Simultaneous detection of dissolved gases and volatile organics using in-situ mass spectrometry

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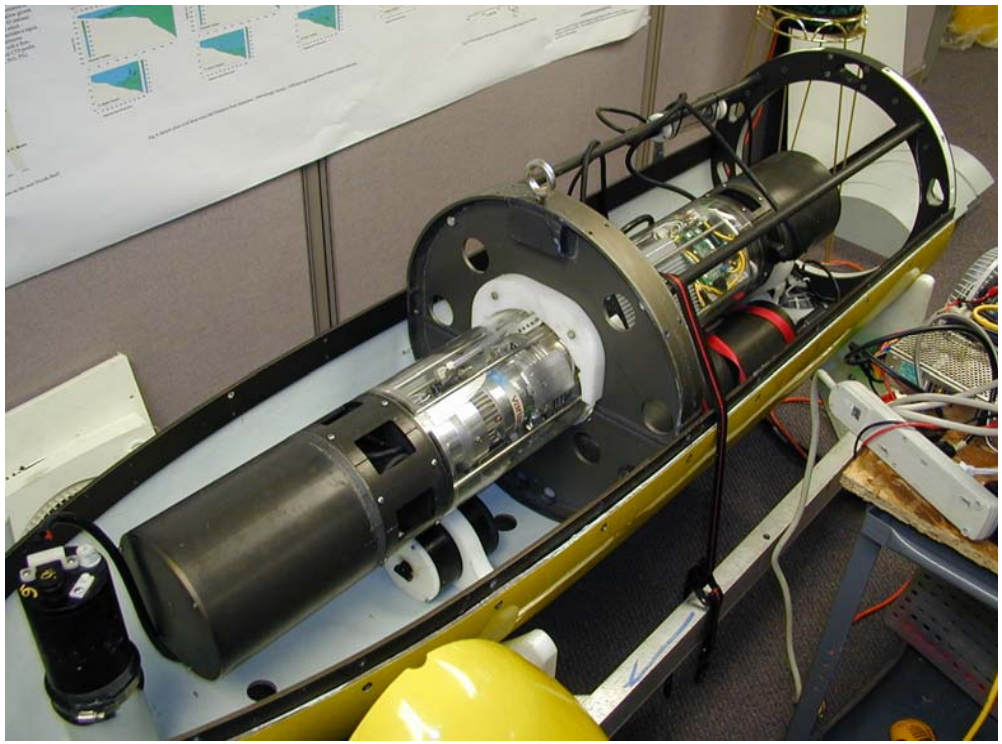
In-Situ MS at USF

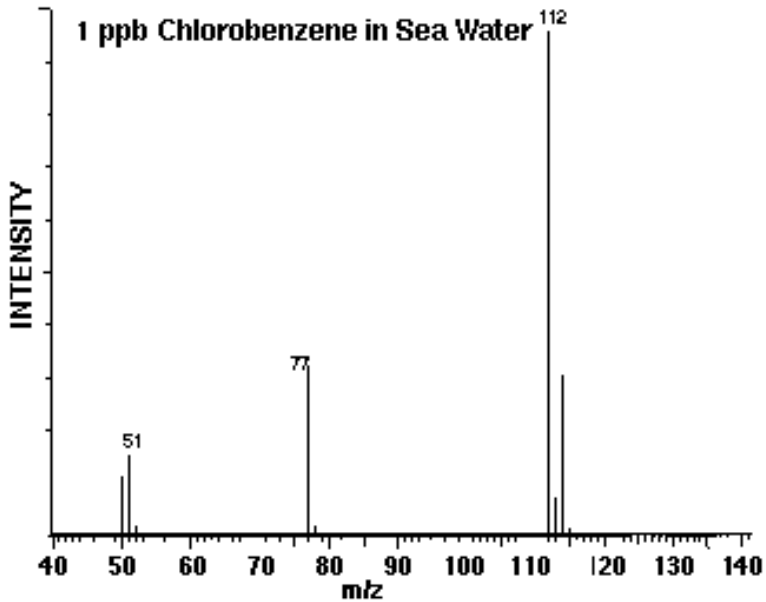
- 200-amu MIMS
- Deployments
  - Tampa Bay
  - Bayboro Harbor
  - Gulf of Mexico
  - Lake Yellowstone
  - Saanich Inlet
  - Lake Maggiore
- The Future…



100-amu UMS in OEX Nosecone

MS: Versatile Chemical Sensor

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



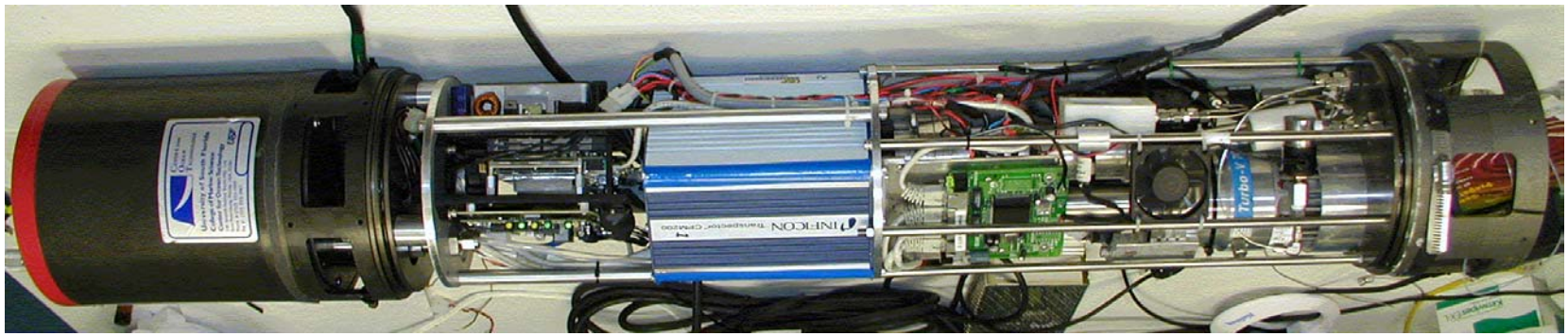
No configuration valid for all analytes

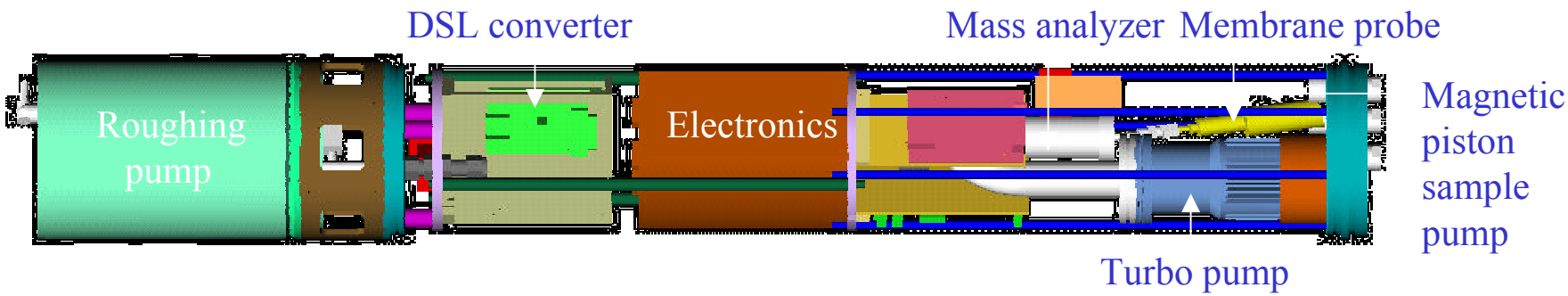
Instrumentation

Principle Features of UMS

Type	Linear quadrupole mass filter
Mass range	200 amu
Inlet System	Membrane introduction system
Power consumption	<100 Watts
Voltage of operation	24 VDC
Deployment time	14-21 days
Dimensions	∅ 19 cm (7.5”)
	L 105 cm (41’’)
Weight	33 kg (72.7 Lb)
Depth	>200 m
DSL tether range	~1600 m (1 mile)

