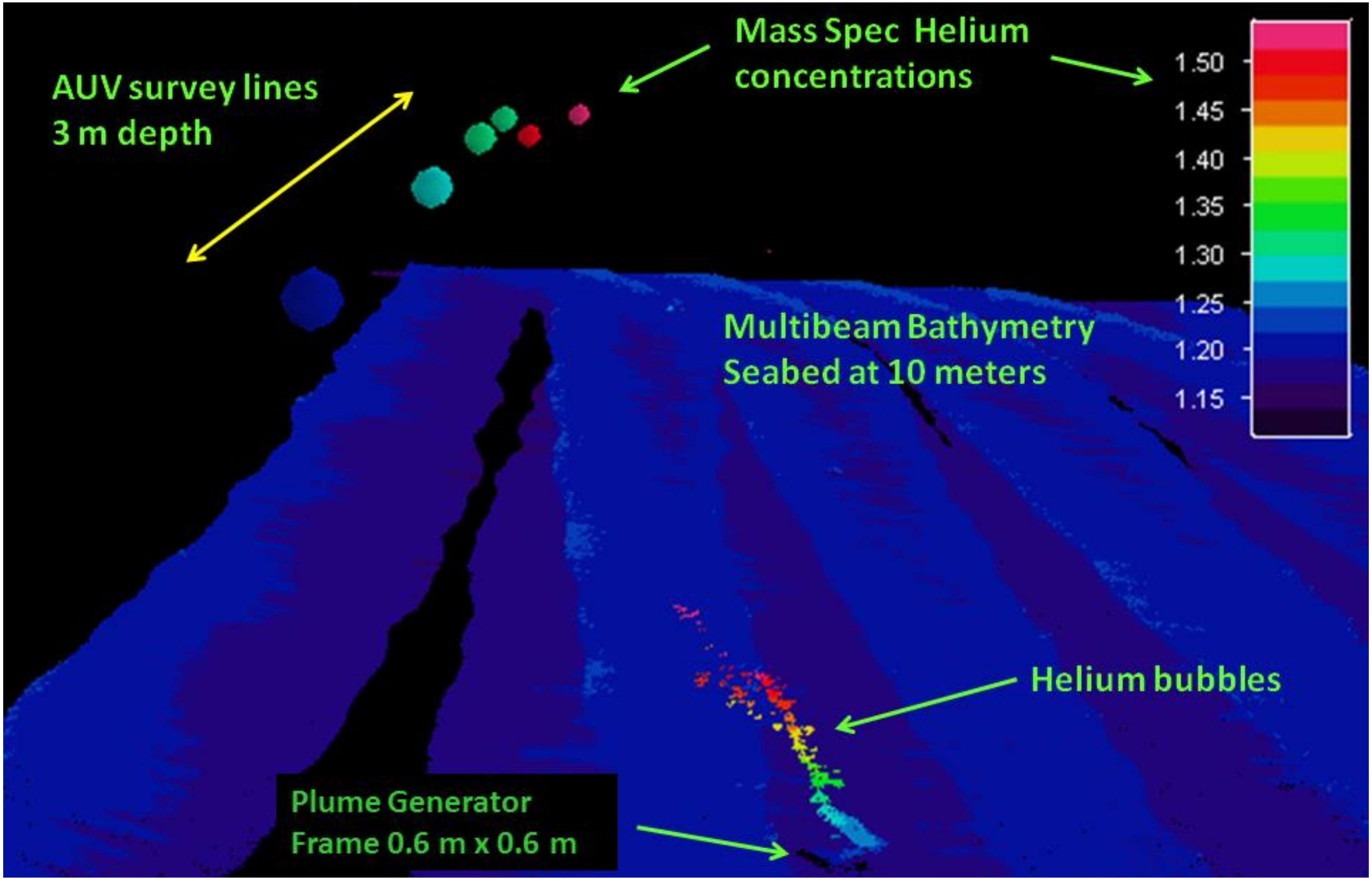
Successfully Detected Helium on Multiple Surveys

