In Situ Mass Spectrometry: Underwater Measurements & Miniaturization


SRI – St. Petersburg & University of South Florida College of Marine Science

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

- Underwater Membrane Inlet MS
- Variety of Deployments
- Cylindrical Ion Trap MS
- Extreme Miniaturization
MS: Versatile Chemical Sensor

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

No configuration valid for all analytes
Membrane Inlet Mass Spectrometry (MIMS)
## Principle Features of UMS

<table>
<thead>
<tr>
<th>Type</th>
<th>Linear quadrupole mass filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass range</td>
<td>200 amu</td>
</tr>
<tr>
<td>Inlet System</td>
<td>Membrane introduction system</td>
</tr>
<tr>
<td>Power consumption</td>
<td>85-90 Watts</td>
</tr>
<tr>
<td>Voltage of operation</td>
<td>24 VDC or 110 VAC</td>
</tr>
<tr>
<td>Deployment time</td>
<td>Configuration dependent</td>
</tr>
<tr>
<td>Dimensions</td>
<td>(\varnothing) 19 cm (7.5'')</td>
</tr>
<tr>
<td></td>
<td>L 105 cm (41'')</td>
</tr>
<tr>
<td>Weight</td>
<td>33 kg (72.7) Lb</td>
</tr>
<tr>
<td>Depth</td>
<td>&gt;1000 m</td>
</tr>
<tr>
<td>DSL tether range</td>
<td>(~1600) m (1) mile)</td>
</tr>
</tbody>
</table>
New 200 amu *In Situ* Mass Spectrometer

- Microcontroller
- Embedded PC
- MS electronics box
- 200 amu linear quadrupole in vacuum housing w/ heating jacket
- Turbo pump
- MIMS probe
- Roughing pump
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

  - Hydrostatic pressure

  \[\{\text{Constant during deployment}\} \quad \text{Variable during deployment}\]
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 at 1 atm (78% N₂, 21% O₂, 1% CH₄)  2/18/05

\[ y = 1.742 \times 10^{-10} x + 2.143 \times 10^{-08} \]
\[ R^2 = 9.999 \times 10^{-01} \]

\[ y = 1.821 \times 10^{-10} x + 5.175 \times 10^{-09} \]
\[ R^2 = 9.999 \times 10^{-01} \]

\[ y = 1.593 \times 10^{-10} x + 1.573 \times 10^{-10} \]
\[ R^2 = 9.995 \times 10^{-01} \]

Concentration (umole/kg)
Instrument Response (A)

Calibration at 200 atm (78% N₂, 21% O₂, 1% CH₄)  2/18/05

\[ y = 7.056 \times 10^{-11} x + 1.690 \times 10^{-08} \]
\[ R^2 = 9.994 \times 10^{-01} \]

\[ y = 7.176 \times 10^{-11} x + 3.614 \times 10^{-09} \]
\[ R^2 = 9.939 \times 10^{-01} \]

\[ y = 6.512 \times 10^{-11} x + 7.765 \times 10^{-11} \]
\[ R^2 = 9.962 \times 10^{-01} \]
Deployment Methods

- AUV
- USV
- Diver
- Moored
- ROV

![Deployment Methods Images](image-url)
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

$O_2$ and $CO_2$ are inversely correlated in areas of active photosynthesis and respiration.
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)

- CH4 Conc. (μmol/kg)
- N2 Conc. (μmol/kg)
- O2 Conc. (μmol/kg)
- Ar Conc. (μmol/kg)
- CO2 Conc. (μmol/kg)

- Mass Spec.
- Calculated Sat.
- Optode

Map showing profile locations.
Future Plans for Underwater MS

• Deployment Opportunities
  – Methane Hydrates: Gulf of Mexico
  – Subglacial Antarctic Lake Environments
  – AUV in Extreme Environments

• Alternative Sampling Interfaces
  – Wider range of analytes

• Unattended Operation/ Full Ocean Depths
  – Ocean Observatories

• Extreme MS Miniaturization
  – MEMS Microfabrication
Miniaturization of Ion Trap Mass Spectrometers

- Hyperbolic Electrodes
- Quadrupole Potential
- Mass Instability Scan
Cylindrical Ion Trap MS Arrays

- Cylindrical Geometry → Miniaturize
- Microtrap → Lower Sensitivity
- Array → Increased Sensitivity
- Microfab → Tolerances
Advantages of Miniaturization of Mass Analyzer

- Lower voltages/lower power
- Reduced vacuum requirements
- Overall system reduction
- Reduced cost
- MS sensor networks
Microfabricated CIT Arrays (MEMS)

Silicon Wafer

Process flow

Cylindrical ion trap
SEM of Half-Array of Micro-Cylindrical Ion Traps in Silicon

Fabricated CIT Half-Ring Electrodes with Endplates
Packaging Method for Micro-CITs

6 x 6 Micro-CIT Array

Gold plated PCB for mounting and electrical connections
Spectrum of TCE recorded with micro Cylindrical Ion Trap (r₀ = 360 microns)
Miniaturization and Integration of Peripherals

Volume of vacuum chamber, overall size and power consumption drastically reduced
Future Plans for Micro MS

- Optimize performance of micro-CIT array
- Optimize and integrate ion source arrays
- Fabrication and integration of other components:
  - Detectors
  - Vacuum and sampling systems
  - Pre-separation stage (e.g., GC)

Handheld MS sensor

- Merge with Underwater MS program
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- Staff at USF MEMS Facility

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