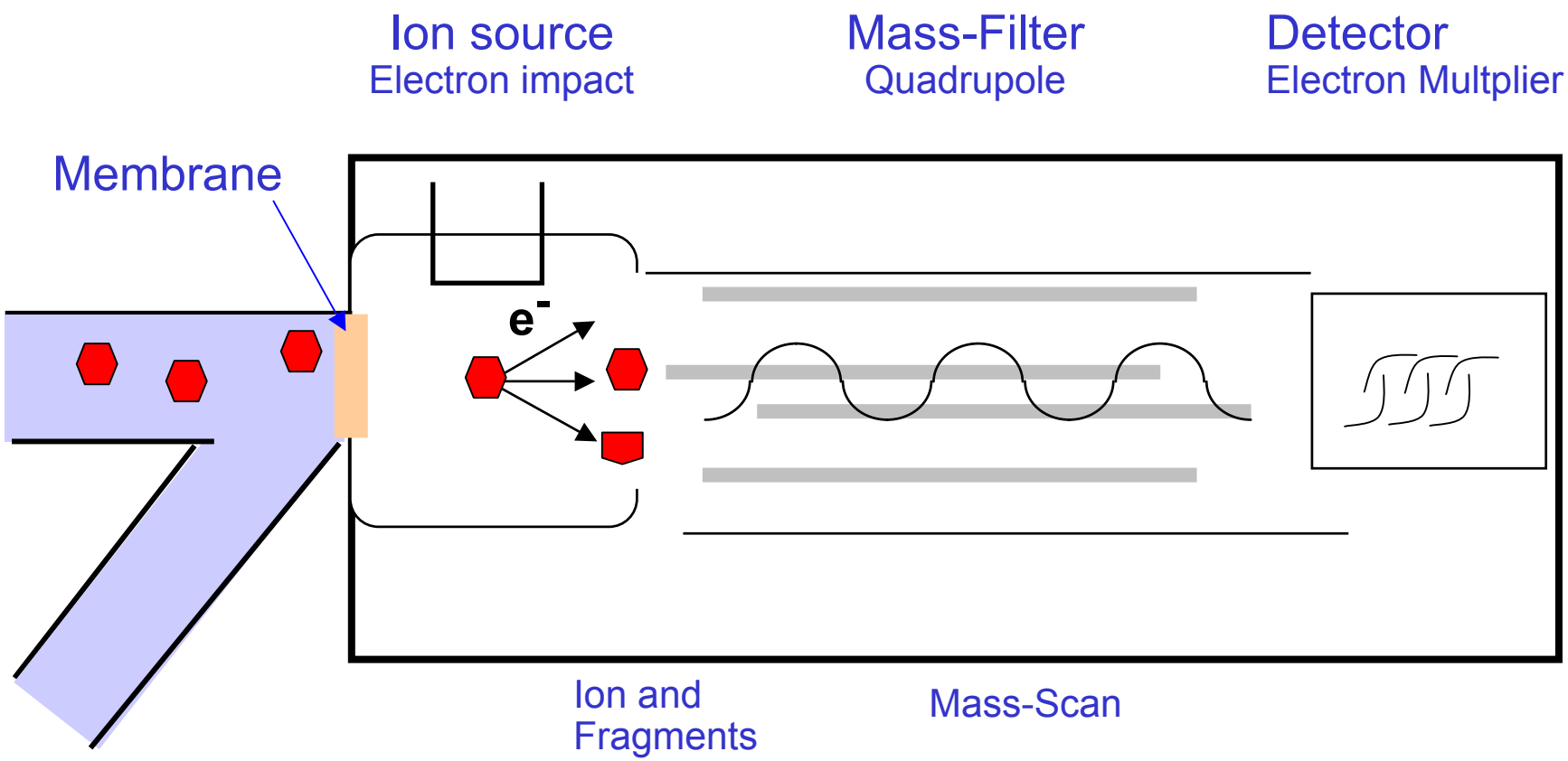
200-amu Linear Quadrupole MIMS



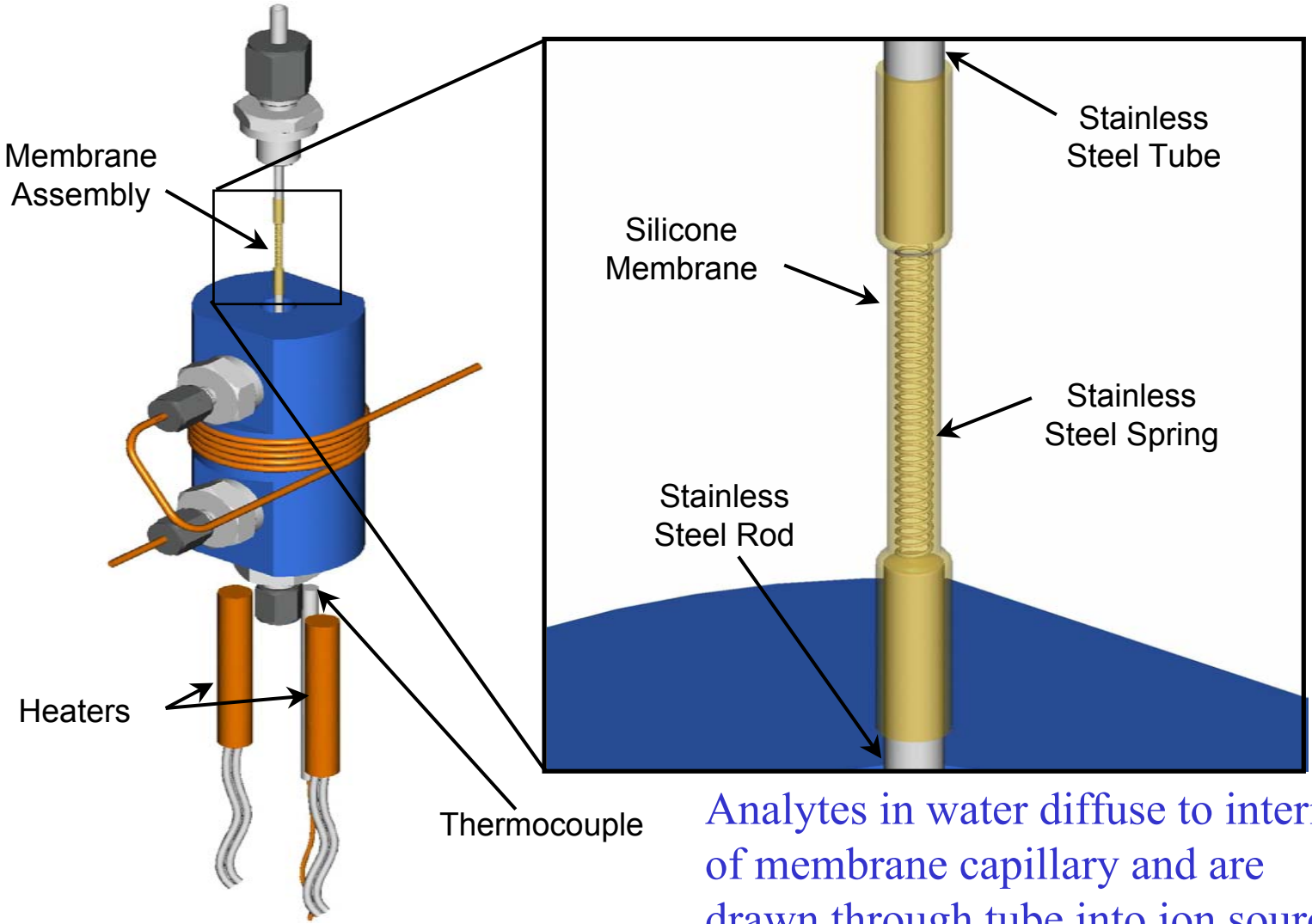


Compact 200-amu RGA with closed ion source

Membrane Introduction Mass Spectrometry (MIMS)



Deep-Water MIMS Probe



Analytes in water diffuse to interior of membrane capillary and are drawn through tube into ion source

Target Analytes for Underwater MIMS

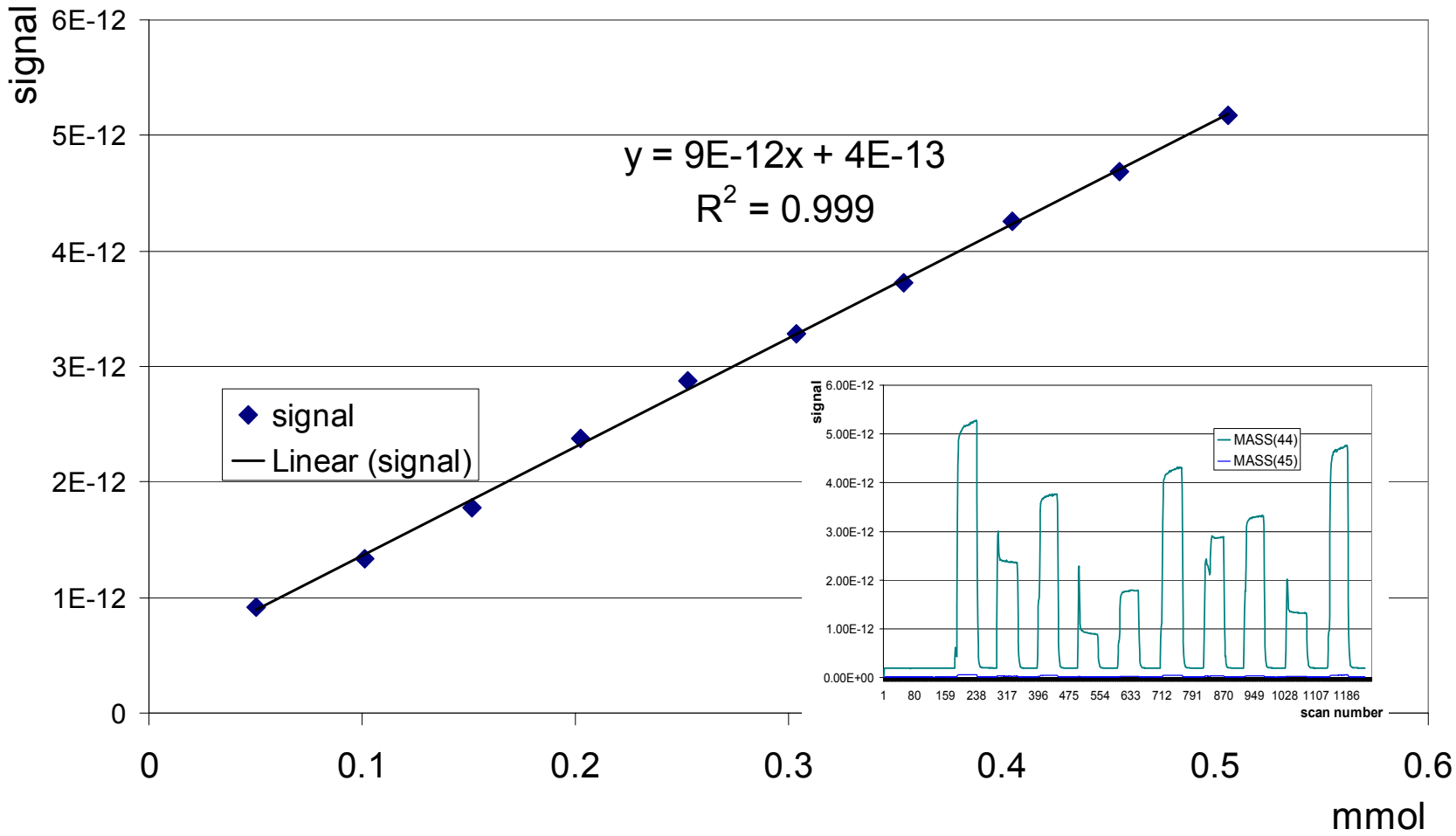
- Gases
  - CH_4, N_2, O_2, CO_2, Ar, etc.

    (very low ppm, ~10 sec response)
- Volatile Organic Compounds
  - Benzene, Toluene, Xylene, Dimethyl sulfide…

    (very low ppb, ~1-5 min response)
- Semi-Volatile Compounds
  - Napthalene, PAHs, Pesticides, etc.