- Three days of AUV "lawnmower" surveys with plume generator
- Helium released from both gas cylinders on Days 1 and 2 (except first survey on Day 1)
- Helium detected on most surveys
- Helium and 2.5% methane in air released on Day 3; both helium and methane detected on last survey
- Fluorescein was not detected by C7 fluorometer





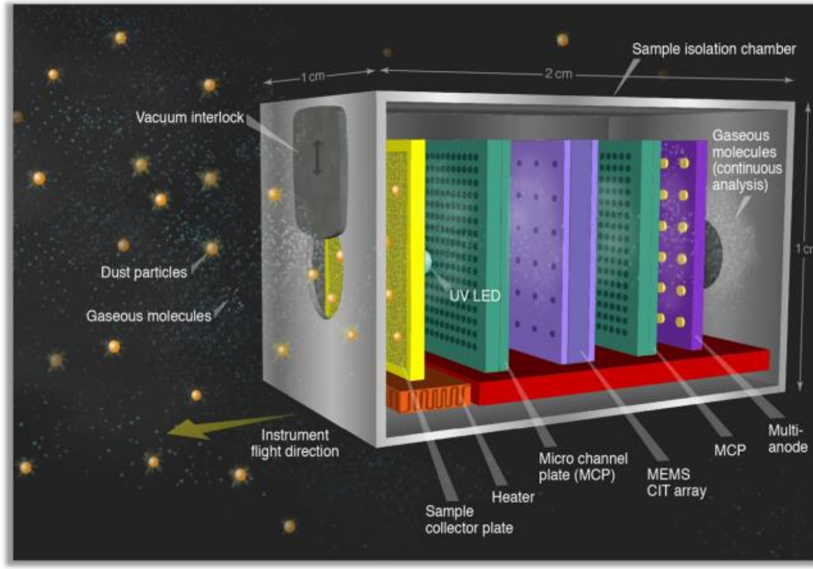
Fledermaus 3D Viewer Display of Multi-sensor Data

