In-Situ Mass Spectrometry: Underwater Measurements and Miniaturization

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Introduction

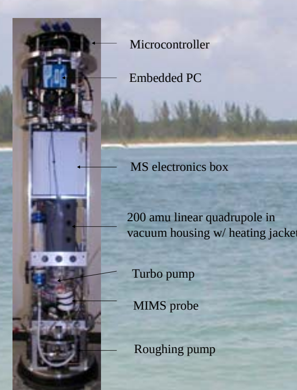
The University of South Florida's Center for Ocean Technology (COT) has developed underwater mass spectrometers for *in situ* chemical analysis of aqueous systems and is presently evaluating the applicability of these instruments to the study of subglacial aqueous environments. All systems employ membrane sampling interfaces that are ideal for sensitive detection of volatile organic compounds and dissolved gases. The design of the membrane interface allows deployments to depths greater than 1000 m. Recent field deployments include depth profiles of dissolved gases to 500 m in the Gulf of Mexico.

COT scientists and engineers have also been using micro-electromechanical systems (MEMS) techniques to fabricate micro-mass spectrometer systems in silicon and other novel materials. In particular, miniature and micro-cylindrical ion trap (μ-CIT) mass spectrometers have been constructed. Array-based techniques are also being investigated to increase sensitivity. Extreme miniaturization will greatly enhance the utility of *in situ* mass spectrometer systems in extreme environments.

Underwater Mass Spectrometer

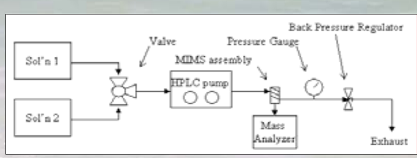
Principal Features of the Underwater Mass Spectrometer

Type	Linear quadrupole mass filter
Mass range	200 amu
Inlet System	Membrane introduction system
Power consumption	80-90 Watts
Voltage of operation	24 VDC or 110 VAC
Deployment time	Configuration dependent
Dimensions	∅ 19 cm (7.5")
	L 105 cm (41")
Weight	33 kg (72.7 Lb)
Depth	>1000 m
DSL tether range	~1600 m (1 mile)

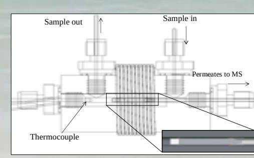


MIMS Dissolved Gas Calibration Apparatus

An apparatus was constructed to allow calibration of MIMS dissolved gas measurements. The apparatus allows automated preparation of dissolved gas standards at various concentrations by mixing two solutions of know concentrations at varying ratios with a rotary switching valve. Sample flow rate, temperature and pressure can be controlled independently to simulate sampling conditions encountered in the environment. The experimental calibration apparatus and MIMS probe assembly are depicted below.



Schematic representation of the experimental calibration setup for introduction of dissolved gases with control of physical parameters.

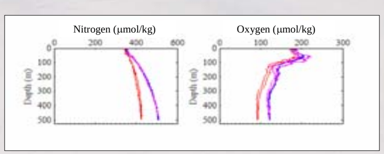


Schematic of MIMS assembly.

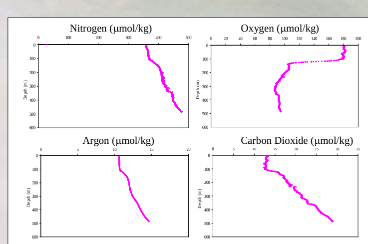
The hollow fiber polydimethylsiloxane (PDMS) membrane is supported by a 1/16" Hastelloy C 10 mm porous sintered rod. The assembly can sustain pressures well in excess of 200 atm. Restrictive dimensions around the membrane generate high flow rates at the membrane surface.

Depth Profiles in the Gulf of Mexico

The underwater mass spectrometer (UMS) was recently deployed from the R/V Suncoaster in the Gulf of Mexico for measurements of dissolved gas depth profiles to 500 m. The UMS was mounted on a shipboard rosette and real-time communications were enabled via a standard UNOLS CTD tether.



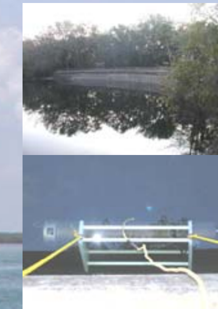
Dissolved gas profiles for *m/z* 28 (nitrogen) and *m/z* 32 (oxygen). Raw mass spectrometer data are plotted in red and pressure corrected data are plotted in blue. Calculated nitrogen saturation profile and the dissolved oxygen sensor profile are plotted in magenta.