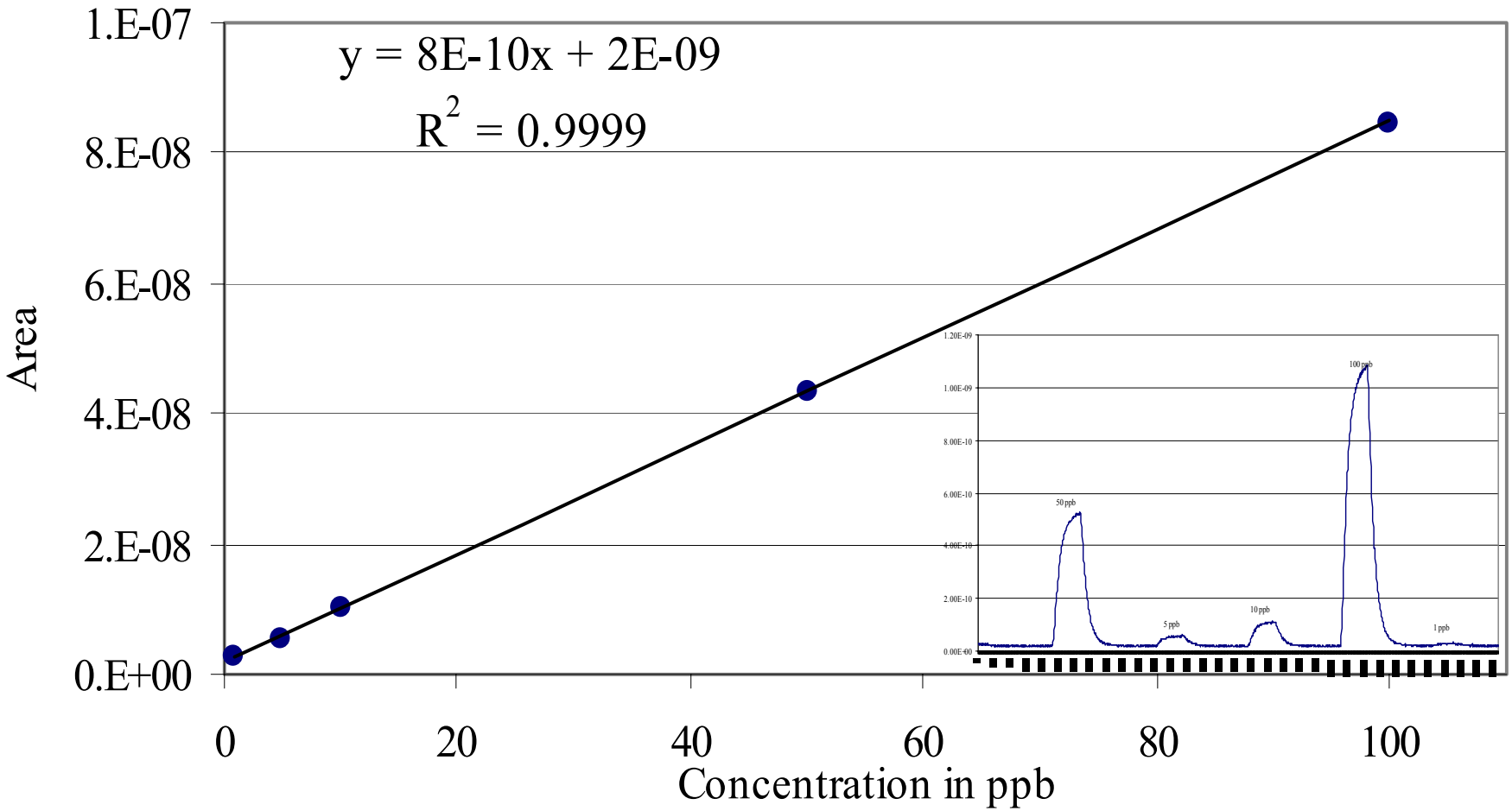
    (low ppb, ~5-20 min response)

