Real-time Monitoring of Aquatic Environments with an Underwater Mass Spectrometer

Peter G. Wenner, F.H.W. van Amerom, S.K. Toler, J.E. Edkins, K. Koehn, R.J. Bell, M. Hall and R.T. Short

University of South Florida Center for Ocean Technology

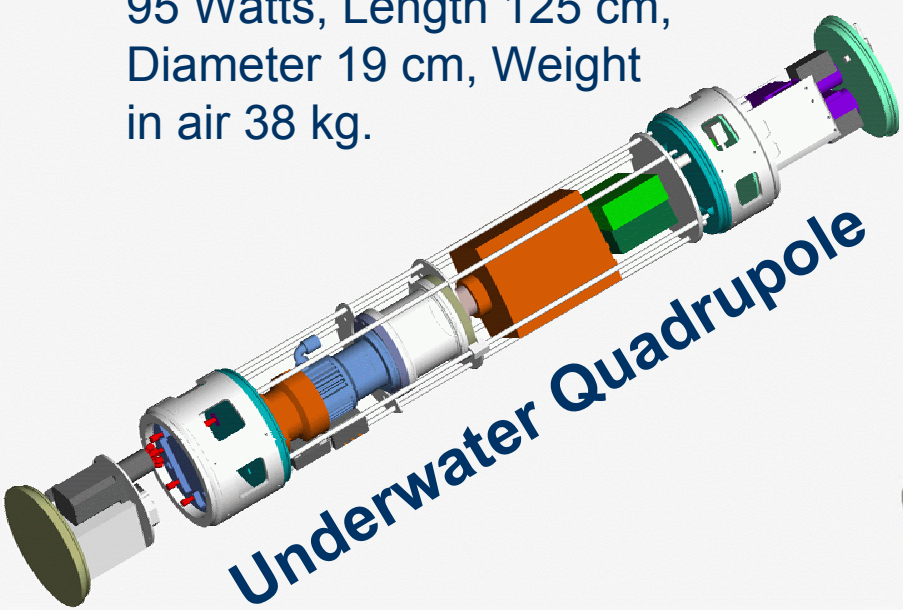
USF/COT Underwater Mass Spectrometry Program

- First generation instruments
  - 100 amu Quadrupole
  - Saturn Ion Trap
- Field deployment instrument
  - 200 amu Quadrupole
- Recent deployments
  - Bayboro Harbor
  - Lake Maggiore
  - Kennedy Space Center
  - Lake Yellowstone
- Future Development

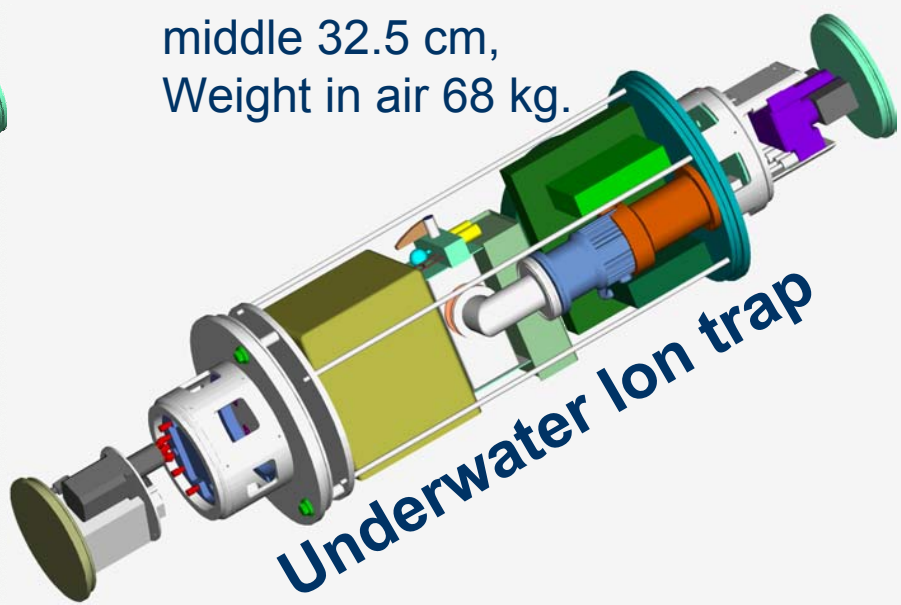
Schematics of underwater MS systems

Hulls: anodized Aluminum, depth 300 m; **Power:** 24 VDC;
Roughing Pump: 2 diaphragm pumps (KNF); **Vacuum**: Turbo pump (Varian)
Membrane Probe: PDMS (in house)

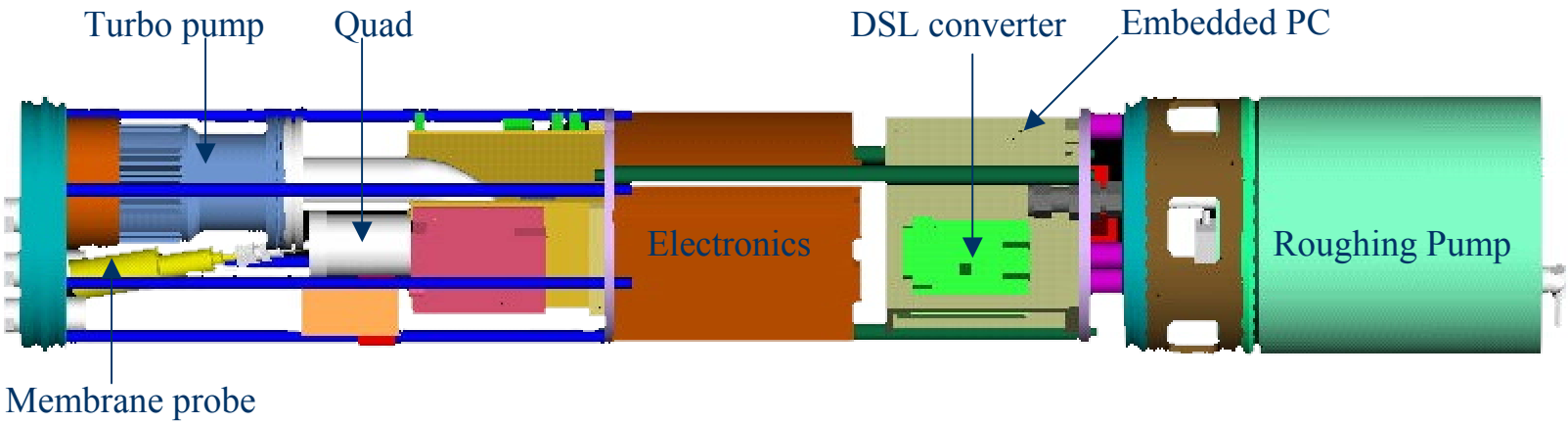
Analyzer Section
Quadrupole 100 amu
(Transpector 2, Inficon)
95 Watts, Length 125 cm,
Diameter 19 cm, Weight
in air 38 kg.



Analyzer Section
Iontrap (Saturn 2000, Varian)
150 Watts, Length 135 cm,
Diameter 19 cm in the
middle 32.5 cm,
Weight in air 68 kg.



200 amu Linear Quadrupole MIMS System



Underwater Mass Spectrometry

- Principle features of MS

Type	Linear quadrupole mass spectrometer
Mass range	200 amu
Inlet System	Membrane introduction system
Power consumption	105 Watts
Voltage of operation	24 V
Deployment time	10-14 days max.
Dimensions	∅ 19 cm (7.5”)
	L 114 cm (45’’)
Weight	33 kg (72.7 Lb)
Depth	200 m max.
DSL tether range	1609 m (1 mile)