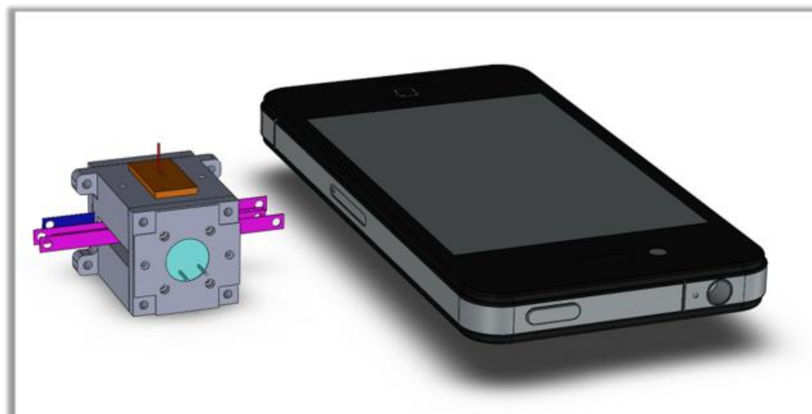


Space Application for NASA

Micro-fabricated MS (μ-MS) for Cometary Missions

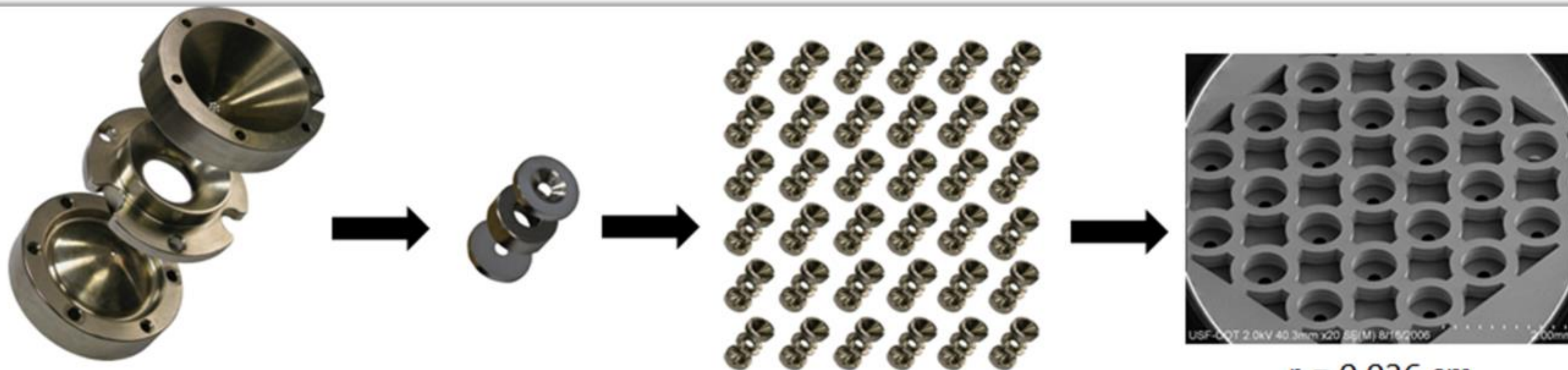
- Comets carry interstellar and nebular materials pivotal to understanding prebiotic molecules that could have initiated life on Earth
- Extremely miniature MSs are optimal for space applications due to less stringent power and vacuum pump requirements
- Goal is to demonstrate use of microelectromechanical systems (MEMS) technology for fabrication of a μ-MS for the chemical exploration of comets to detect low-molecular-weight biomarkers





SRI and Goddard Space Flight Center (GSFC)