Calibration of CO_2

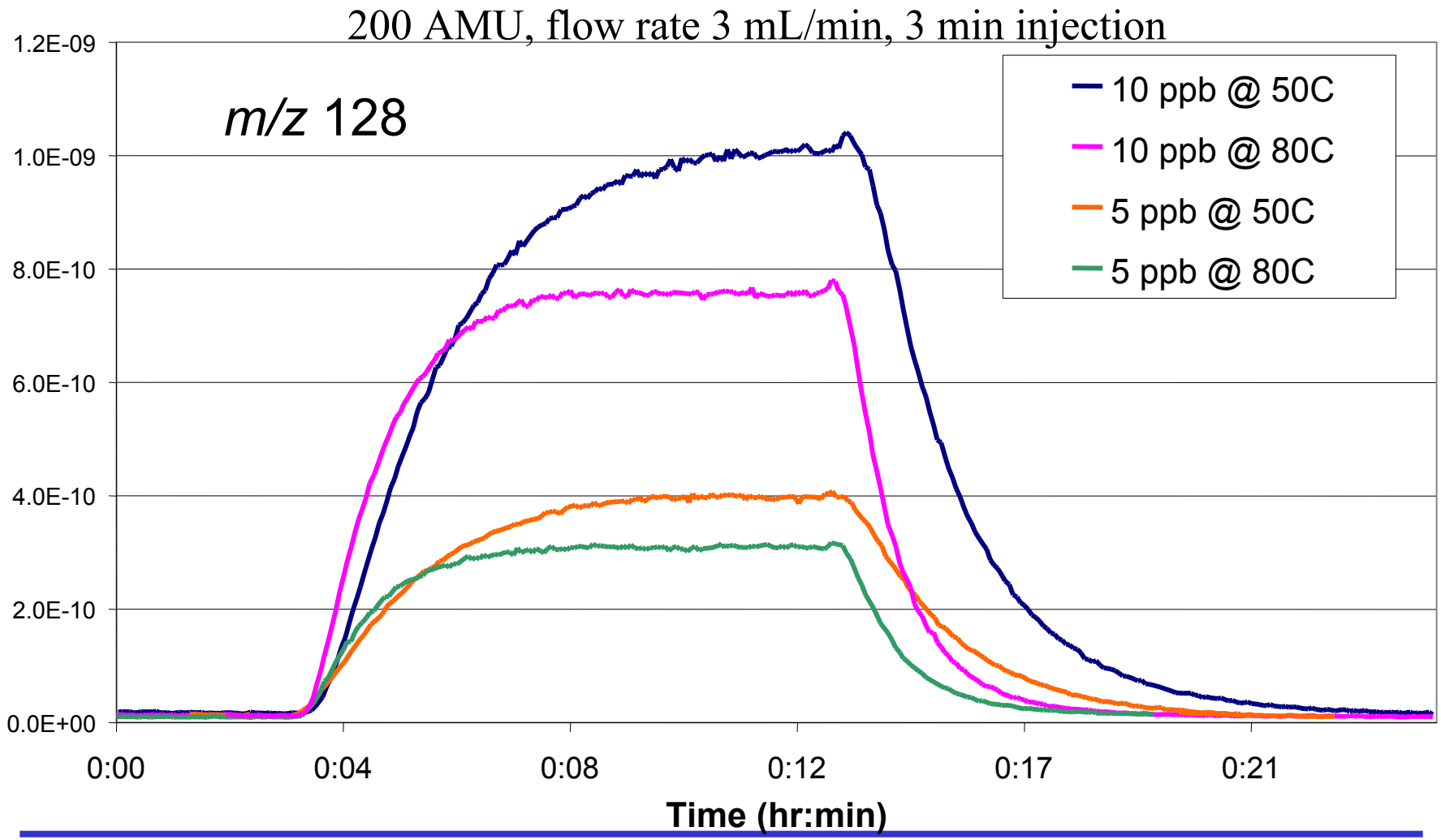


$NaHCO_3$ in 1 L water, 100 ml aliquote + 0.5 ml of 1 mol/L HCl

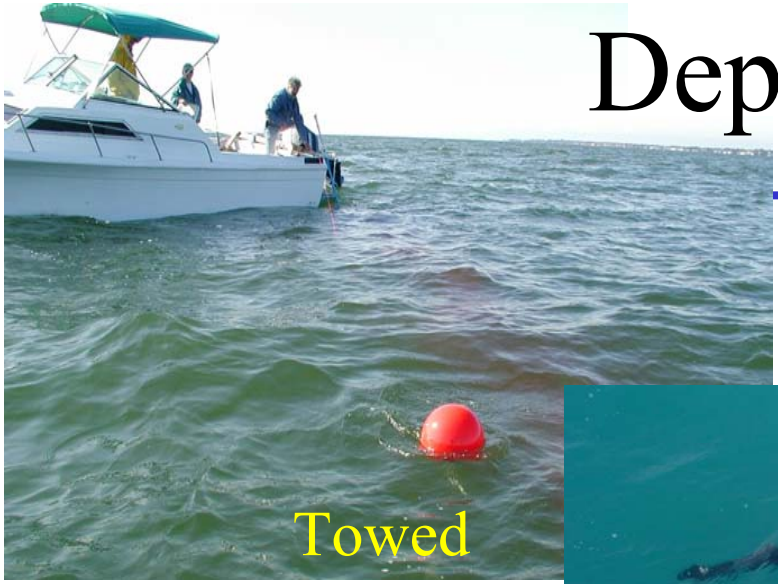
Calibration of Chloroform



Naphthalene in Seawater



Deployments

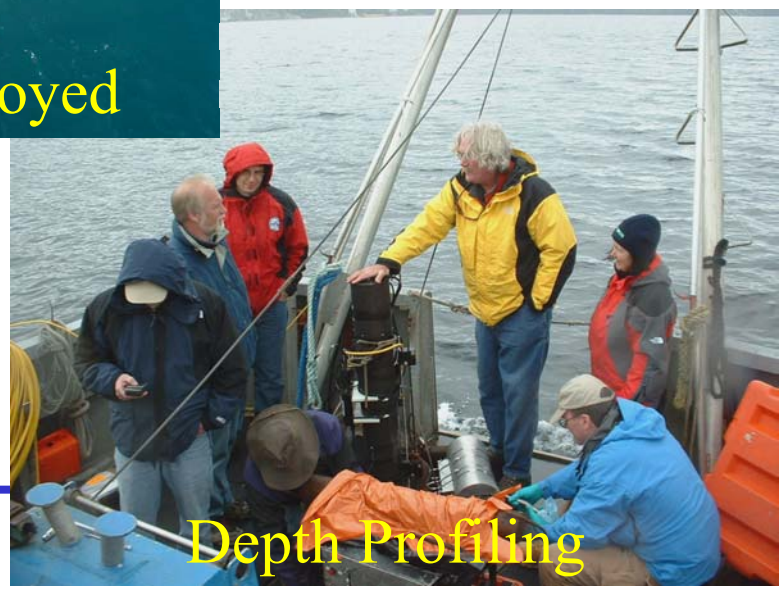


Towed

Guided Surface Vehicle

Diver Deployed

Remotely Operated Vehicle



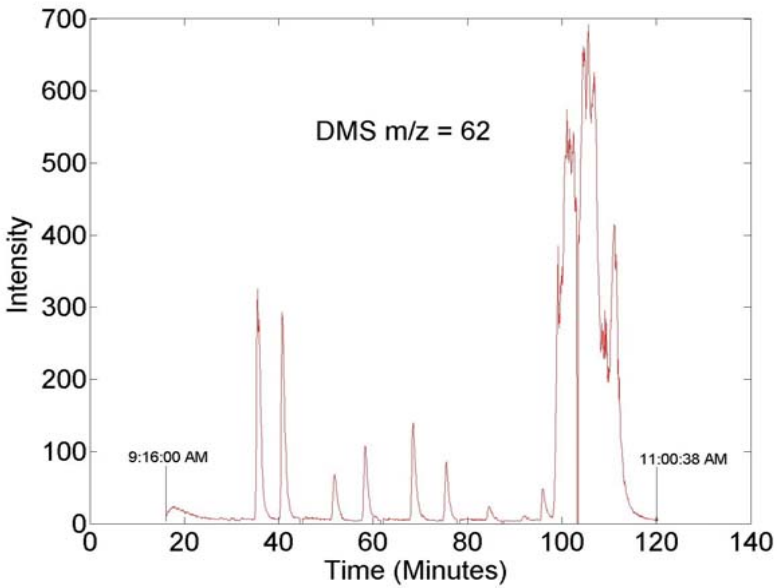
Depth Profiling

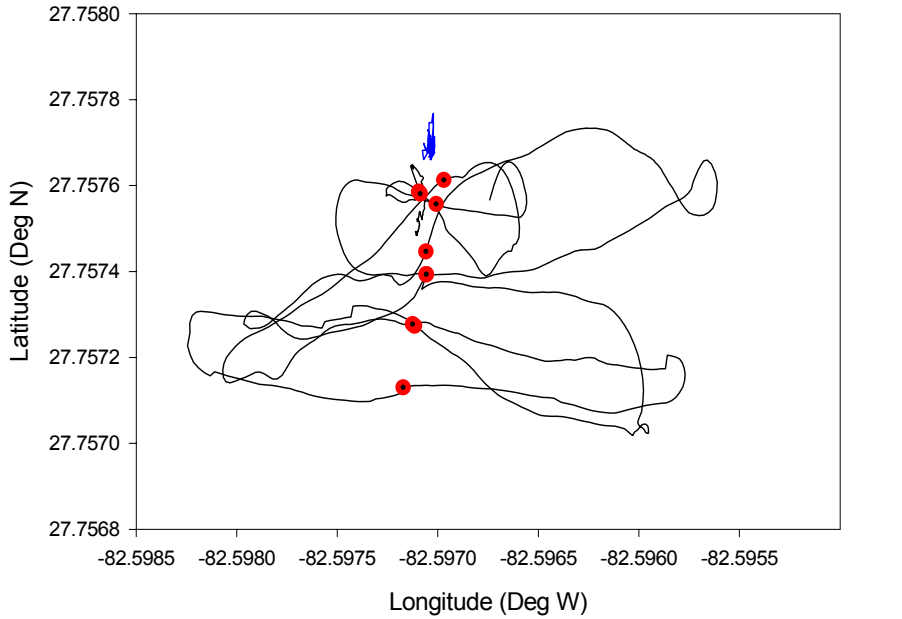
Logistics of Plume Mapping

- 2L DMS/1 hour with Dye
- Anchored boat
- Steady tidal current

- MS navigated through DMS plume w/ GPS
- Multiple transects
- Varying distances

Merged MS Data/GPS Record Identifies Location of Plume



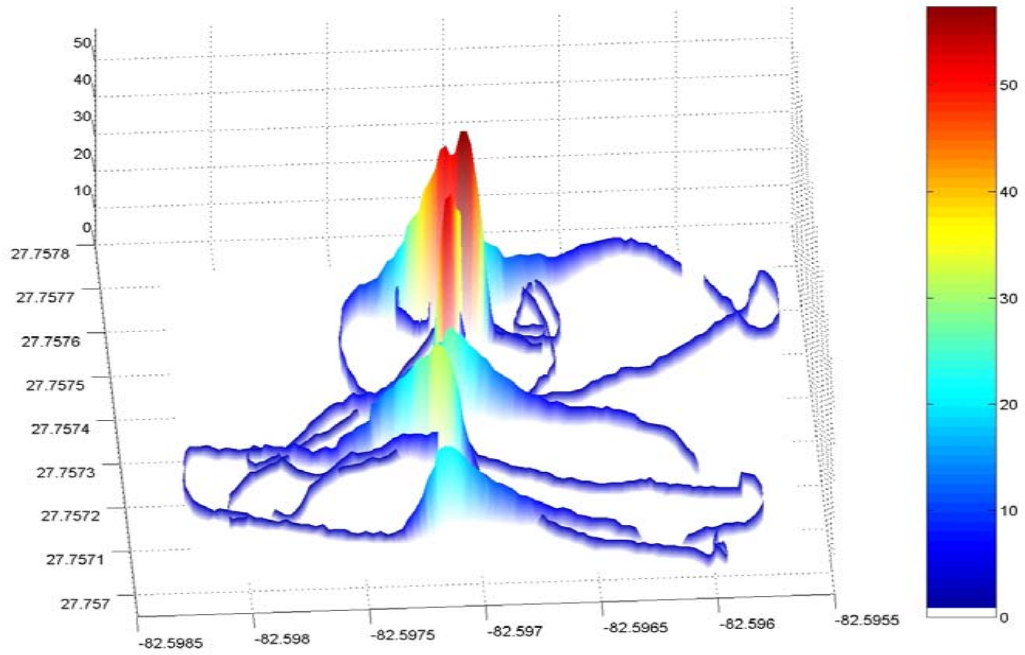


Mass Spectrometer Data

- Peaks = crossing the plume
- Largest peak = closest to dispense boat
- Peaks line up to show where plume was located

3-D Visualization of MS/GPS Data

MS Data Superimposed onto Boat Route

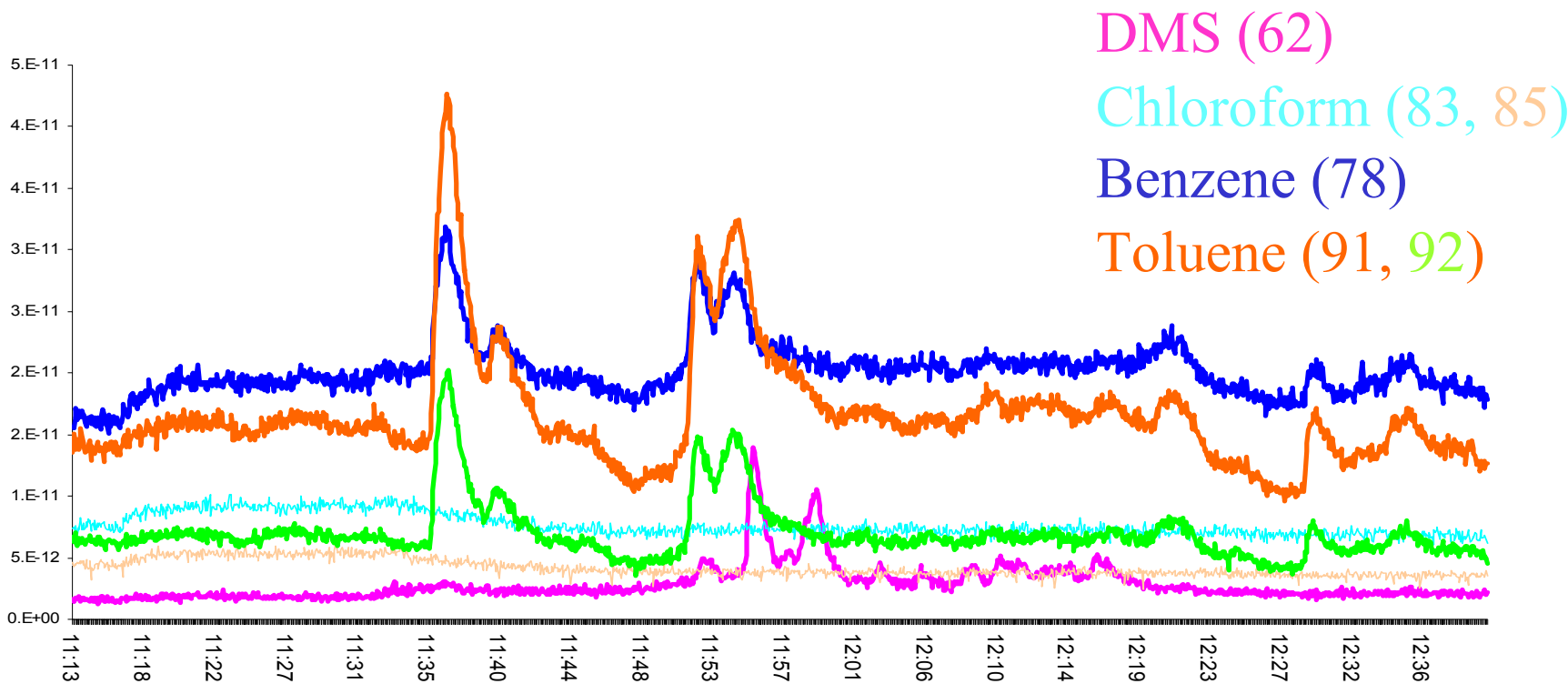


- Ion intensity scale superimposed on position
- Mapped as Lat and Lon on the horizontal scales
- Peaks wider than plume