Modular Stepwise MS Approach

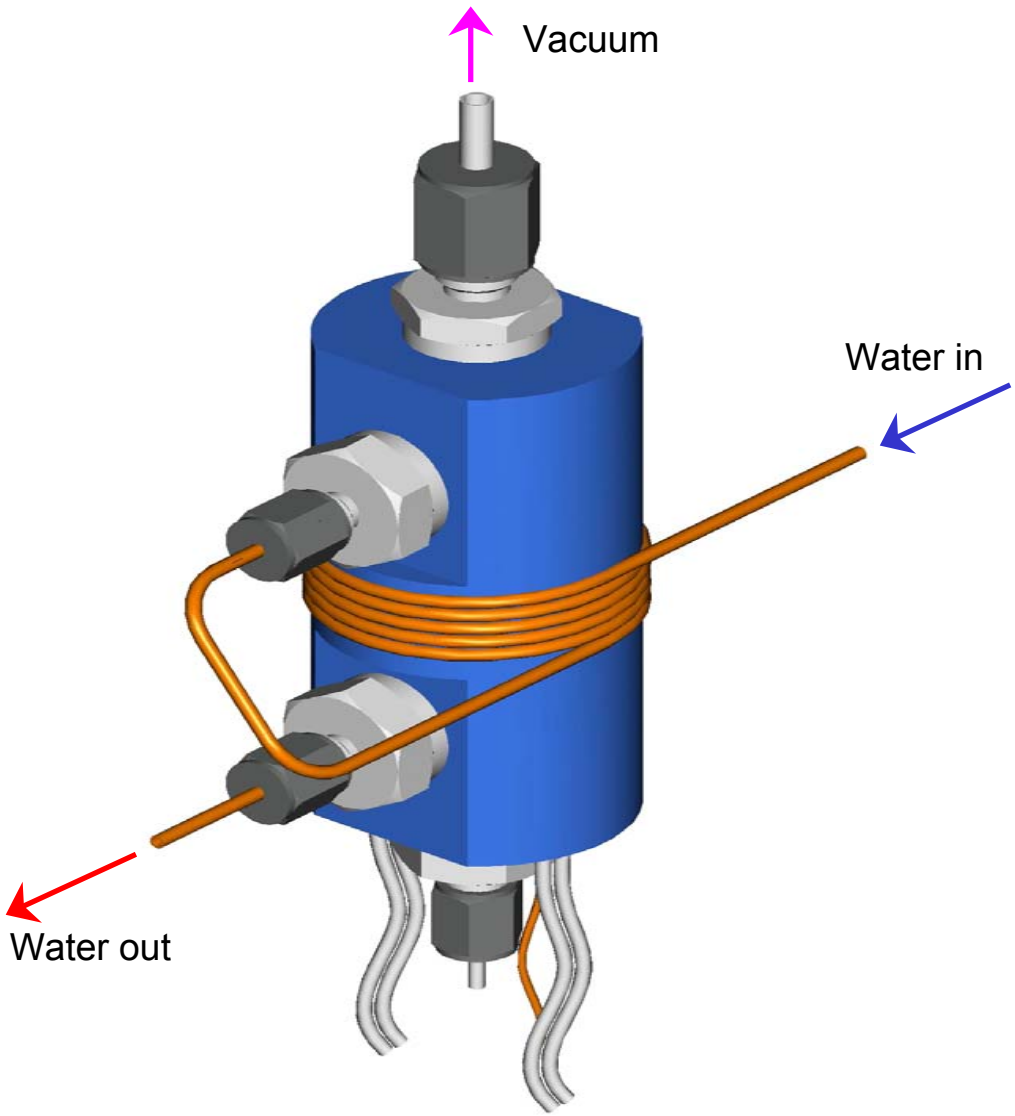
- No configuration valid for all analytes
- Less complex configuration first
  - Membrane introduction/quadrupole MS
  - Shallow water applications
- Progressive versions
  - Solid-phase micro-extraction interface
  - Magnetic Sector MS for DIC, CO_2
  - Increased depth
- Use common components

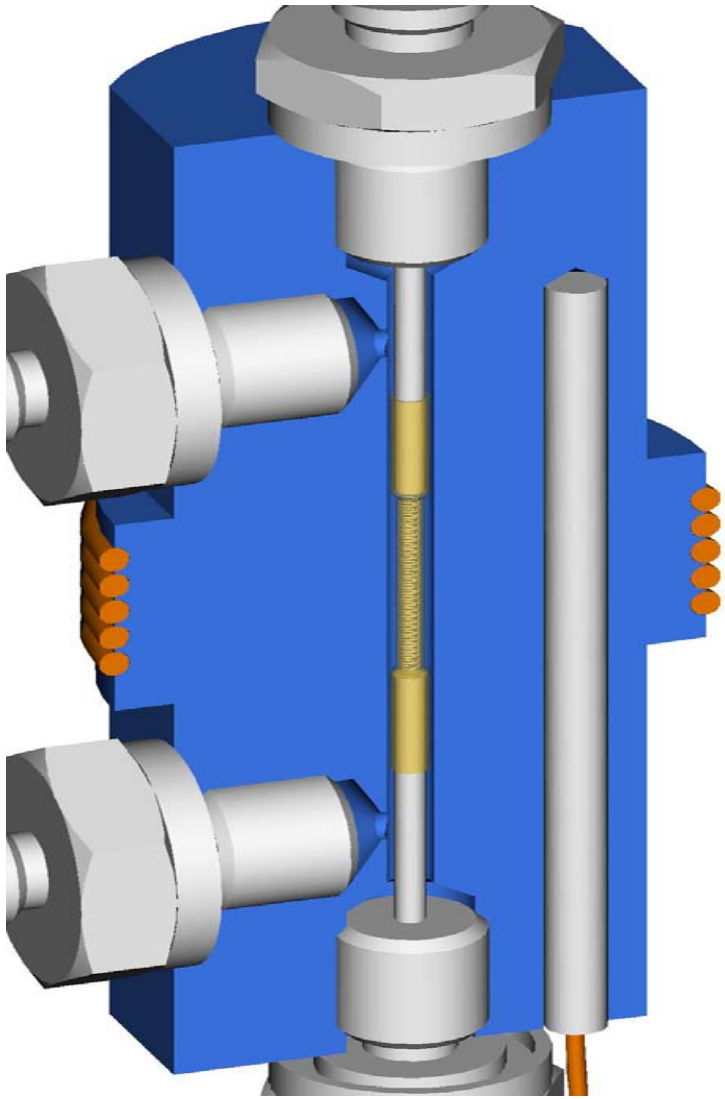
Membrane Introduction for In-Situ Analysis

- Simple Interface
- PDMS Capillary
- VOCs, Dissolved Gases No Sample Prep
  - In-line Sample Heating

