

In Situ Mass Spectrometry for Environmental Measurements in Aqueous Systems

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In Situ Mass Spectrometer Activities at USF & SRI – St. Petersburg

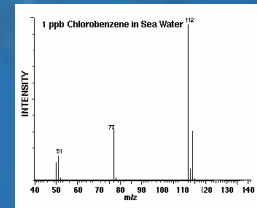
- Description of Underwater Membrane Introduction MS
- Calibration Issues
- Variety of Deployments
 - 2-D chemical mapping
 - Depth profiling
 - Long term monitoring
- Alternative Sampling Interface

In Situ Analysis Advantages

- Reduced Sample Contamination
- Increased Sampling Speed/Density
- Gradient Mapping
- Real-Time Feedback
- Self-Directed Sensors

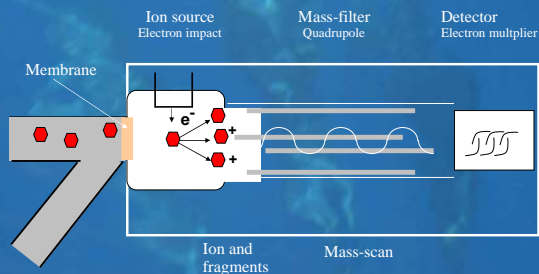
MS: Versatile Chemical Sensor

- Trace Elements
- Isotope Ratios
- Pollutants/VOCs
- Dissolved Gases
- Proteins/Amino Acids
- Bacterial Signatures

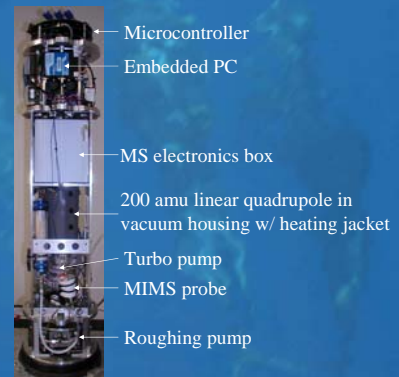


No configuration valid for all analytes

Membrane Introduction Mass Spectrometry (MIMS)



200 amu In Situ Mass Spectrometer



Principle Features of UMS



Type	Linear quadrupole mass filter
Mass range	200 amu
Inlet System	Membrane introduction system
Power consumption	85-90 Watts
Voltage of operation	24 VDC or 110 VAC
Deployment time	Configuration dependent
Dimensions	Ø 19 cm (7.5")
	L 105 cm (41")
Weight	33 kg (72.7 Lb)
Depth	>1000 m
DSL tether range	~1600 m (1 mile)

Simultaneous Detection of Multiple Analytes

- Dissolved Gases
 - e.g. Nitrogen, Oxygen, Argon, Carbon Dioxide, Methane, Hydrogen Sulfide
- Volatile Organic Compounds
 - e.g. Toluene, Benzene, Dimethyl Sulfide, Chloroform
- Larger MW Compounds with Modification
 - e.g. PCBs, Pesticides, Drugs, Toxins

Calibration - Instrument Parameters

- Physical parameters that affect instrument response:
 - Detector settings
 - Filament settings
 - Residual gas
 - Membrane geometry
 - Membrane temperature
 - Sample velocity

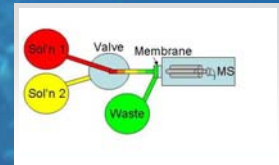
} Constant during deployment

 - Hydrostatic pressure

} Variable during deployment

Calibration - Method

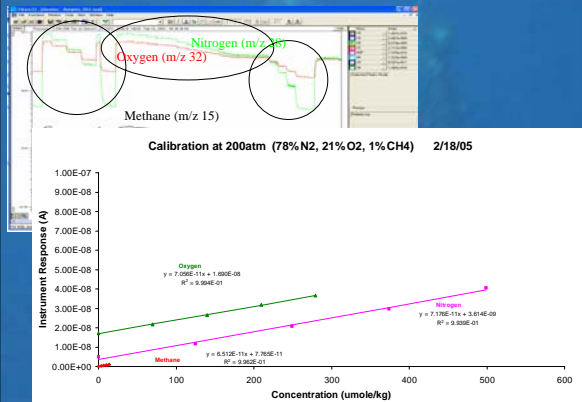
- Two solutions with known gas concentrations are mixed at various ratios to allow for intermediate concentrations and *in situ* automated calibration



- Shipboard apparatus allows in-field sample preparation and calibration



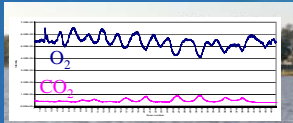
Calibration - Screenshot



Deployment Methods



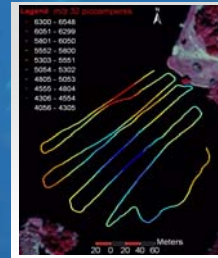
Lake Maggiore Chemical Surveys



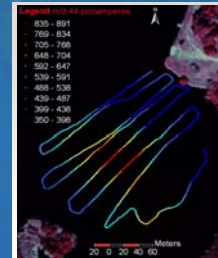
- Mass spectrometer deployed aboard an unmanned surface vehicle
- Mapping variation of dissolved gas ion intensities
- Develop surface contour maps based on gas ion intensity data
- Carbon dioxide & oxygen data displayed