Rationale for Fabricating μ-MS Arrays in Silicon



r_0= 0.036 cm

QIT r_0= 1 cm

- Hyperbolic ion trap used in most commercial instruments
- Difficult to machine
- High voltages required

CIT r_0= 0.2 cm

- Cylindrical ion trap (CIT)
- Similar trapping potential
- Easier to further miniaturize

Array Approach

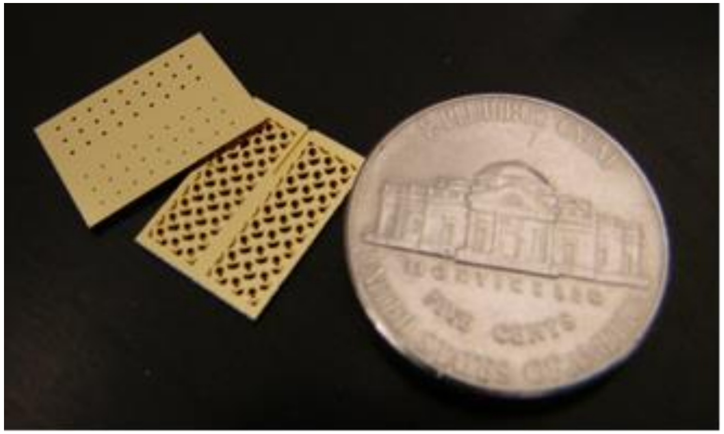
- Regain sensitivity by increased trapping volume
- Parallel analysis through multiple sub-arrays

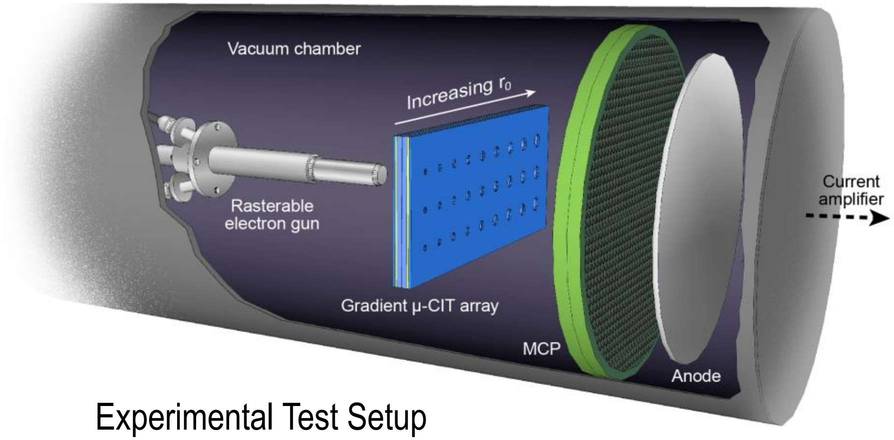
Microfabrication Approach

- High machining precision
- Batch fabrication leads to cost effective and repeatable process
- High uniformity across the micro (μ)-CIT array