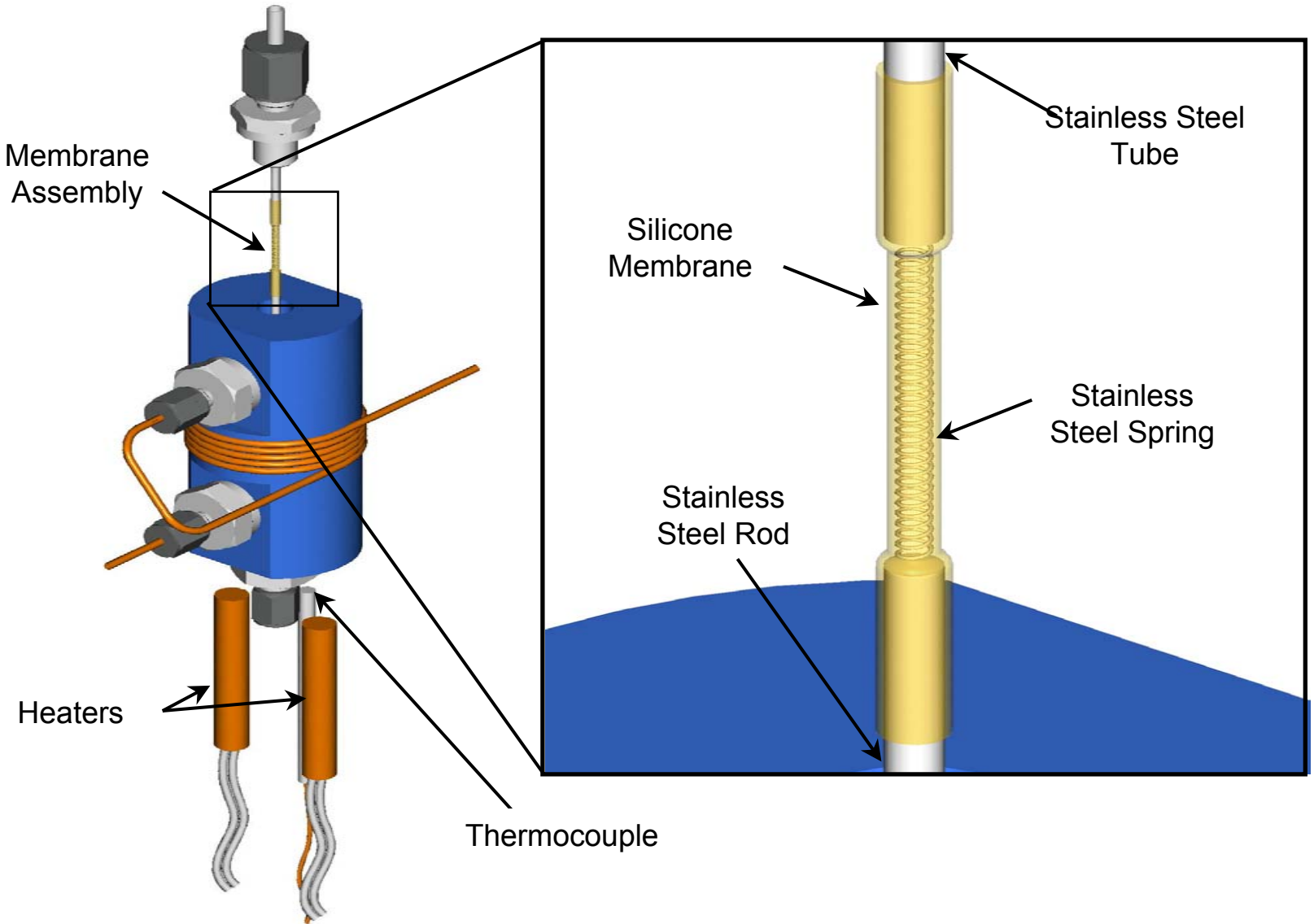
Membrane Probe Construction

Membrane Introduction
Sample Interface for High Pressure



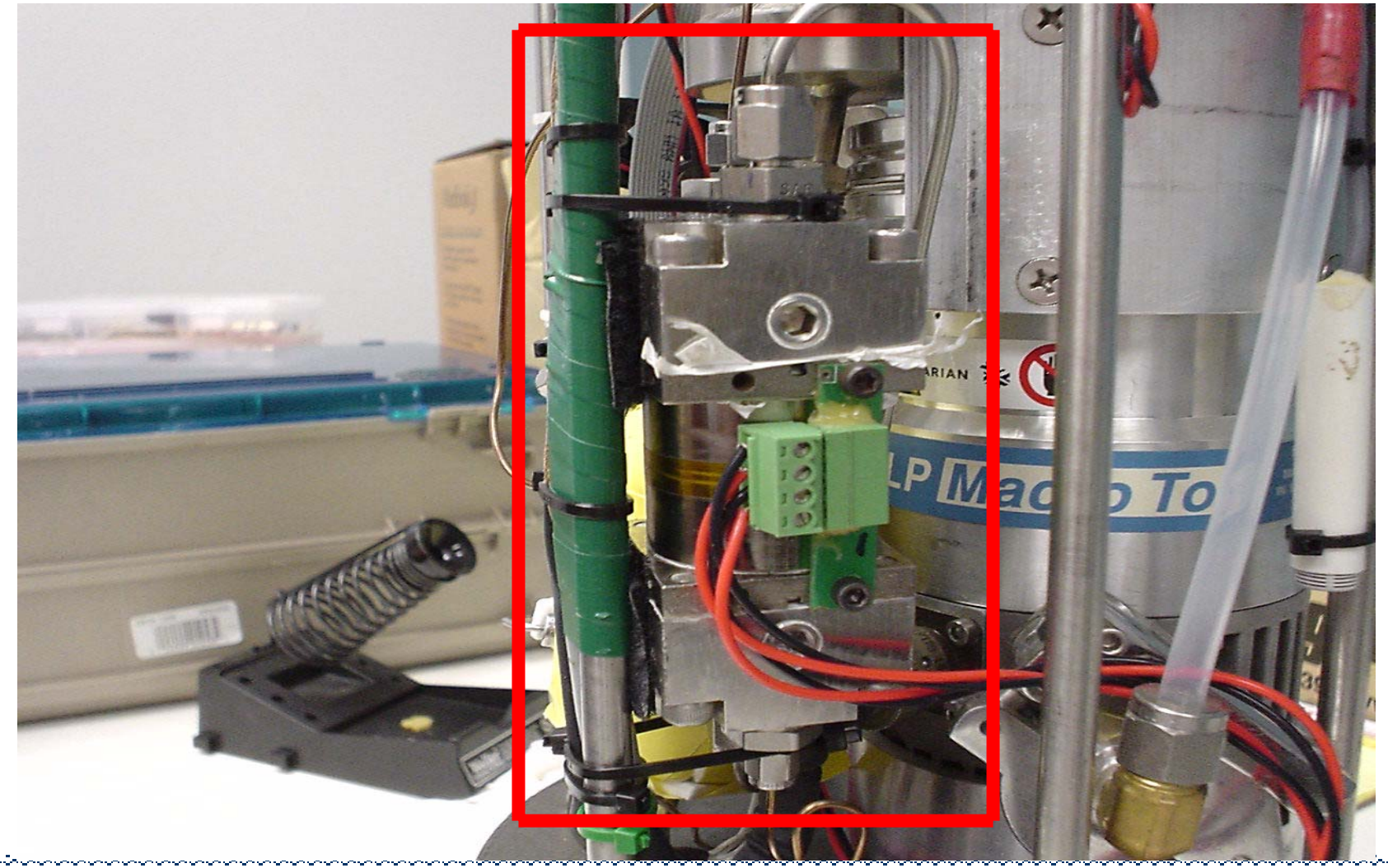


Membrane Introduction Sample Interface



Magnetic Piston Sample Pump

For Sampling at Depth

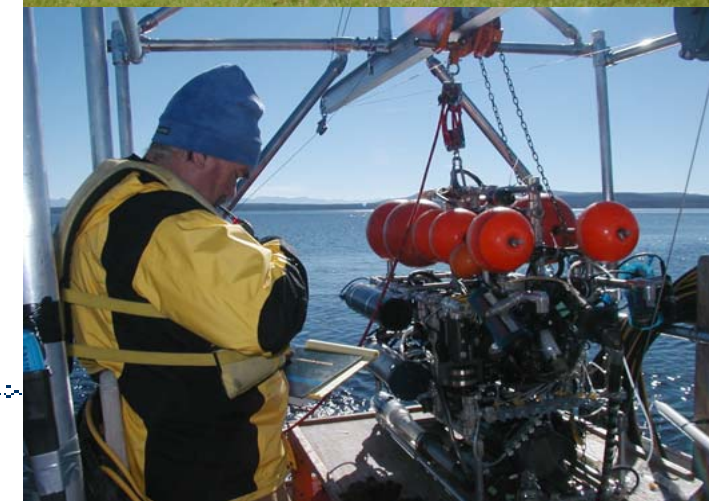


Target Analytes for Underwater MIMS

- Gases
  - CH_4, N_2, O_2, CO_2, Ar, etc.
    (very low ppm, ~10 sec response)
- Volatile Organic Compounds
  - Benzene, Toluene, Xylene, Dimethyl sulfide, etc.
    (very low ppb, ~1-5 min response)
- Semi-Volatile Compounds
  - Napthalene, PAHs, Pesticides, etc.
    (low ppb, ~5-20 min response)

Deployments

- Moored
  - Monitoring marinas and shipping channels, tidal changes, river effluent
- Guided surface vehicle
  - Mapping of voc's and gases
- Remotely Operated Vehicle
  - Chemical characterization of geothermal plumes in Lake Yellowstone