Lake Maggiore, St Petersburg, FL

O₂ and CO₂ are inversely correlated in areas of active photosynthesis and respiration



m/z 32 - Oxygen



m/z 44 - Carbon Dioxide

Logistics of Plume Mapping

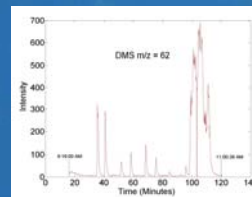


- 2L DMS over 1 hour with Dye
- Anchored Boat
- Steady Tidal Current

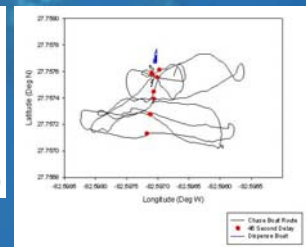
- MS Navigated through DMS Plume w/ GPS
- Multiple Transects
- Varying Distances



Merged MS / GPS Data Identify Location of Plume



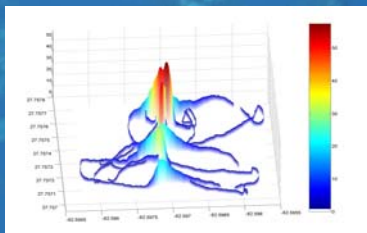
Mass Spectrometer Data



- MS Peaks at plume crossings
- Largest peak closest to dispense boat
- Peaks line up to show where plume was located

3-D Visualization of MS/GPS Data

MS Data Superimposed onto Boat Route



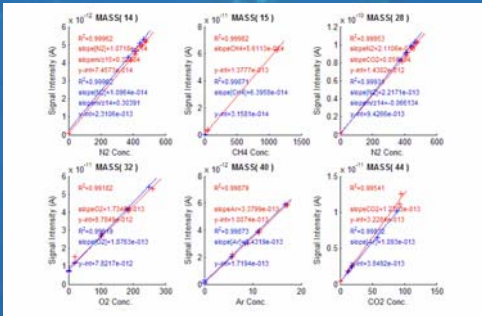
- Ion intensity scale superimposed on position
- Mapped as Lat and Lon on the horizontal scales
- Peaks wider than plume due to membrane diffusion

Depth Profiles of Dissolved Gases

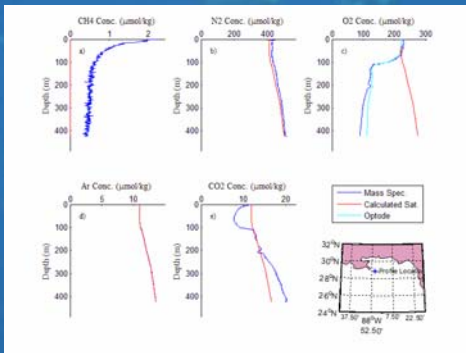


- Vertical profiles of dissolved gases with underwater mass spectrometer in Gulf of Mexico
- Mount instrument on custom frame along with CTD, DO and pH Sensors
- Communicate with instrument through standard UNOLS CTD tether using Seabird Modem
- Determine dissolved gas concentrations from mass spec data with the aid of a portable calibration unit

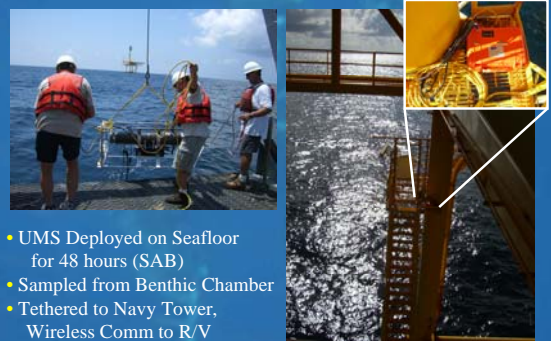
Pre-Deployment Calibration



Depth Profile Data (MC118)

