Underwater Membrane Introduction Mass Spectrometers: Recent Developments and Deployments

R. Timothy Short\textsuperscript{1}, Strawn K. Toler\textsuperscript{1}, Ryan Bell\textsuperscript{1}, and Robert H. Byrne\textsuperscript{2}

\textsuperscript{1}SRI International, Marine Technology Program
\textsuperscript{2}University of South Florida, College of Marine Science
St. Petersburg, Florida

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Need for In-water Chemical Monitoring and Profiling

• Oceans and coastal regions
  – Biogeochemical studies
  – Hydrothermal vent analysis
  – Pollution monitoring and tracking
  – Bloom and plume diagnostics
  – Energy source discovery
    ▪ Methane and natural gas
    ▪ Oil reservoirs

• Harbors and internal waterways
  – Port safety and security
    ▪ Inadvertent chemical release
    ▪ Deliberate chemical release
  – Water supply monitoring
  – Ecosystem health (global climate change)
Approach of In Situ Analysis Provides Benefits

• Reduced sample contamination
• Increased sampling speed/density
• Real-time feedback
  – Rapid response
  – Adaptive sampling
  – Gradient mapping
• Self-directed sensors

Mass spectrometry allows sensitive simultaneous detection of multiple chemical species with high specificity
Portable Underwater Mass Spectrometry (UMS)

- Membrane introduction mass spectrometry (MIMS)
  - Simultaneous in situ detection of multiple analytes
  - Dissolved gases
  - Volatile organic compounds (VOCs)
  - Light hydrocarbons

- Recent developments
  - Dissolved inorganic carbon (DIC) measurements
  - Effect of salinity on MIMS measurements

- Recent deployments
  - Santa Barbara (SB) Channel: 2-D mapping
  - Gulf of Mexico: MC118 gas hydrates research
  - Gulf of Mexico: MC252 deep tow surveys
Membrane Introduction Mass Spectrometry (MIMS)

- **Ion source**: Electron impact
- **Mass-filter**: Quadrupole
- **Detector**: Electron multiplier
- **Ion and fragments**
- **Mass-scan**
High Pressure Membrane Assembly

• Flow-over membrane interface design
  – Polydimethylsiloxane (PDMS)

• Temperature regulated

• Pressure tested to 200 bar
  (2000 m depth)
Oceanic Carbon System Measurements Using Underwater Mass Spectrometry

- Method for measuring gaseous dissolved carbon dioxide (pCO₂) and total dissolved inorganic carbon (DIC) with UMS
  - Calculate total alkalinity and pH
- Dual membrane probe system (also possible with single membrane)
- Switching valve for rapid changing between acidified and non-acidified samples (DIC/ pCO₂)

![Diagram of Oceanic Carbon System Measurements Using Underwater Mass Spectrometry](image)

![Graph showing relationship between dissolved inorganic carbon and ion current](image)
DIC Linearity Experimental Setup

- Na$_2$CO$_3$ standards for DIC were infused with acid and analyzed by MIMS to determine instrumental linearity and precision.
MIMS Response to DIC is Linear over Expected Range

Baseline was subtracted prior to linear fit
Residuals indicate a possible small quadratic component

\[ DIC = \beta_1 I_{44} \]

@ 35°C, \( \beta_1 = 31.9 \pm 0.3 \)

@ 30°C, \( \beta_1 = 40.2 \pm 0.3 \)
Salinity Dependence Experimental Setup

- Acidified NaCl solutions of various ionic strength were simultaneously equilibrated with a gas standard (1% CO$_2$ in N$_2$)
  - Each sample was of equal fugacity, but varied in concentration
Salinity Dependence Results (PDMS Membrane)

- MIMS response is salinity-dependent and the degree of dependence changes with hydrostatic pressure (two diffusion mechanisms?)

[Graph showing data normalized at $m = 0$]
Deployment Methods

- AUV
- ROV
- USV
- Depth Profiling
- Diver
- Towed
- Moored
In Situ Methane Measurements in the Santa Barbara Channel Using UMS Analyses (Sept. 2009)

- Surface tow surveys of dissolved gases and VOCs with UMS in SB Channel
- UMS mounted on custom towfish along with conductivity, temperature, and depth (CTD) sensor and battery vessel
- Communicated with instrument through a tethered Ethernet connection
Transects and Interpolated UMS Data in SB Channel

Day 1, Sept. 28, 2009

Day 3, Sept. 30, 2009
UMS for Hydrates Research in the Gulf of Mexico (March 2009)

- Vertical profiles of dissolved gases with UMS in Gulf of Mexico (MC118)

- UMS mounted on custom frame along with CTD, dissolved oxygen (DO), and pH sensors

- Communicated with instrument through standard UNOLS CTD tether using Seabird modem

- Determined dissolved gas concentrations from UMS data with the aid of a portable calibration unit
Depth Profile Data – Gulf of Mexico

- [CH₄] (umol/kg)
- [N₂] (umol/kg)
- [O₂] (umol/kg)
- [CO₂] (umol/kg)

Argon Corrected

- Mass Spec.
- Calculated Sat.
- Optode

Profile Location

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Deepwater Horizon Incident – Subsurface Oil
UMS Deployment at MC118 (June 2010)

- Vertical profiles of dissolved gases with UMS in Gulf of Mexico (MC118)

- UMS mounted on custom frame along with CTD, DO, and pH sensors

- Communicated with instrument through standard UNOLS CTD tether using Seabird modem
Vertical Methane Concentration Profiles at MC118

Cast 1

Cast 2

Cast 3
Analysis of Collected Samples at MC118

Methane profiles June 2010

Location of UMS Cast 1

Provided by Jeff Chanton, Florida State University
Deep Tow Surveys Southwest of MC252 (Sept. 2010)

• Deep tow surveys of dissolved gases and VOCs with UMS in Gulf of Mexico

• UMS mounted on deep tow sled with CTD, sampling rosette, USBL, and multiplexer vessel to provide communication and power

• Sled deployed from A-frame of M/V Arctic for deep tow operations as part of Broader Gulf of Mexico Survey Cruises
Tow-yo Between 900 and 1500 m Along 225° Heading

Radial Line 225 (027 to 401 km from DWH) 11/09/10 to 14/09/10

Plot of tow sled depth during deep tow transect
Conclusions

• Need for in-water chemical monitoring and mapping
  – Wide variety of motivations

• In situ MIMS analysis
  – Simultaneous detection of dissolved gases and VOCs
  – Real-time information on chemical distributions

• DIC measurements possible with in-line acidification

• Salinity dependence of MIMS response is pressure dependent

• Deployment methodologies
  – Towed (2-D or 3-D)
  – Vertical profiling (1-D)

• Application to subsurface spills
  – Real-time mapping of dissolved gases, methane, and volatile organics
  – Adaptive sampling
  – Guide water sampling strategies
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