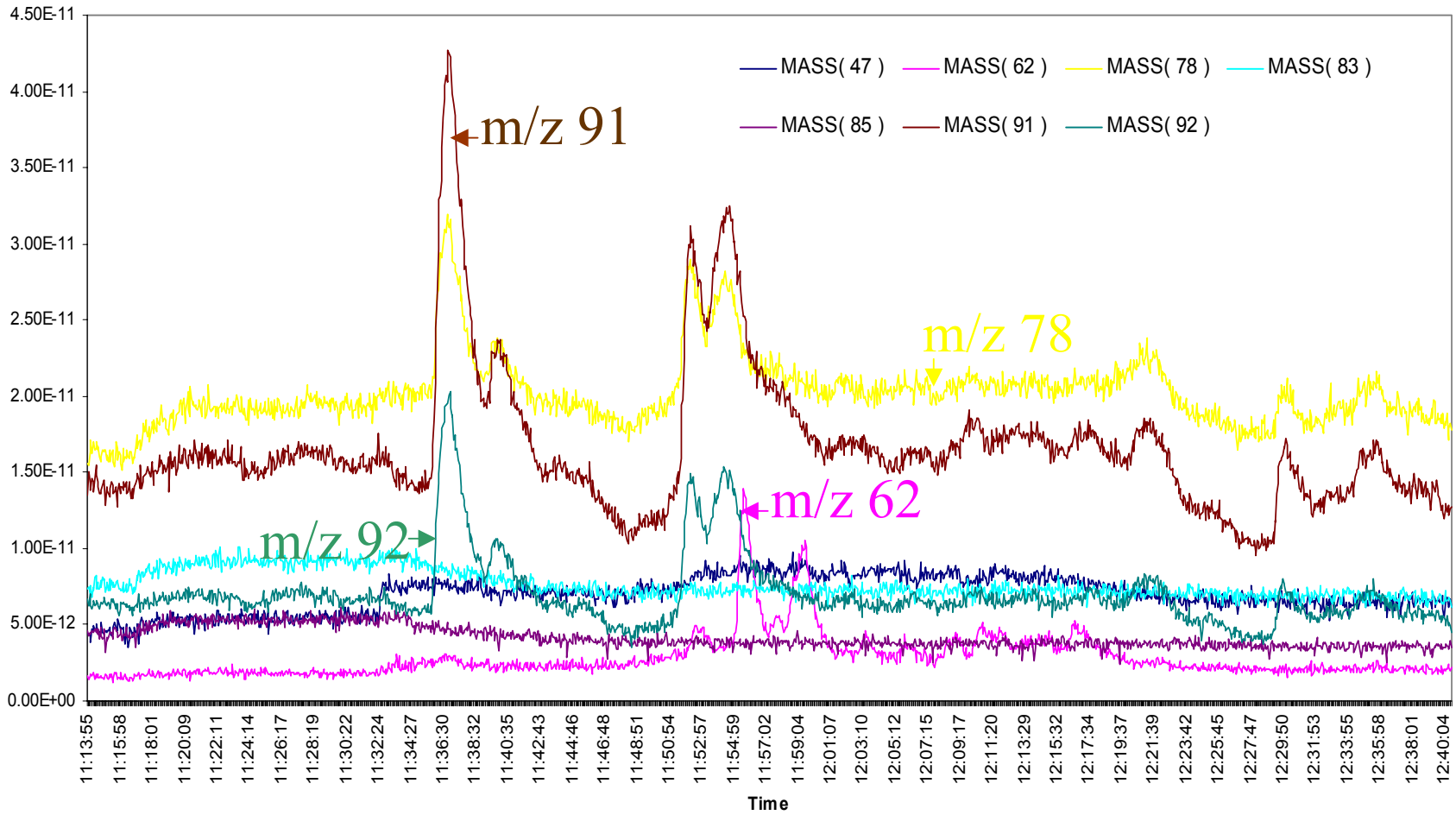


Chemical Surveying using Surface Vehicle

Deployment in Bayboro Harbor

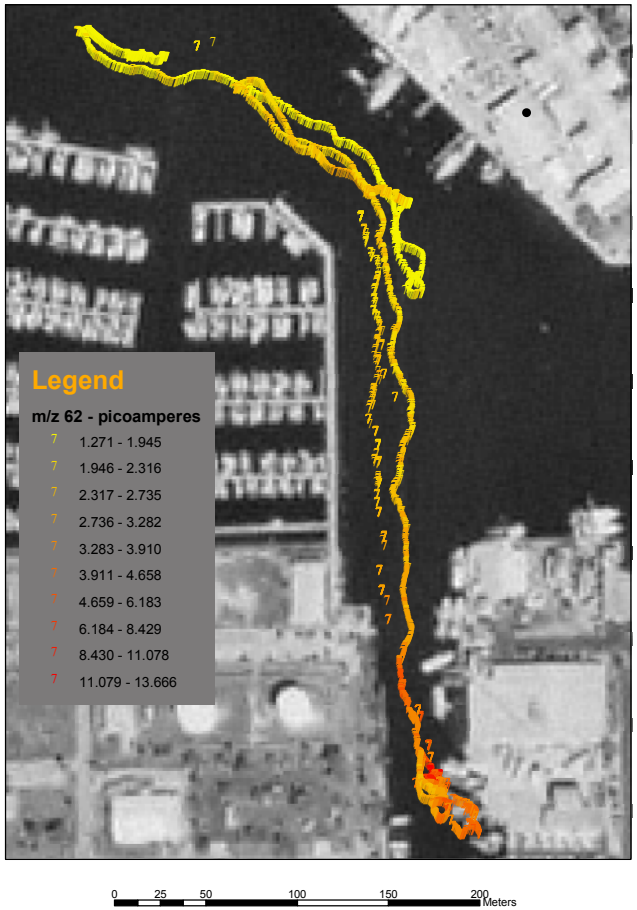
ENG Concepts Guided Surface Vehicle

MS Data from Survey of Bayboro Harbor

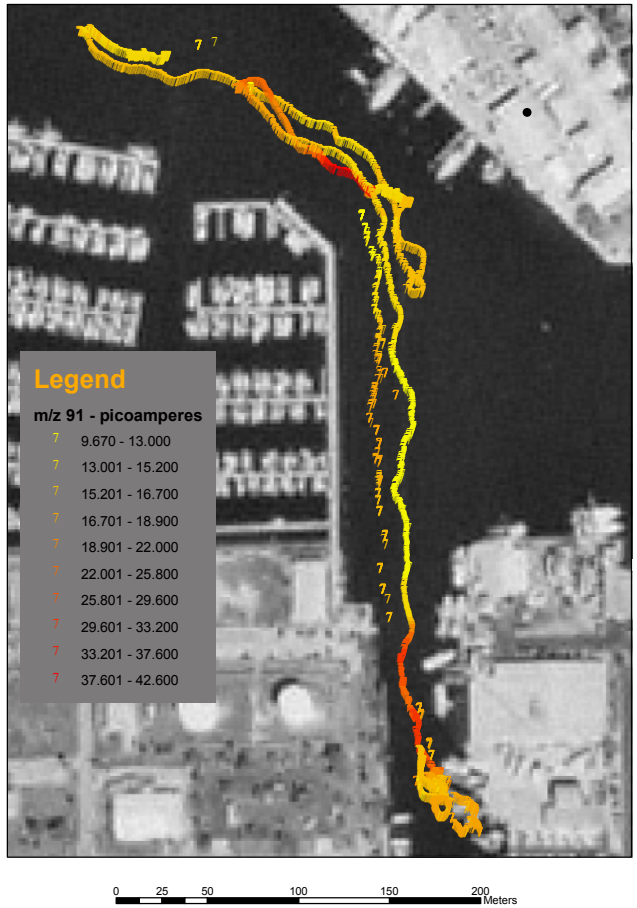


Mapping of Dimethyl Sulfide and Toluene

m/z 62



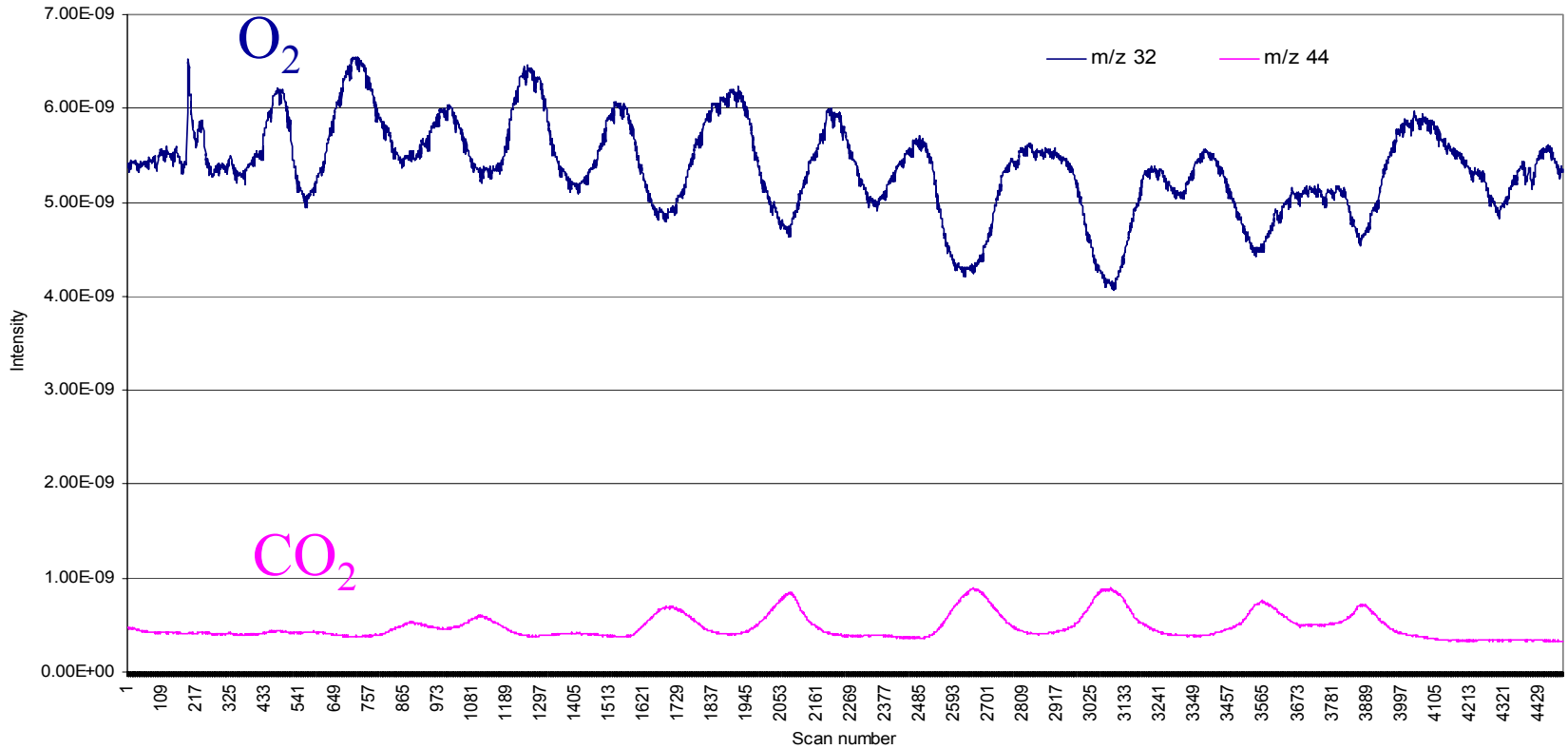
m/z 91



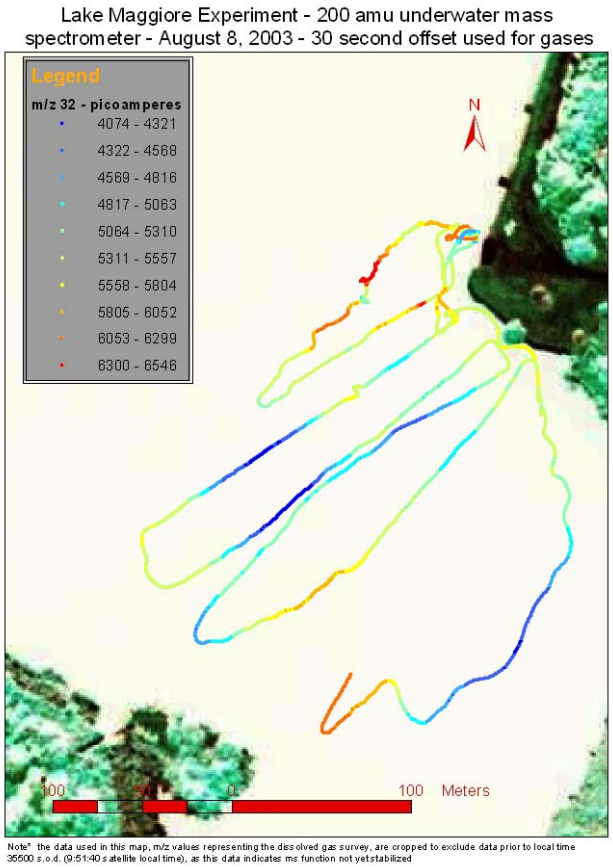
Chemical Surveying of Lake Maggiore

Updated *ENG Concepts Guided Surface Vehicle*

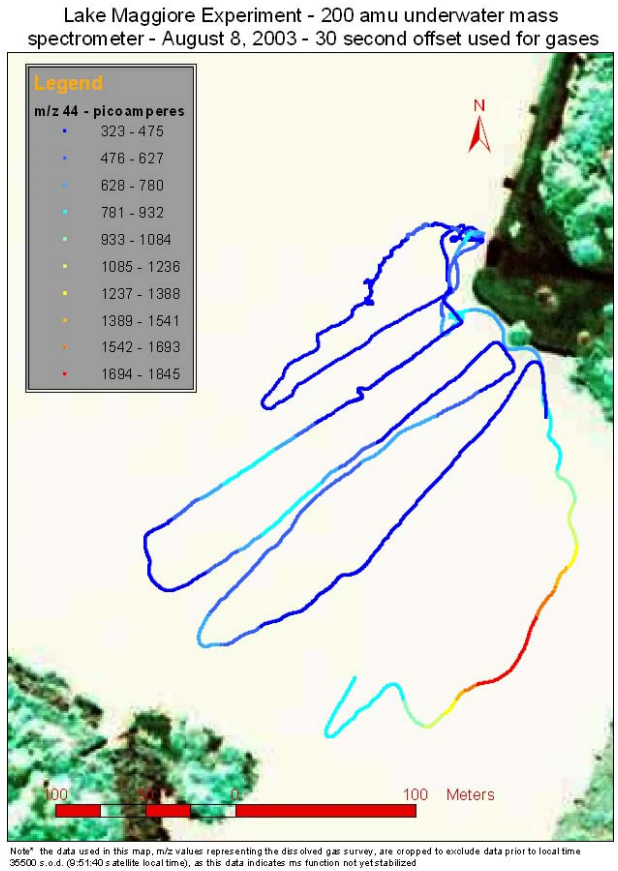
