

## IN SITU MASS SPECTROMETRY FOR CHEMICAL MEASUREMENTS IN THE WATER COLUMN AND ON THE SEA FLOOR

**Theme 4: Frontiers of Global Ocean Observations**  
**Session 4A: Frontiers in In-Situ Observing Technology**

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Among the techniques used in modern elemental and molecular analysis, none surpasses mass spectrometry (MS) in analytical access to elements, isotopes (stable and radioactive), and complex molecules (including natural and anthropogenic organics). Interest in the development of MS as an in situ analytical technique is a consequence of the demonstrated versatility, sensitivity, and reliability of MS characterizations. As an in situ technique, MS provides a means of simultaneously monitoring many types of chemicals with high temporal and spatial resolution.

SRI International and the University of South Florida have developed underwater membrane introduction mass spectrometry (MIMS) systems capable of in situ detection and quantification of dissolved gases and volatile organic compounds (VOCs) [1,2]. The instruments are based on a 200 amu (atomic mass unit) linear quadrupole mass analyzer with a closed ion source (Transpector CPM-200 Residual Gas Analyzer, Inficon, Inc., Syracuse, New York). Introduction of analytes into the mass spectrometer occurs through a high-pressure polydimethylsiloxane membrane introduction system that has been tested at pressures equivalent to oceanic

depths of  $\leq 2000$  meters. The membrane interface used in these systems provides parts-per-billion level detection of many VOCs and sub parts-per-million detection limits for many dissolved light stable gases.

The underwater MIMS systems have been deployed on a wide variety of platforms for a number of applications in coastal oceanographic, estuarine, and freshwater research. Types of deployments include shallow-water monitoring for pollutants (VOCs) in tethered/moored scenarios, as well as onboard autonomous and remotely controlled unmanned vehicles [3–5] (e.g., see Figure 1). By recording the position of the vehicle/MS system using global positioning system or ultra-short baseline navigation technology, and time matching to concurrent MS data, we have demonstrated that chemical maps can be created to show spatial chemical concentration variations with unprecedented resolution [3,4]. The underwater MIMS systems have also been used in vertical profile studies of dissolved gases to approximately 900 m depths. Methods to calibrate for effects of hydrostatic pressure at depth have been devised to provide in situ dissolved gas concentrations [6].

More recently, a sediment probe and syringe pump system has been developed to provide additional in situ analytical capability (Figure 2). The syringe pump system provides a very constant sample flow rate over a wide range of sampling speeds, and allows the introduction of reagents to convert non-volatile analytes to volatile species that can be detected by the underwater MIMS system. For example, dissolved inorganic carbon can be converted to gaseous carbon dioxide in order to quantify total carbon in aqueous environments. The sediment probe can be programmed to sample pore water at various depths in the sediment to measure vertical gradients of dissolved gases.

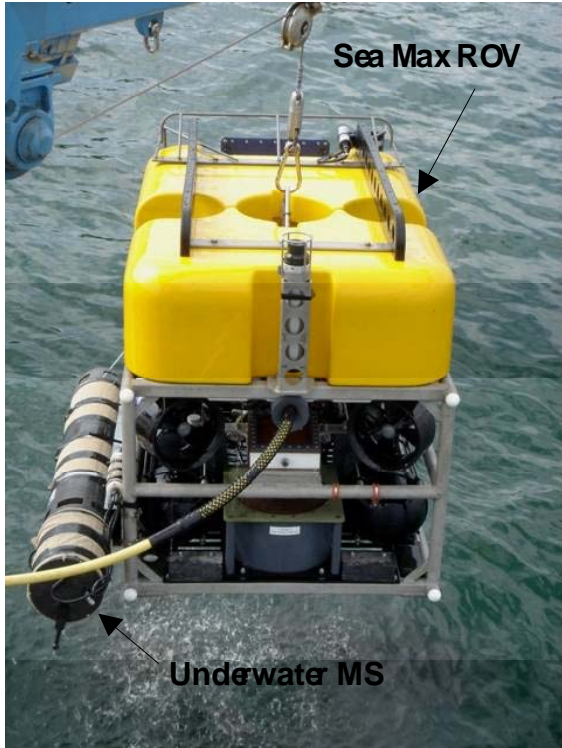


Figure 1. The underwater MS being deployed on the *Sea Max Mk1* remotely operated vehicle (ROV) in Bayboro Harbor, Florida.

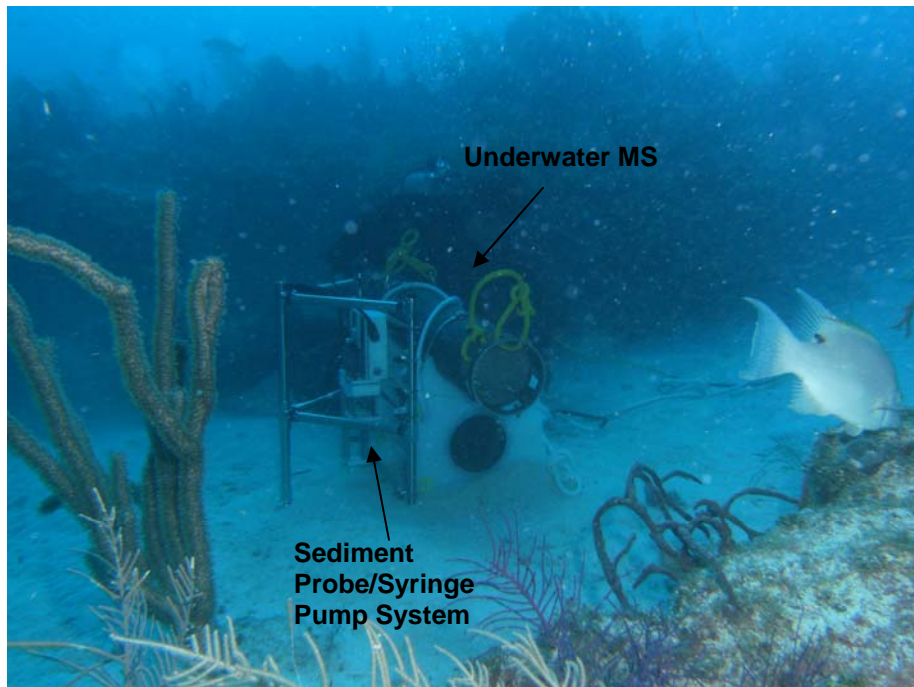


Figure 2. The underwater MS and sediment probe/syringe pump system deployed at the Aquarius Reef Base (Florida Keys National Marine Sanctuary).

Future goals include development of an in situ mass spectrometer capable of long-duration deployment, further miniaturization of MS systems, and development of new sampling interfaces. Several innovations and improvements relative to current underwater MS technology are required to meet these goals. Providing the capability to make stable measurements over periods of weeks to many months (with in situ recalibration or minimal drift from calibration) will immensely expand the utility of in situ mass spectrometry technology for ocean observing applications.

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