- MEMS processing provides a method to create arrays of sub-millimeter-diameter cylindrical ion traps (CITs) with high precision in silicon
- A custom-designed broad-beam electron source and detector system are also being developed for simultaneous operation of μ-CITs

Validation of μ-CIT Operation in a Prior Effort

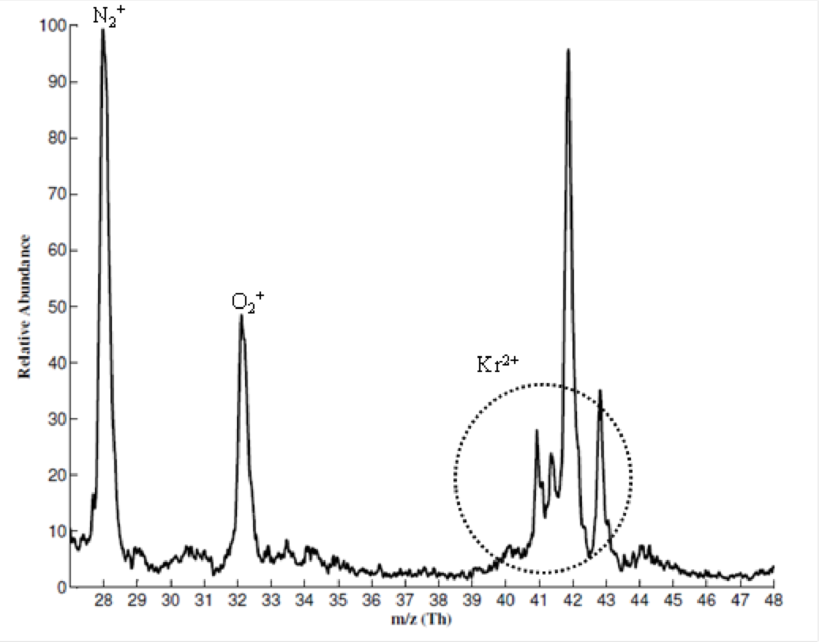




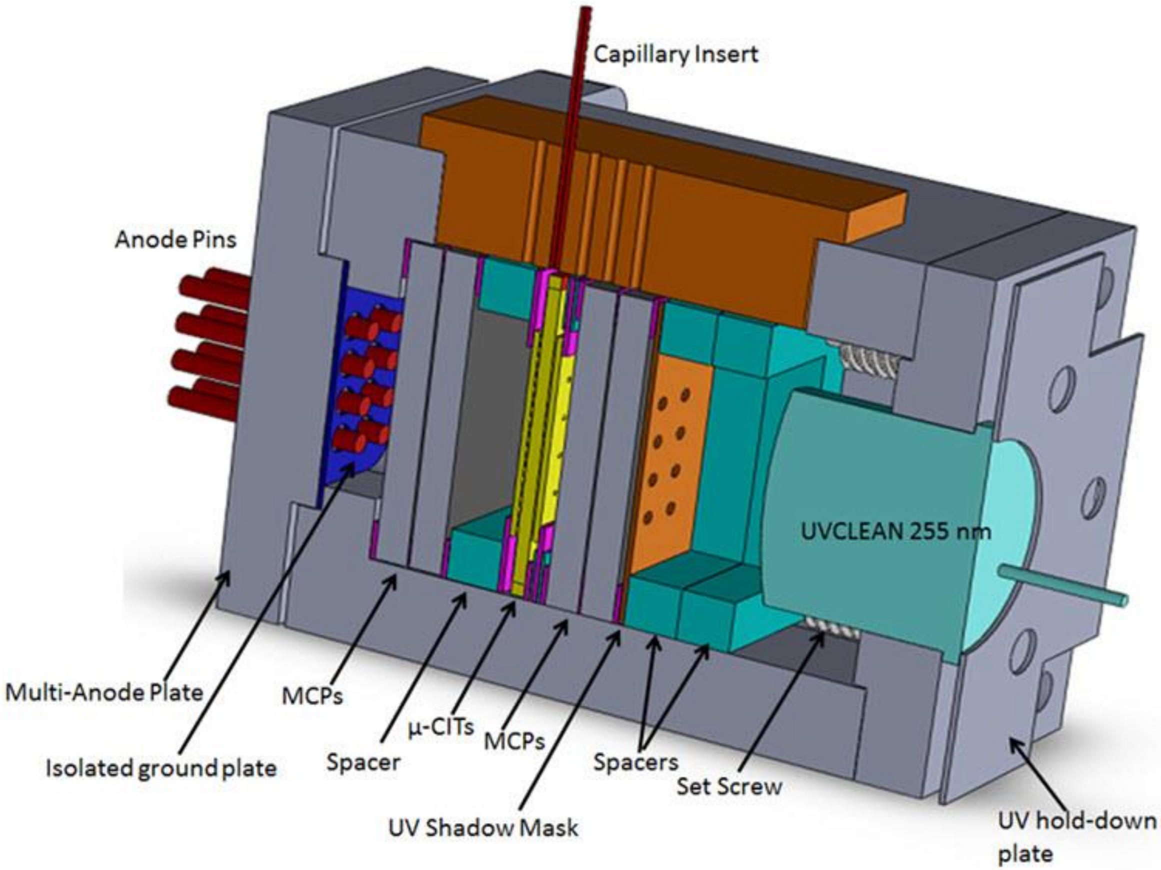
Experimental Test Setup

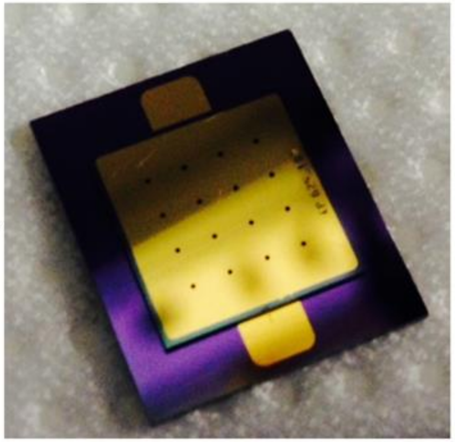
- An array of 54 μ-CITs was fabricated in silicon
- Each μ-CIT was tested individually using a rasterable electron gun
- Spectra with a mass resolution of approximately 1 atomic mass unit were obtained