MS Data from Survey of Lake Maggiore



Mapping of Dissolved Gases



Map variation in m/z 32 intensity



Map variation in m/z 44 intensity

Joint Environmental Science Investigations Conducted at the Kennedy Space Center

KENNEDY SPACE CENTER (KSC)
JOINT ENVIRONMENTAL SCIENCE INVESTIGATIONS (JESI)
TEST PLAN

AUGUST 2003

Principle Point of Contact:

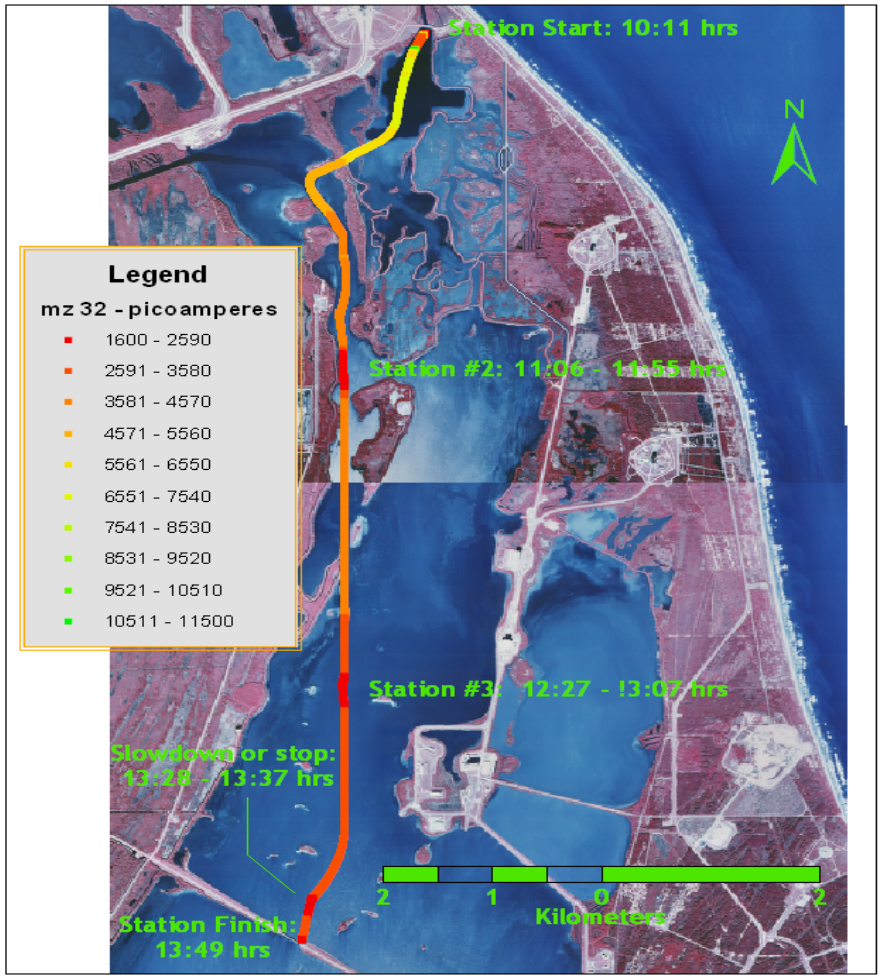
Denise M. Crimmins
Code 82201
Naval Undersea Warfare Center
401-832-9411
crimminsdm@npt.nuwc.navy.mil

Alternate Point of Contact:

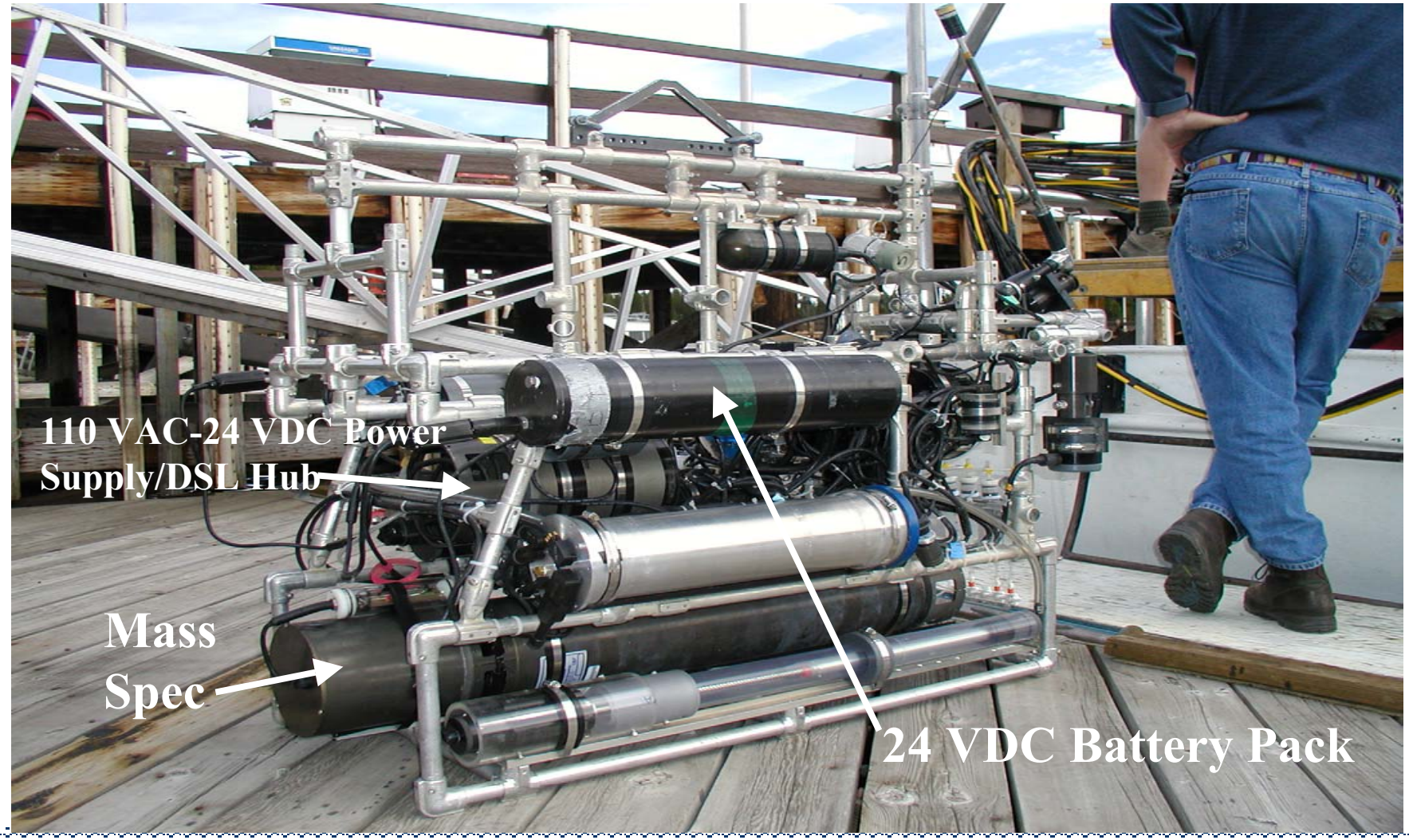
Jason A. Yozura
Code 82201 Contractor
Naval Undersea Warfare Center
401-832-2395
yozuraja@npt.nuwc.navy.mil

UMS Deployed on the FMRI's MARVIN Platform at Kennedy Space Center

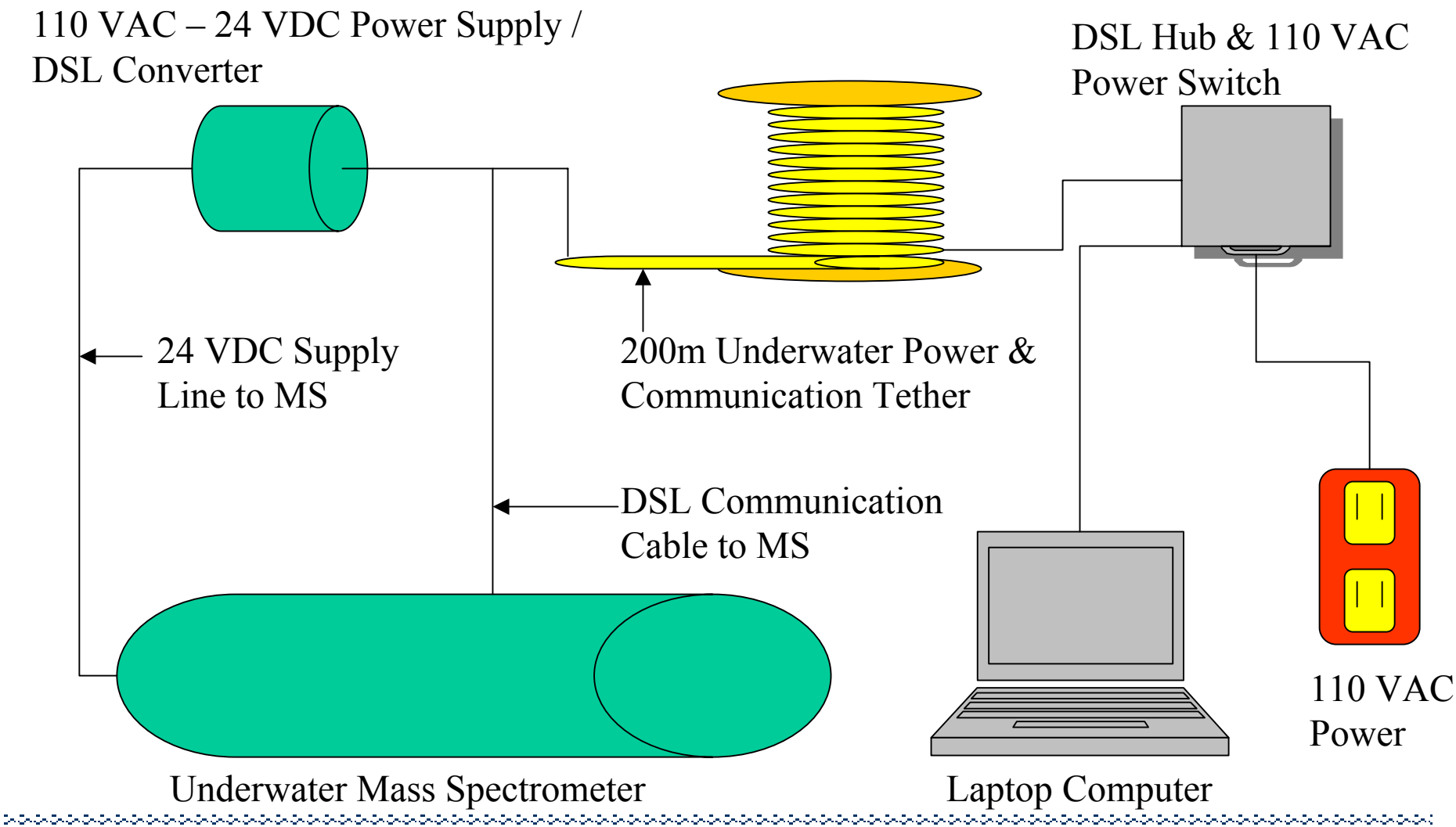
Mapping of O_2 during transect of the Banana River