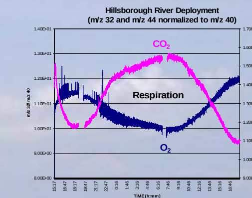


Depth profiles were obtained for multiple gases during a single cast to 500m.

Hillsborough River Analysis

The Hillsborough River is a valuable resource to the Tampa Bay region. It provides drinking water to many residents of the area and is also utilized for recreational purposes. Given the importance of the river to the surrounding community and observed strong temporal variations in the river's chemistry, the underwater mass spectrometer will be deployed to monitor dissolved gas concentrations. The benefit of this research will be a greater understanding of the spatial, seasonal and diurnal variations of dissolved gas concentrations in the river and further understanding of the implications of these changes for the health of the environment.





Time-series data obtained from the Hillsborough River. Signal for oxygen and carbon dioxide are normalized to argon to reduce effects of instrumental drift.

μ-Cylindrical Ion Trap (μ-CIT) Mass Spectrometer Arrays

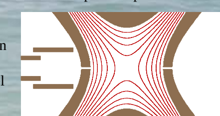
Miniaturized mass spectrometers (MS) can be especially powerful sensors for on-site identification and characterization of a wide variety of chemicals. Miniaturization is desirable for field-deployed mass spectrometers because of the corresponding reduction of electrical power requirements, simplification of vacuum systems, and the possibility for rapid parallel chemical analysis. Recent efforts in extreme miniaturization of mass spectrometers and their components have been stimulated by opportunities arising from micro-fabrication techniques and advances in materials sciences.

Traditional commercially available ion trap mass spectrometers employ hyperbolic electrodes to obtain a quadrupole trapping potential by applying an rf voltage to the ring electrode. By scanning the amplitude of the rf trapping potential, the low-mass cutoff of the ion trap is gradually raised and ions are sequentially ejected by mass-to-charge ratio (*m/z*) into a detector to obtain a mass spectrum.

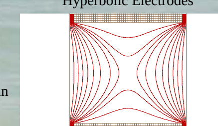
Since cylindrical geometries are much easier to fabricate and miniaturize than hyperbolic surfaces, recent efforts by several groups have focused on the development of cylindrical ion traps (CITs). By proper choice of the dimensions of a cylindrical ion trap, the quadrupole potential found in hyperbolic traps can be reproduced. Miniaturization of ion trap mass spectrometers can result in a reduction of sensitivity, however, since trapping capacity is reduced as traps are made smaller. Creation of arrays of miniature CITs, operating in unison, should provide adequate sensitivity, while maintaining all of the advantages of miniaturization discussed above.

A systematic approach to develop miniature and micro CIT mass spectrometers and arrays has been undertaken at USF, with the ultimate goal of microfabrication of extremely low-cost high-performance monolithic mass spectrometer devices. In particular, novel materials and fabrication methods for CIT mass spectrometers have been investigated. Theoretical analysis and modeling of miniature and micro mass spectrometers have guided the experimental development of CITs.

Electric potential inside an ion trap mass spectrometer.



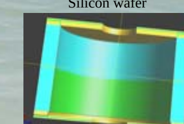
Hyperbolic Electrodes



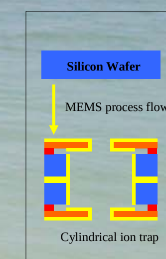
Cylindrical Geometry

A micro-electromechanical systems (MEMS) process flow must be created to fabricate μ-CIT arrays in silicon .

Silicon wafer

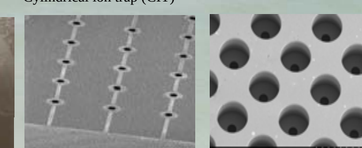


Cylindrical ion trap (CIT)

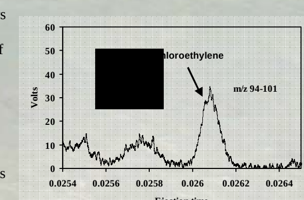


Cylindrical ion trap

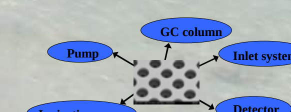
μ-CIT arrays mounted and ready for testing



Secondary electron microscopy (SEM) images of half arrays of apertures and ring electrodes.



Spectrum of TCE recorded with micro Cylindrical Ion Trap (ro= 360 microns)



Peripheral devices will also be miniaturized to achieve total system reduction.

Acknowledgements

The authors gratefully acknowledge the staff at the Center for Ocean Technology for their help in design and development. This research is funded by the US Office of Naval Research (ONR) Grant No. N00014-03-1-0479 and by Grant No. DASG60-00-C-0089.