International Journal of Mass Spectrometry 371 (2014) 17–27

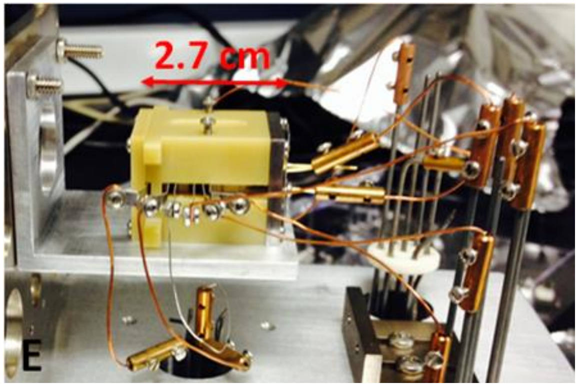


μ-MS Design Concept - ULTEM Package for Prototype



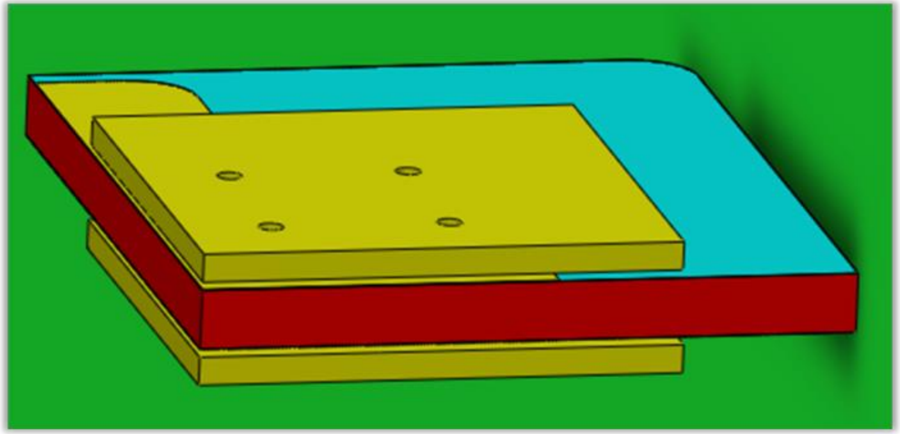


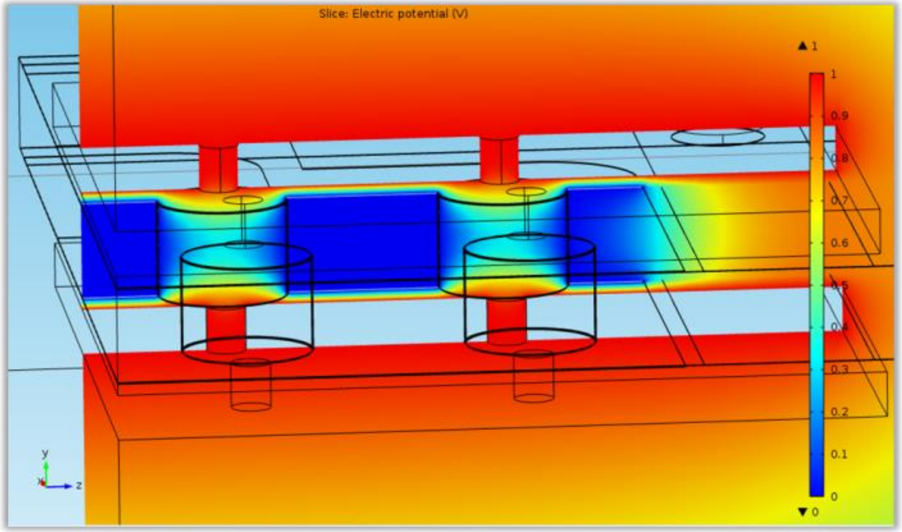
Final μ-CIT array (4x4)



µ-CIT Chip Capacitance Modeling in COMSOL

- Target µ-MS total power consumption is 4 W for a 0-250 amu mass range
- Low capacitance of the µ-CIT array chip is crucial for low-power operation
- A 1/4th model of the actual size µ-CIT array was simulated using COMSOL to calculate expected chip capacitance (C_p)
- Calculated total C_p is in the range of 20-30 pF