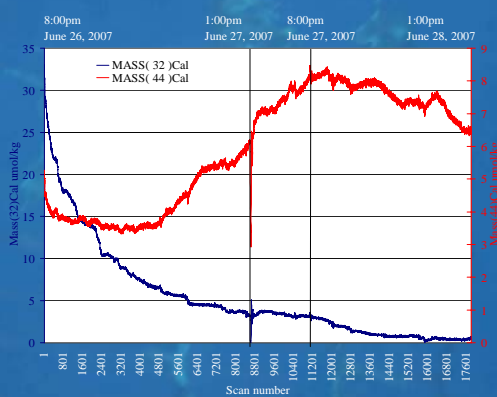


Benthic Boundary Layer Studies

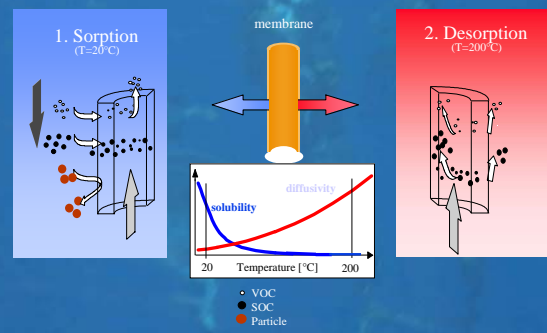


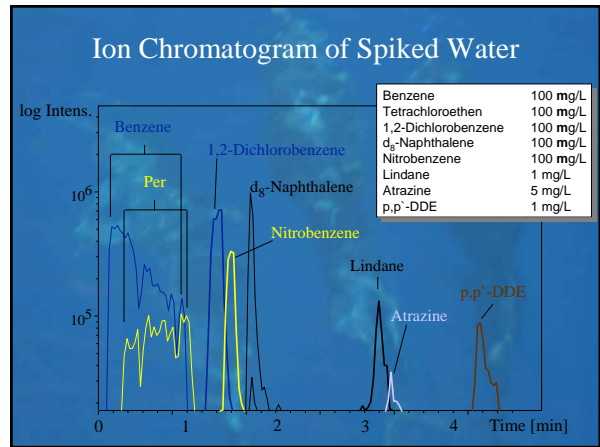
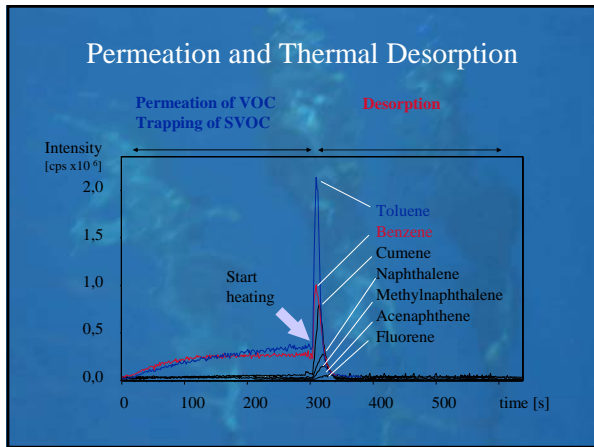
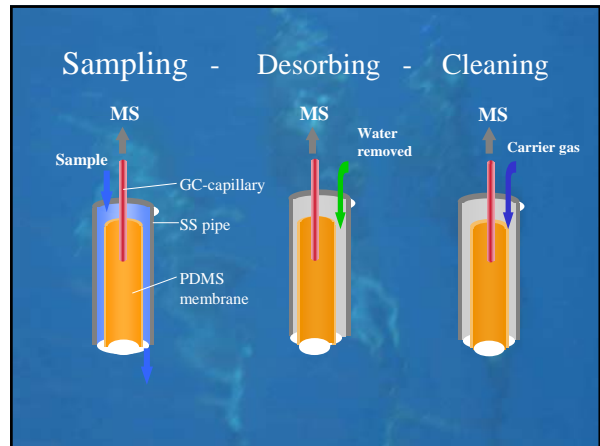
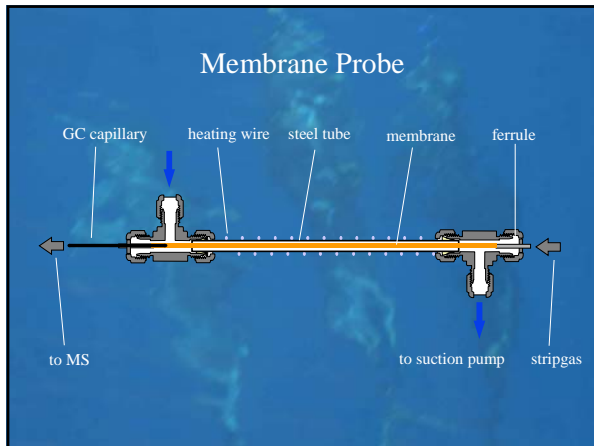
- UMS Deployed on Seafloor for 48 hours (SAB)
- Sampled from Benthic Chamber
- Tethered to Navy Tower, Wireless Comm to R/V

Continuous MS Data from Seafloor



Thermal Desorption "MIMS"





- ### Future Plans for Underwater MS
- Deployment Opportunities
 - Methane Hydrates: Gulf of Mexico
 - Benthic Boundary Layer: SAB
 - Subglacial Antarctic Lake Environments
 - Alternative Sampling Interfaces
 - Wider range of analytes
 - Unattended Operation/ Full Ocean Depths
 - Ocean Observatories
 - Extreme MS Miniaturization
 - MEMS Microfabrication

- ### Acknowledgements
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