Deployment: Guided Surface Vehicle Surveying Chemical profiling and plume mapping

- UMS mounted on ENG Concepts Guided Surface Vehicle
- Bayboro Harbor and Salt Creek, St. Petersburg, FL
  - Regular boat traffic
  - Number of marinas

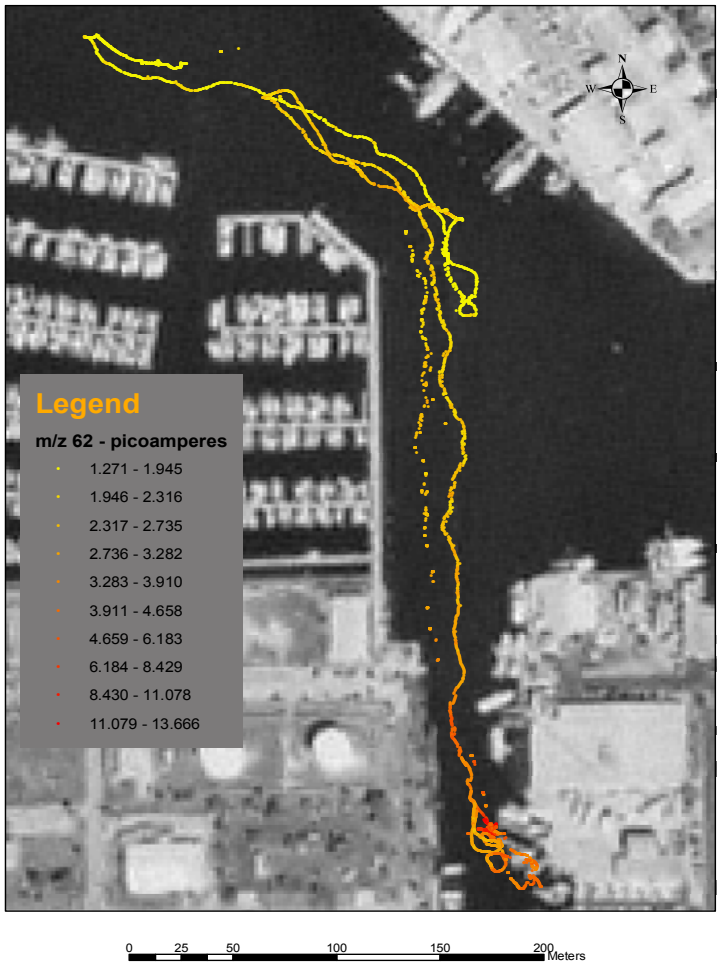
UMS Data from Survey of Bayboro Harbor



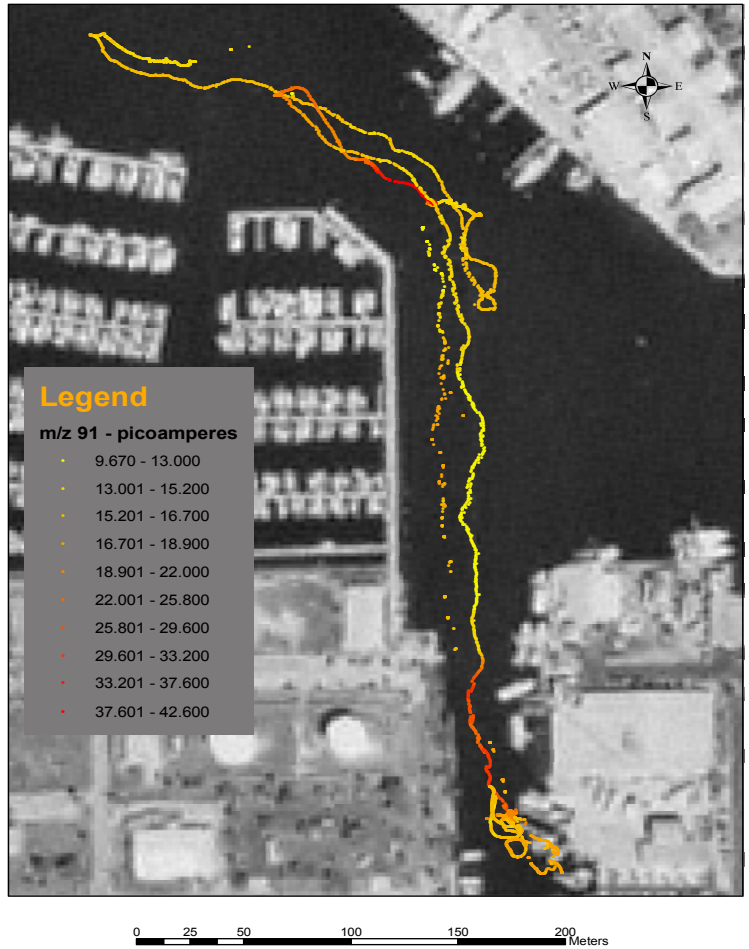
- Characteristic VOC's detected
- Benzene and toluene found in motor boat gas exhaust
- DMS algae byproduct
- Single instrument can monitor multiple plumes at the same time

Mapping of Dimethyl Sulfide and Toluene

DMS



Toluene



Time matched GPS and MS data plotted on aerial photos

Higher concentration in Orange and Red

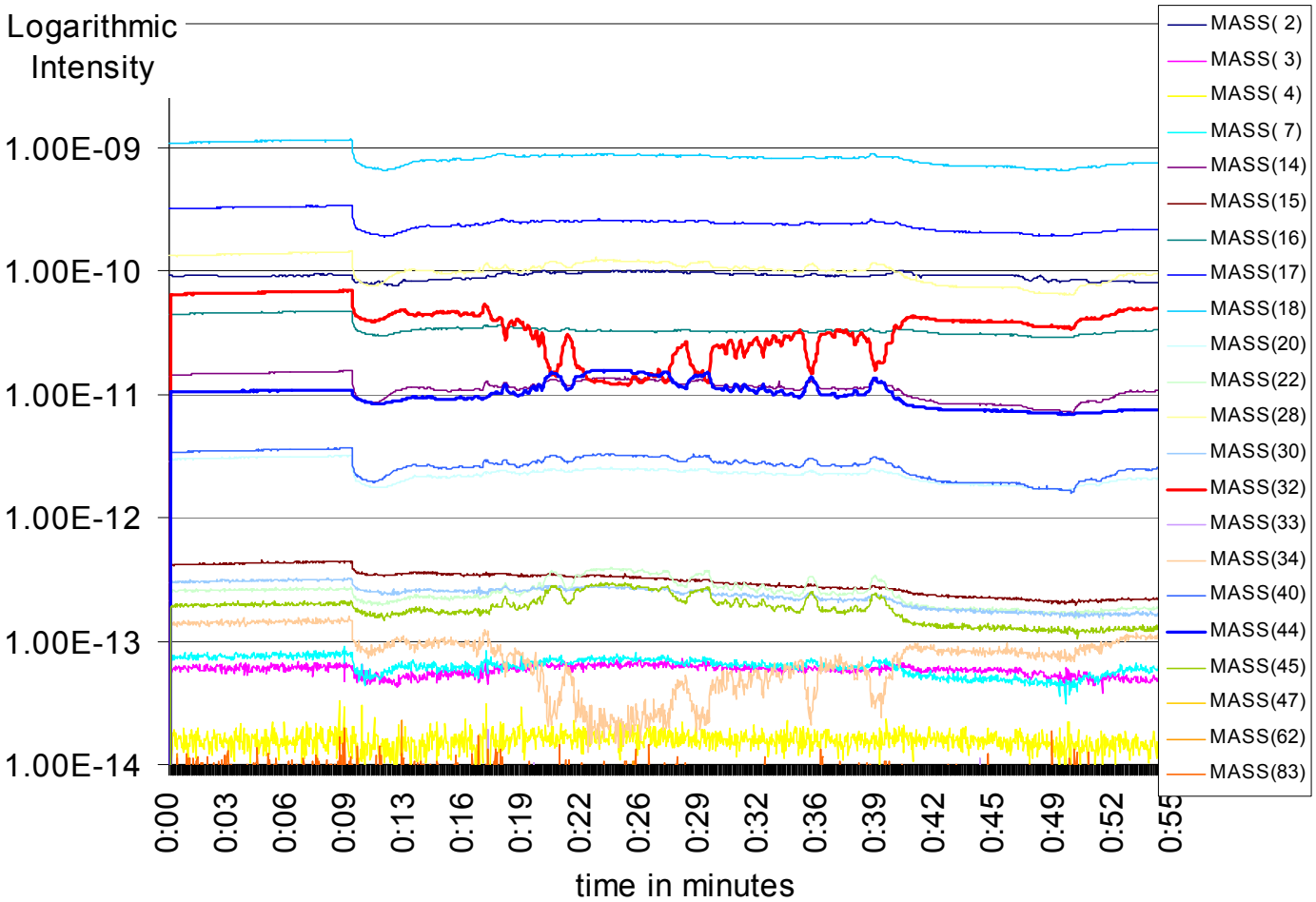
Exploration of Hydrothermal Vents with UMS