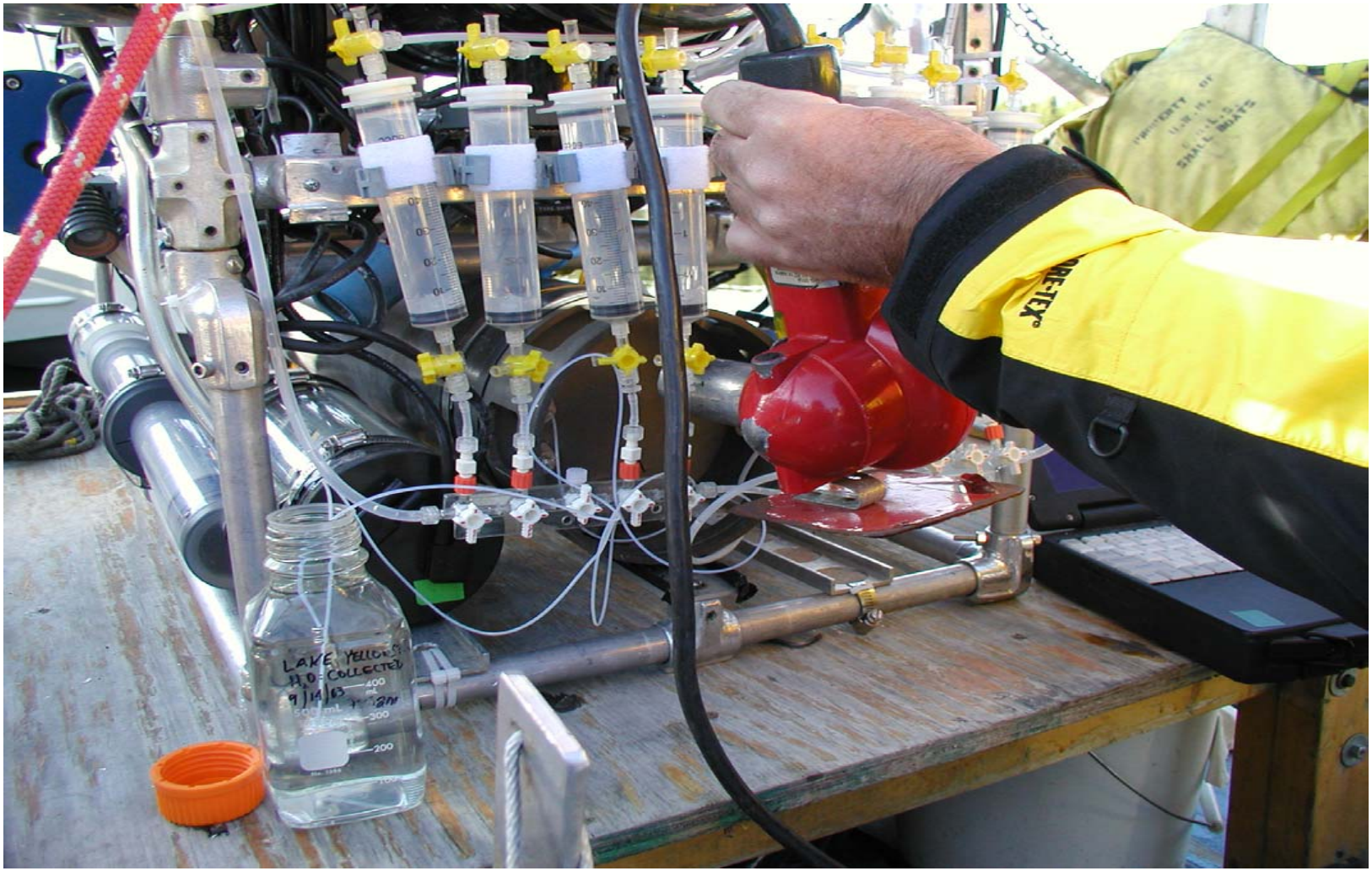
Deployment of UMS aboard a ROV at Lake Yellowstone