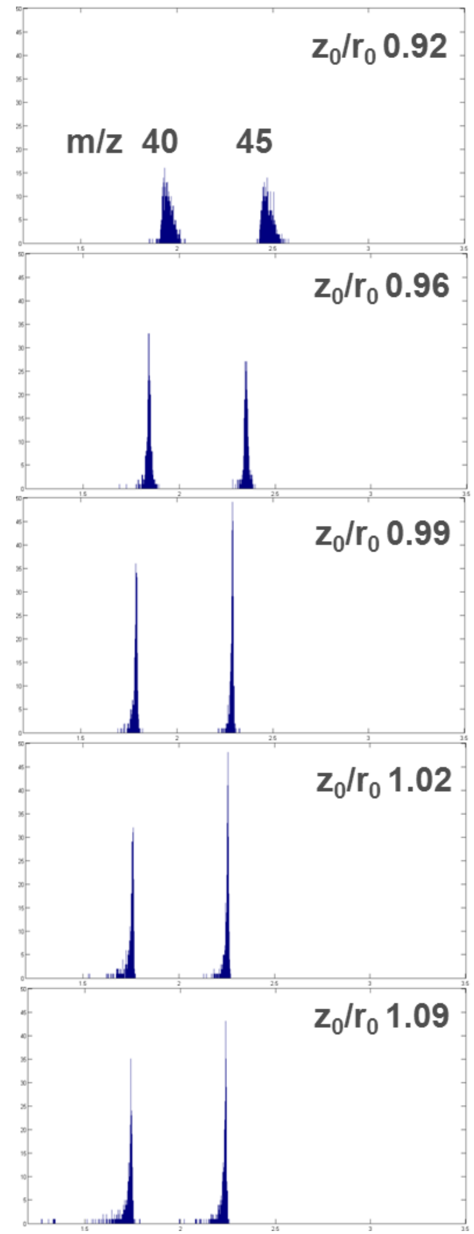


Simulations Guide Design of μ-CIT Axial-to-radial Dimension Ratio (z_o/r_o)

- Individual μ-CITs were modeled and simulated in SIMION
- Simulations were performed with

  z_0 = 262.5 μm (fixed)

  r_0 = 275 – 350 μm
- Optimized mass resolution is for $z_0/r_0 \approx 0.99$
- Ultra-high-vacuum test setup constructed (10^{-10} Torr)
- Initial results from a stainless steel μ-CIT array in the ULTEM package
- Experimental testing of silicon μ-CIT array chips to begin soon (fabricated at GSFC)



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 deployment 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
- μ-MSs are ideal for space flight applications
  - Significant SWaP savings
  - Can provide previously infeasible MS capabilities for some missions
- Prototype μ-MS for cometary missions
  - Initial design, simulations, and micro-fabrication nearly complete
  - Experimental testing on μ-CIT arrays from GSFC to begin soon

The Ocean is a Harsh Environment

"If you put an instrument in the ocean and you get it back…that's a gift"

Professor John Noakes
University of Georgia
Center for Applied Isotope Studies

Acknowledgements

- Friso van Amerom, Strawn Toler, A. Chaudhary, Andres Cardenas, Michelle Cardenas, Jwalant Dholakia, and Rich Parniawski (SRI Marine and Space Sensing, St. Petersburg, FL)
- John Kloske, Steve Untiedt, Mark Ryder, and Charles Cullins (SRI Marine Operations, St. Petersburg, FL)
- David Walker, Tom Almeida (SRI Communications, Radar, and Sensing, Ann Arbor, MI)
- Ryan Bell (DeFuca Analytics, formerly SRI)
- Keith VanGraafeiland (CSA Ocean Sciences)
- Ira Leifer (Bubbleology Research International)
- Michael Schlueter and Torben Gentz (Alfred Wegener Institute, Germany)
- Naomi Kato (Osaka University, Japan)
- Paul Mahaffy, Will Brinckerhoff, Daniel Glavin, Tomoko Adachi, Emily Barrentine, and Yun Zheng (NASA Goddard Space Flight Center [GSFC])
- Patrick Roman (Florida International University, formerly NASA GSFC)

Funding Acknowledgements

- CSA Ocean Sciences (Job 2400 PO 8172)
- Osaka University (ERC 12-021 Rev 5)
- NASA Astrobiology Science and Technology Instrument Development Program (#NNX12AQ26G)
- US Space and Missile Defense Command (2500-1193-00-A)

Thank You!

Tim Short

timothy.short@sri.com

727/498-6752

SRI International

Headquarters: Silicon Valley

333 Ravenswood Avenue
Menlo Park, CA 94025-3493
650.859.2000

St. Petersburg, FL Office

450 Eighth Avenue SE
St. Petersburg, FL 33701

Additional U.S. and international locations

www.sri.com

timothy.short@sri.com