- Rusty Springs
- Gulf of Mexico

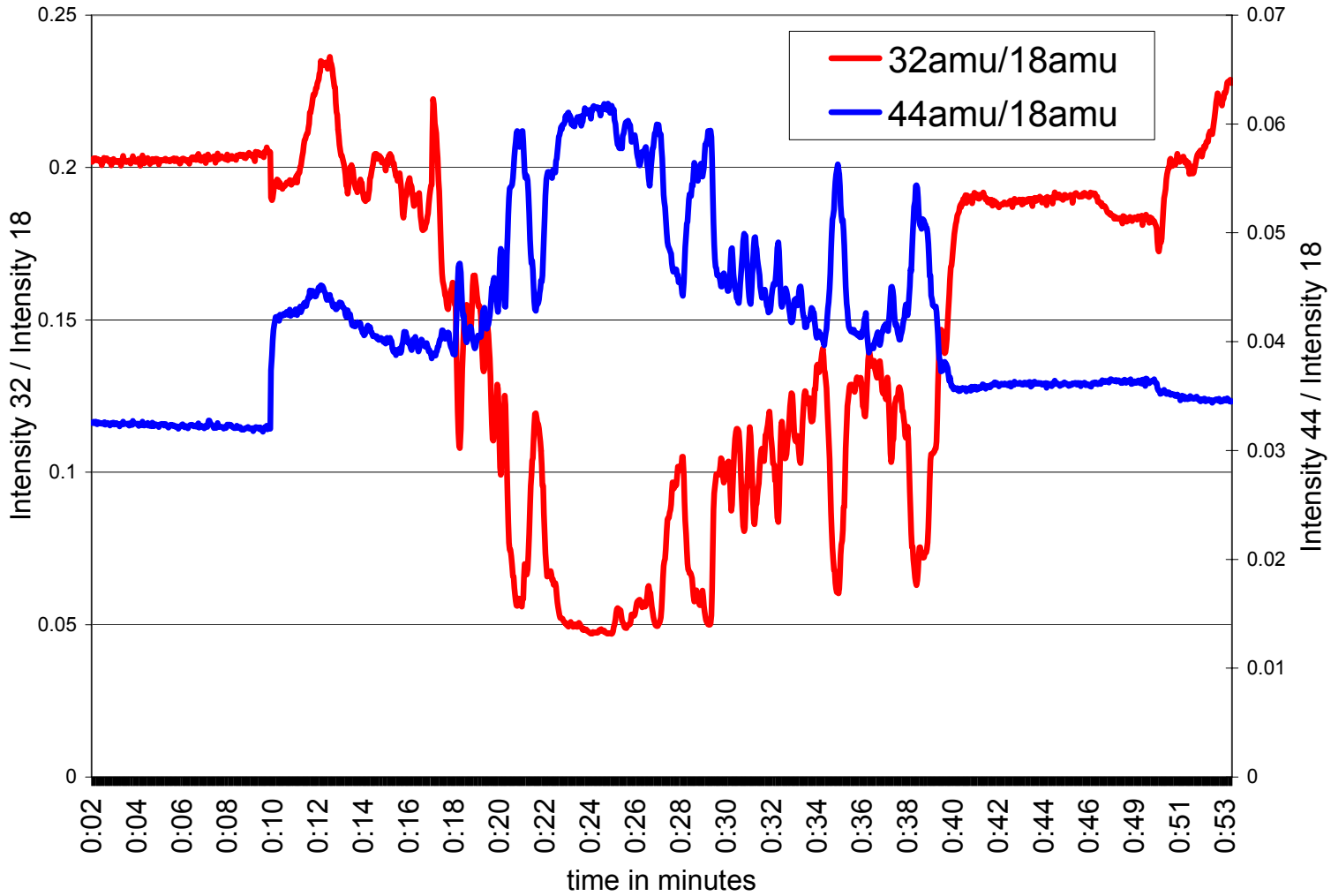
- Diver Deployed
- <20m Depth

UMS Data from Gulf Vent

@ 26° 14' 41.29" N; 82° 00' 52.47" W; depth 15 m



Normalized CO_2 & O_2 Data

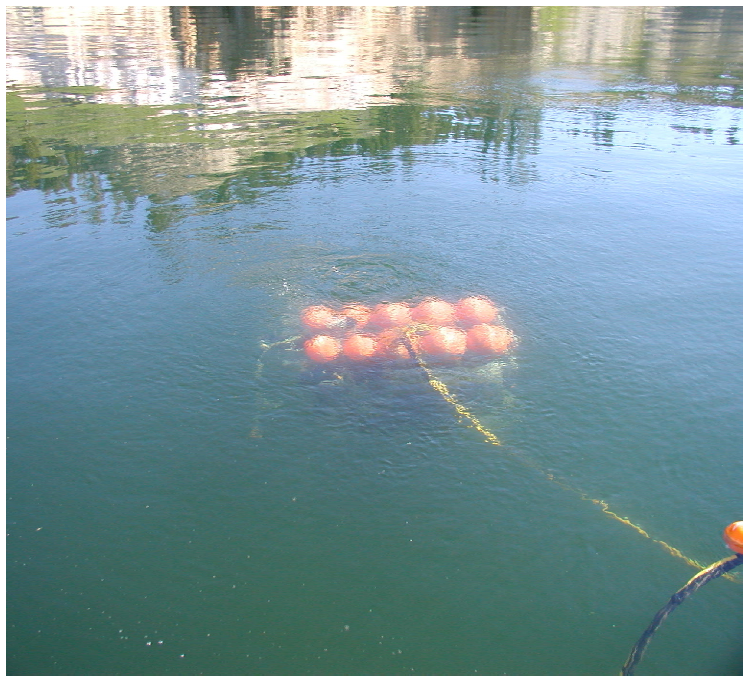


Lake Yellowstone Hydrothermal Vents

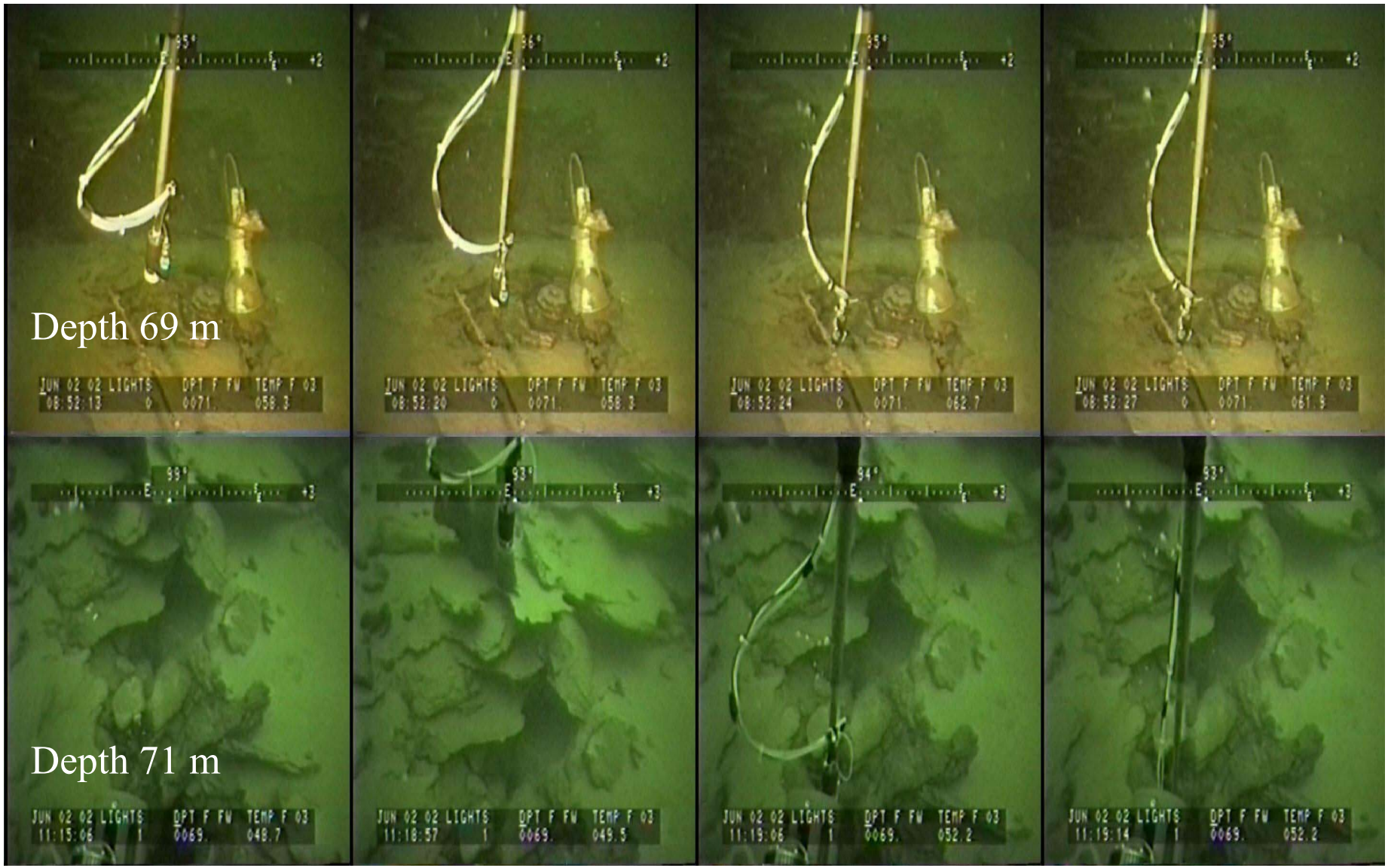
Observation of vent dissolved gas compositions

- Deployed on Eastern Oceanics ROV
- 72m depths
- MS at bottom of vehicle

- Remotely operated vehicle deployment
- Distinct geothermal conditions beneath lake