Tethered Deployment Scheme of UMS for Lake Yellowstone

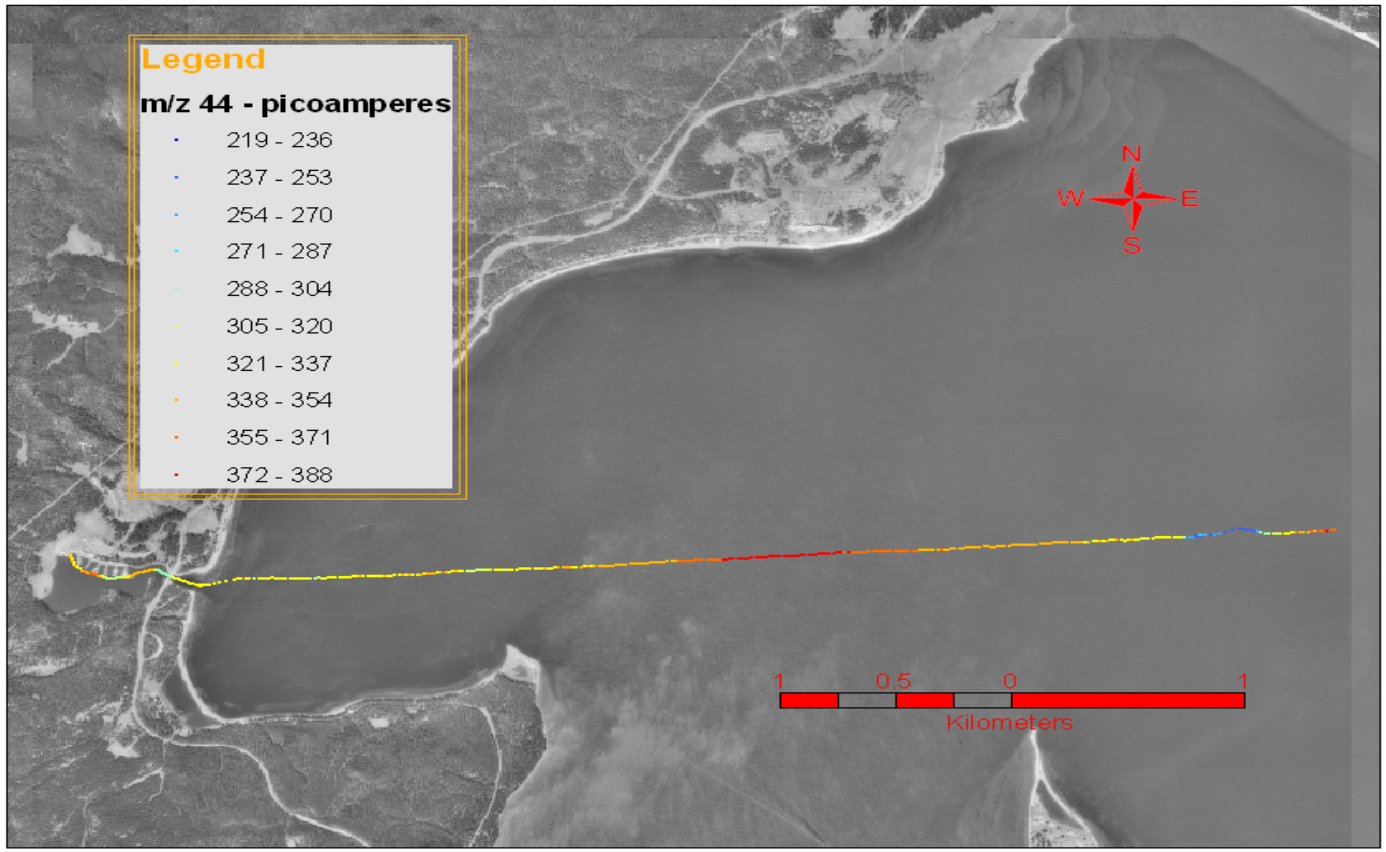


Step One: Freeze the Mass Spec

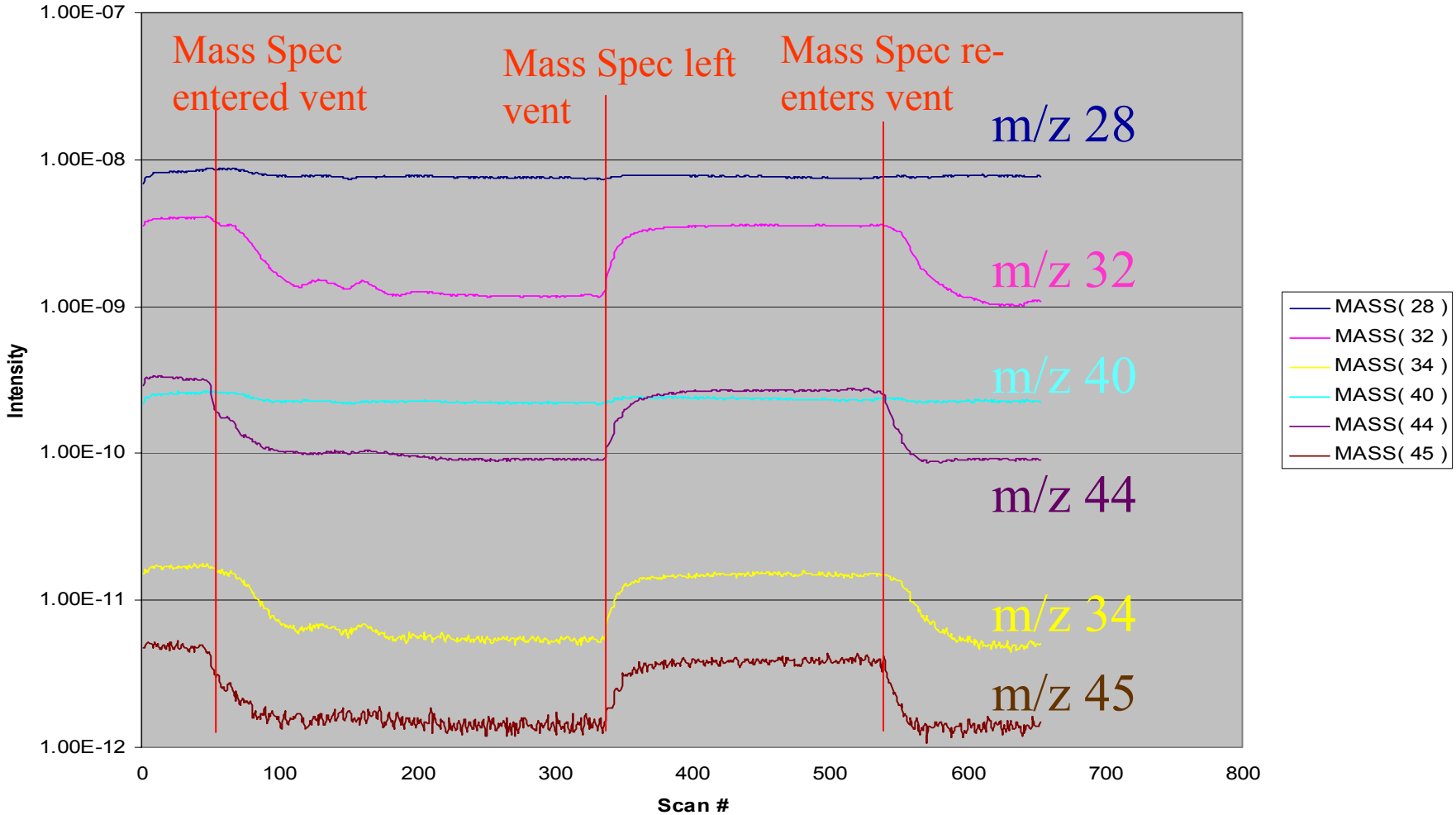


Step Two: Deploy in a Blizzard

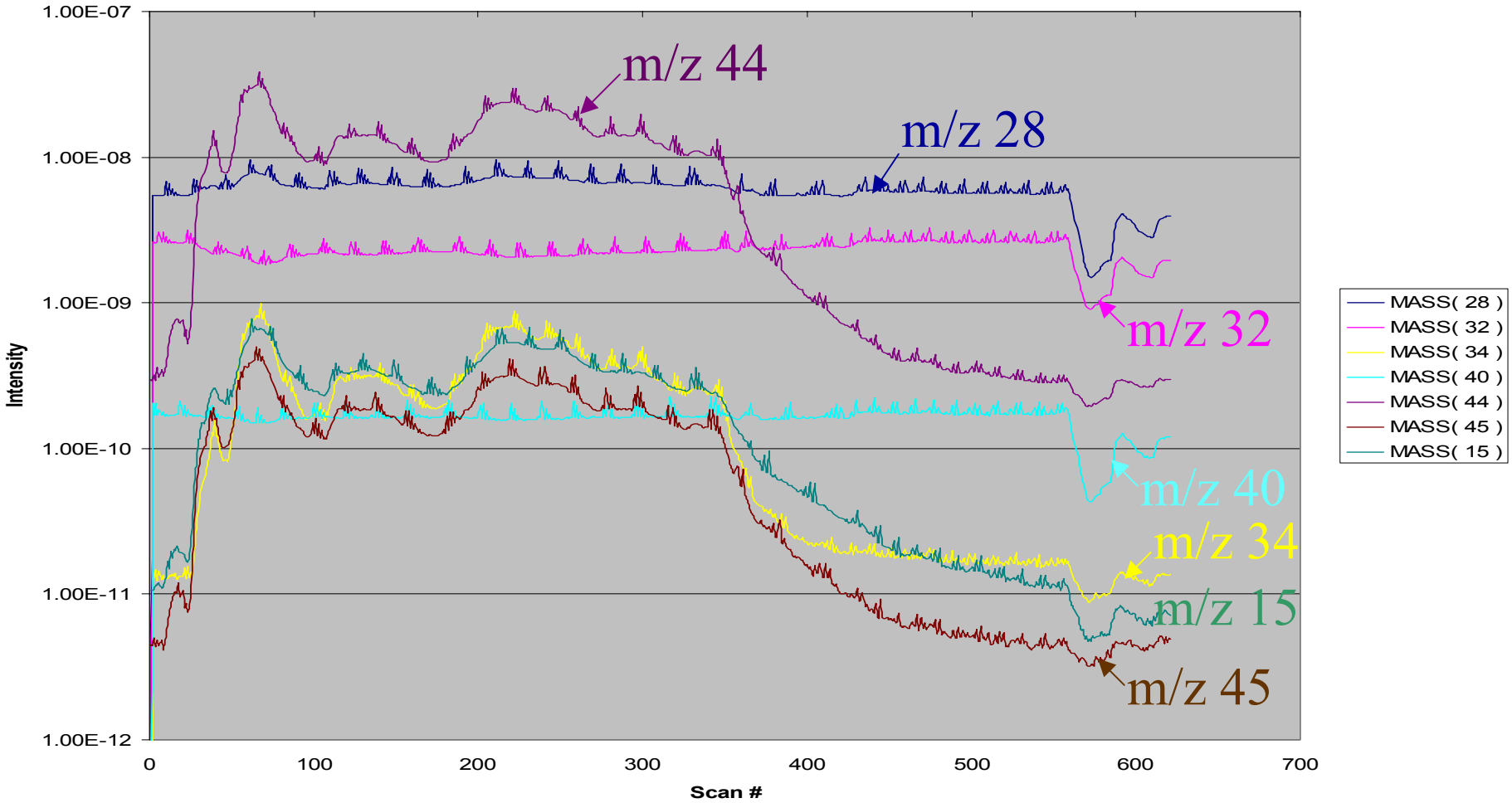
Lake Yellowstone transect
Bridge Bay to Mary Bay (m/z 44)



m/z 28, 32, 34, 40, 44 & 45 Intensities at Otter Vent (3m), Lake Yellowstone



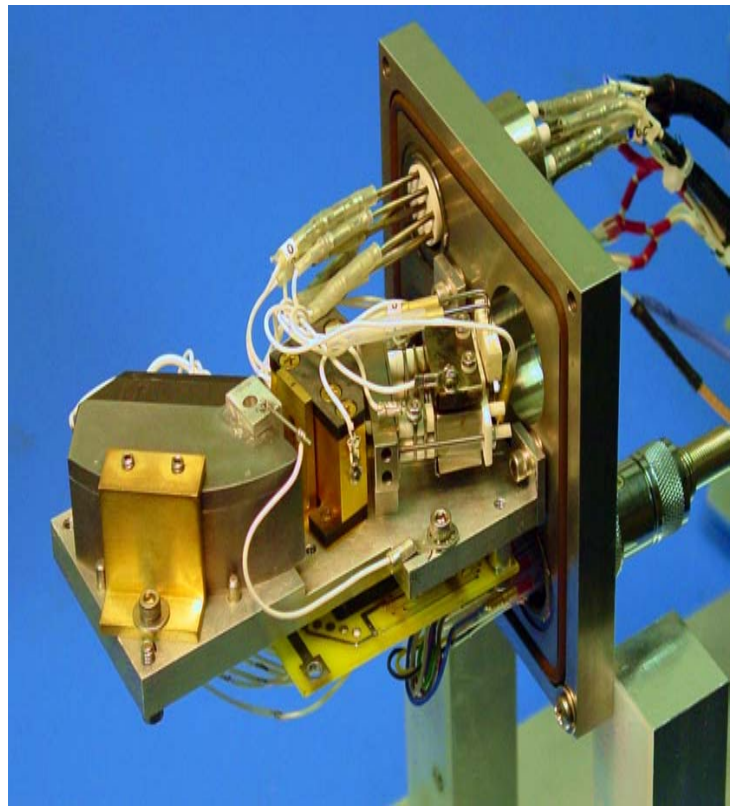
m/z 15, 32, 34, 44, 45 Intensities at Vent (30 m) in Lake Yellowstone



Even an Underwater Mass Spectrometer needs a Break

Future Development Plans

- Alternative Sampling Interfaces
  - Solid Phase Extraction (SPME)
- In-line Acidification
  - DIC to CO_2
  - In-situ Magnetic Sector Instrument Intelligent Ion, Inc.
- Unattended Remote Operation
  - Ocean observatory
- Full Ocean Depths



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