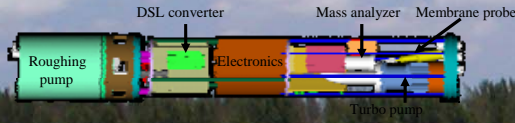


### Introduction

Field-deployed chemical sensors add a new dimension to studies of marine processes by facilitating adaptive sampling and exceptionally rapid, high-resolution chemical mapping. Mass spectrometers add to these attributes the capability for simultaneous measurements of multiple analytes. In view of such capabilities, the University of South Florida (USF) has developed a portable underwater membrane introduction mass spectrometer. Recent field deployments include diurnal monitoring of primary productivity in the Hillsborough River (Tampa, FL) by continuous measurements of dissolved gases (e.g., oxygen and carbon dioxide), mapping of a local lake to generate contour maps detailing the distributions of biologically relevant dissolved gases, and measurements of dissolved-gas depth profiles to 500 m in the Gulf of Mexico. Construction of a new underwater mass spectrometer system allows deployments to depths in excess of 1000 m.

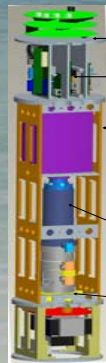
### Underwater Mass Spectrometer



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	22.19 cm (47.5")
	L: 105 cm (41")
Weight	33 kg (72.7 lb)
Depth	>1000 m
DSL tether range	~1600 m (1 mile)

The underwater mass spectrometer can be operated in a tethered mode providing real-time communication and power, or in an autonomous battery-operated mode. Wireless Ethernet can also be used to communicate with the system for remote analysis.

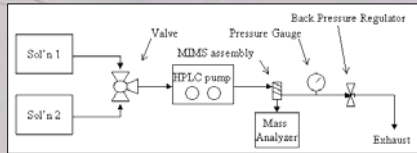
### Next Generation Underwater Mass Spectrometer



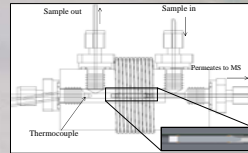
- Redesign of microcontroller with expanded capability
- Embedded PC upgrade with 1 GHz processor running XP OS
- Modular carriage for easy disassembly of component systems
- Integrated system allows removal of external pressure vessel without compromising vacuum
- Redesigned vacuum chamber with heating jacket allowing bakeout of chamber
- Roughing pump mounted on dampers, reducing noise and vibration

### 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 of two solutions of known 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 setup for introduction of dissolved gases.



Schematic of MIMS assembly.

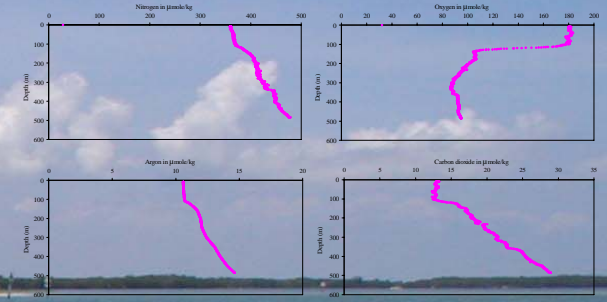
The hollow fiber polydimethylsiloxane (PDMS) membrane is supported by a 1/16" Hastelloy C 10 mm porous sintered rod. The assembly can sustain pressures well in excess of 200 atm. Restrictive dimensions around the membrane generate high flow rates at the membrane surface.

### Acknowledgements

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

### Depth Profiles in the Gulf of Mexico

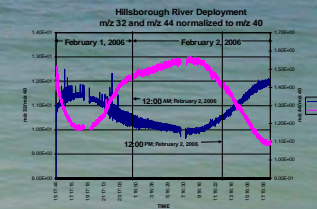
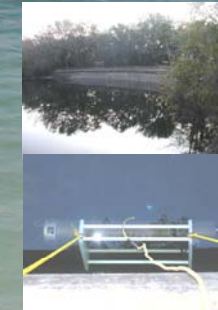
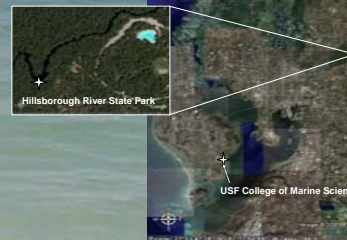
The mass spec was recently deployed off the R/V Suncoaster in the Gulf of Mexico for measurements of dissolved gas depth profiles to 500 m. The UMS was mounted to a shipboard rosette and real-time communications were enabled via a standard UNOLS CTD tether to which the rosette was attached.



Depth profiles were obtained for multiple gases during a single cast to 500m. The raw data were post processed using calibration coefficients determined in the laboratory.

### Hillsborough River Analysis

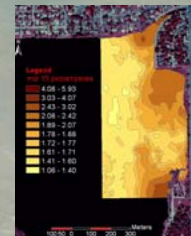
The Hillsborough River is a valuable resource to the Tampa Bay region. It provides drinking water to many residents of the area and is also utilized for recreational purposes. Given the importance of the river to the surrounding community and observed strong temporal variations in the river's chemistry, the underwater mass spectrometer will be deployed on a monthly basis, over the next year, to monitor dissolved gas concentrations. The benefit of this research will be a greater understanding of the 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.



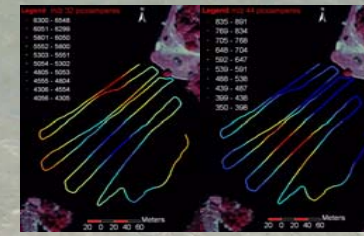
Preliminary time-series data obtained from the Hillsborough River. Signal for oxygen and carbon dioxide are normalized to argon to reduced effects of instrumental drift.

### Surface Contours – Lake Maggiore, St Petersburg, FL

The UMS was deployed in surface waters on a guided surface vehicle while real time data were transmitted via wireless Ethernet. Real time observations allow intensive sampling of areas with strong chemical gradients. Vehicle-mounted UMS deployments have been used to generate contour maps detailing the distributions of dissolved gases in local water bodies. Oxygen and CO<sub>2</sub> vary inversely in response to biological activity. The response of m/z 15 (methane) was observed to depend on the mass spectrometer's proximity to organic rich sediments.



A contour map for m/z 15 shows a strong dependence on proximity to the shoreline. This is likely due to the influence of organic rich sediments in shallow waters close to shore.



Observations of m/z 32 (O<sub>2</sub>) and m/z 44 (CO<sub>2</sub>) were inversely proportional. The m/z 32 and m/z 44 graphs show fine-scale variations indicating localized biological activity.



The mass spectrometer is located beneath the surface vehicle.

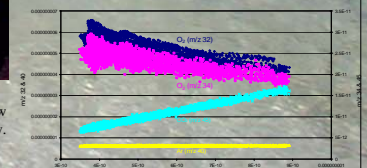


Illustration of the inverse relationship between O<sub>2</sub> isotopes, m/z 32 and m/z 34, to m/z 44 and the positive correlation between CO<sub>2</sub> isotopes 44 and 45. There is no correlation between Argon (m/z 40) and CO<sub>2</sub>.