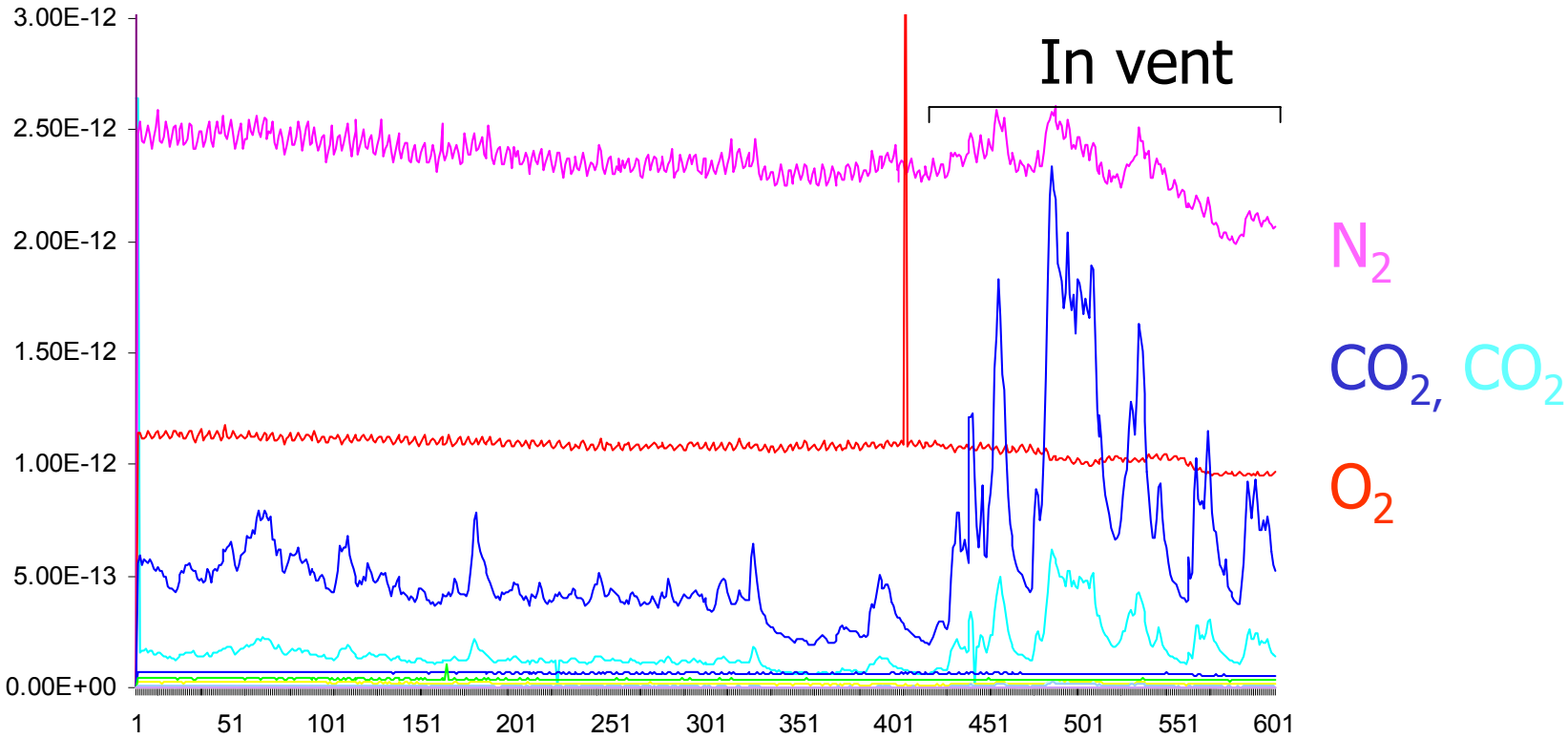


MS Inlet on ROV Extendable Probe

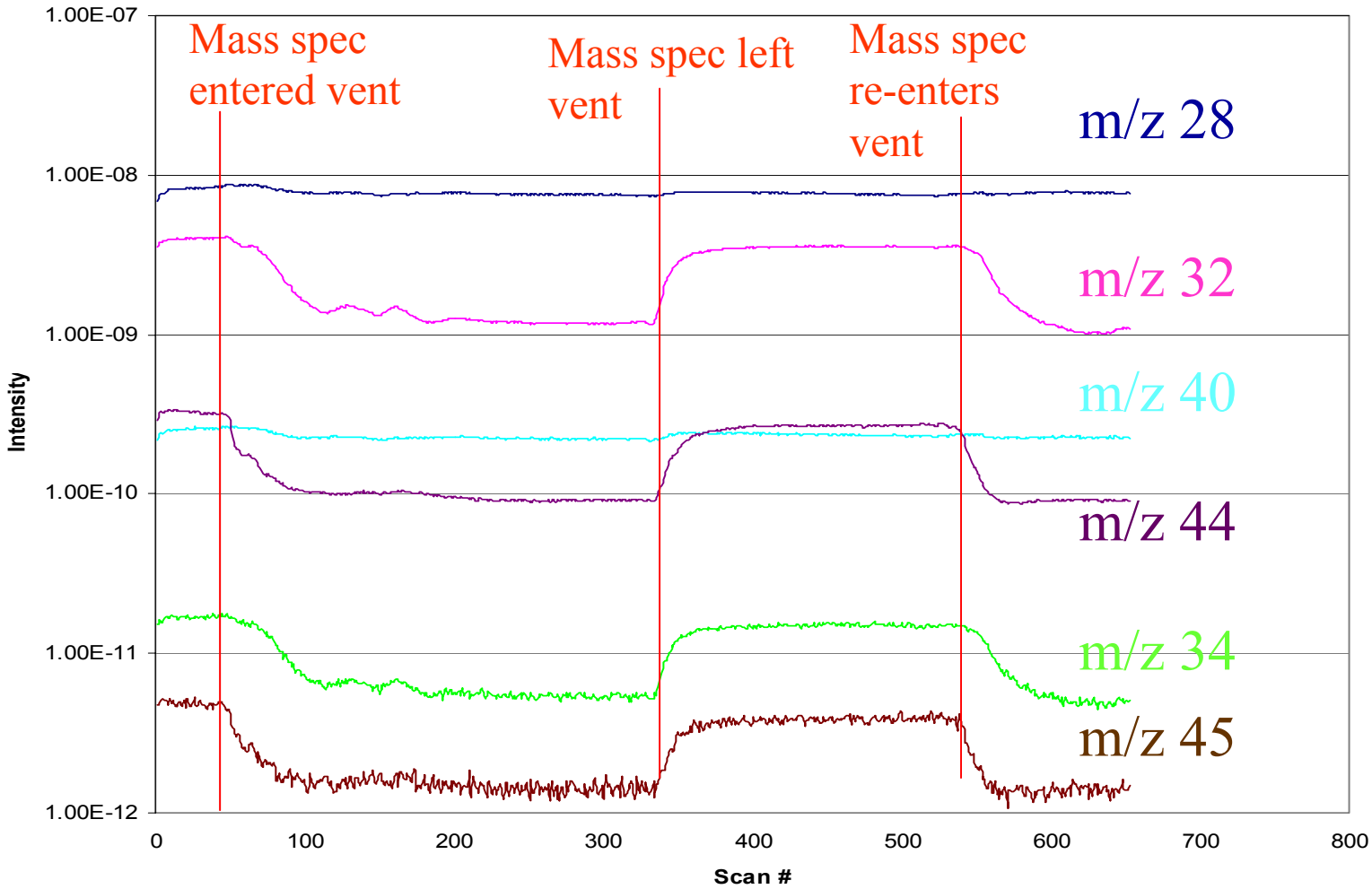


Hydrothermal Vent Gas Analysis

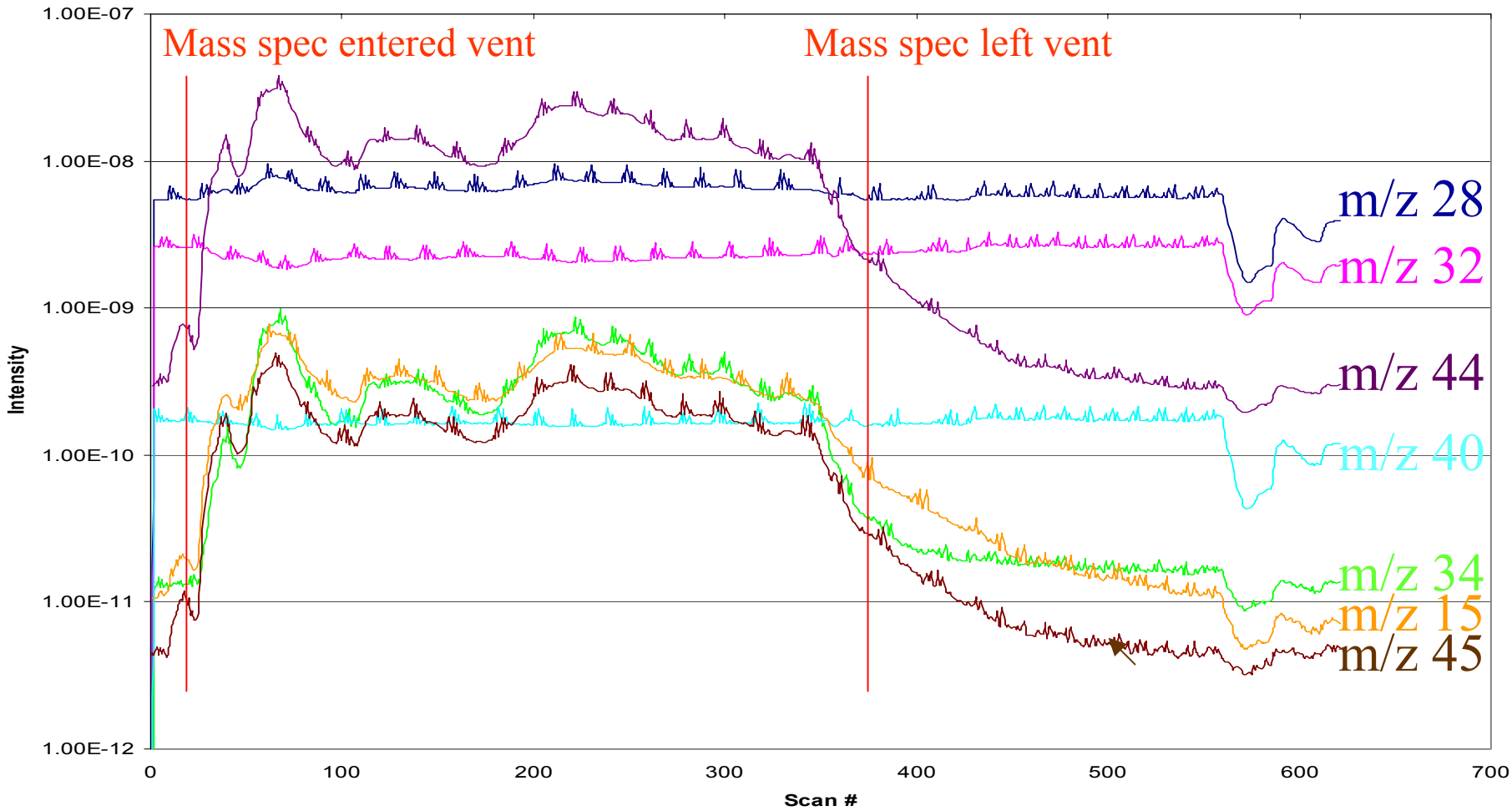
- Distinct differences in vent dissolved gas compositions
- Rapid response to gas compositions



MS Data from 3m Vent



MS Data from 30mVent

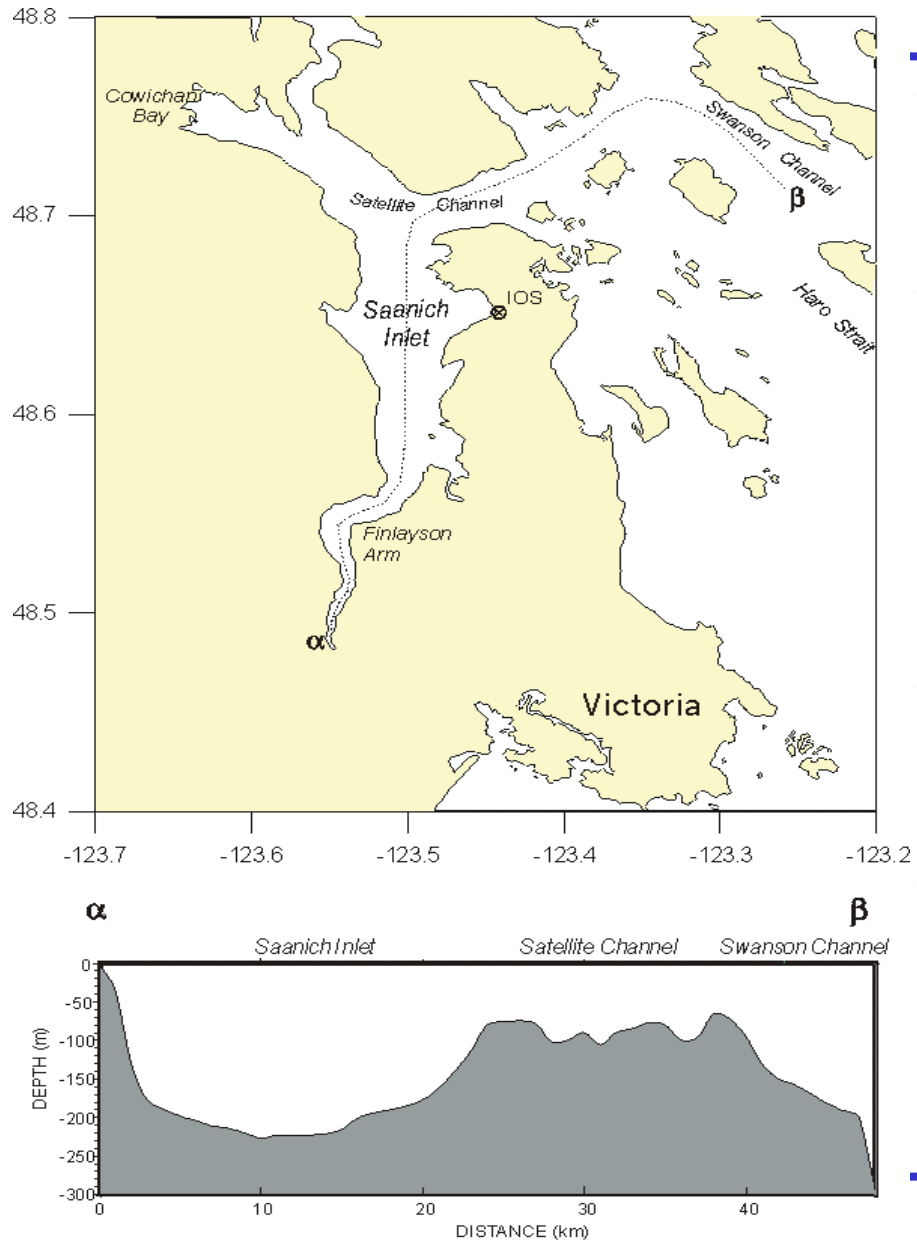


Depth Profiles Saanich Inlet Victoria, B. C.

- 200m depths
- Shipboard tethered deployment for power & communication

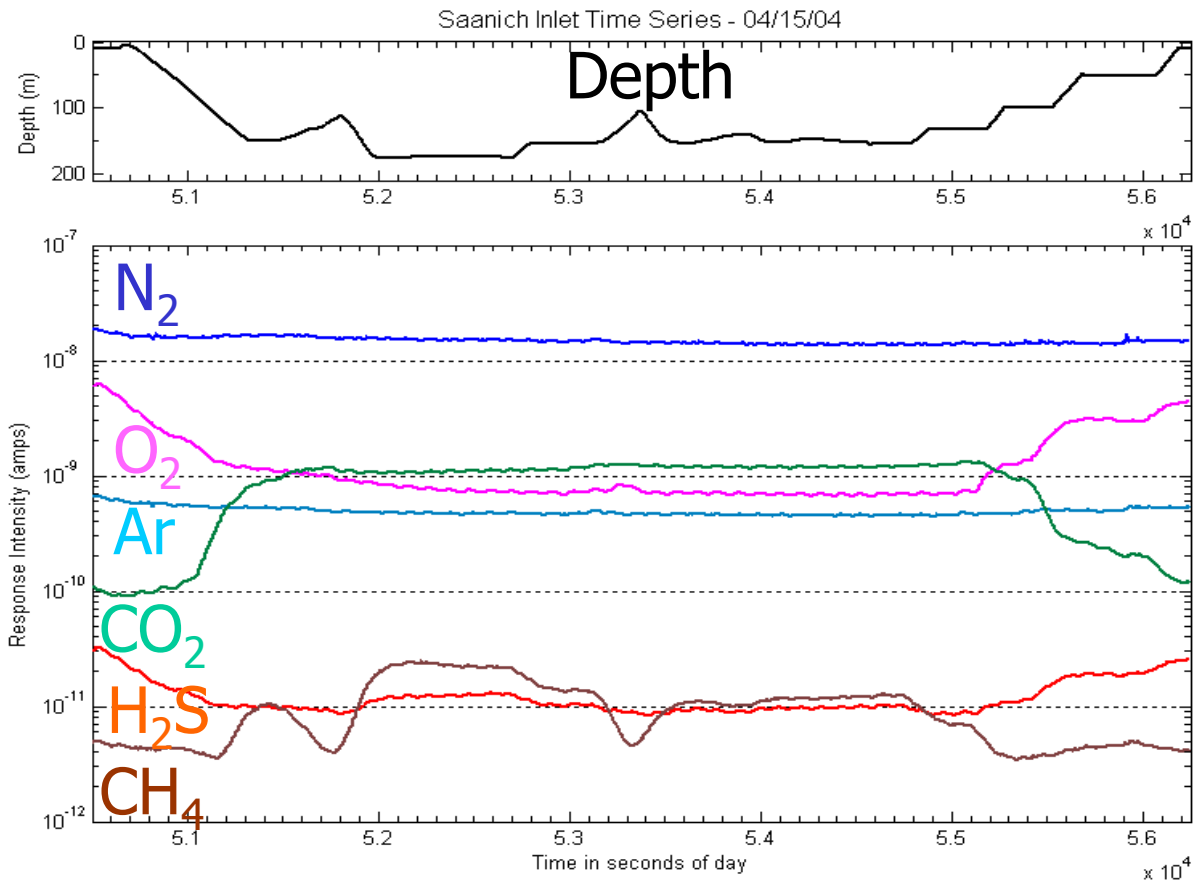
- Deep water is anoxic
- Rich in methane, CO_2, sulfur compounds

Saanich Inlet



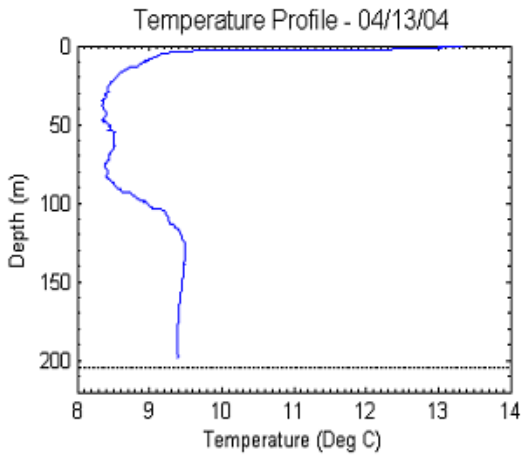
- The inlet is located just north of Victoria, BC
- Maximum depth: 225 m
- There is a ledge at 70 m located at the northern mouth of the inlet
- The ledge restricts bottom water circulation and turnover
- Bottom waters are anoxic with presence of reduced species, ie. CH_4, H_2S

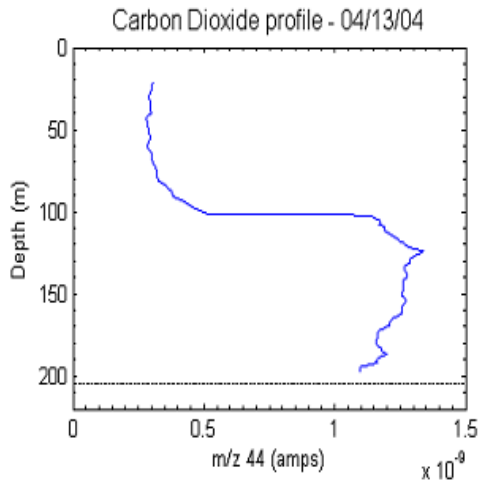
Saanich Inlet Time Series

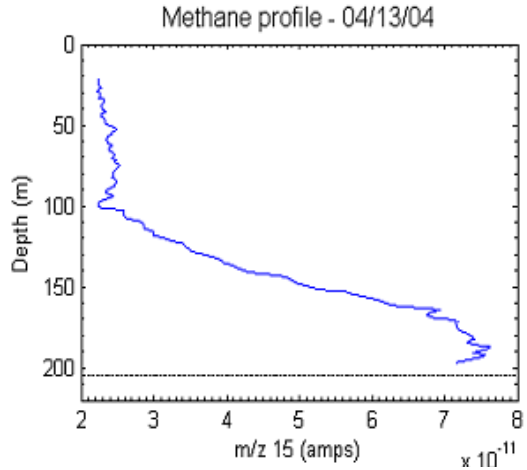


- Many gases show strong variations
- Strong changes in methane were detected below 100

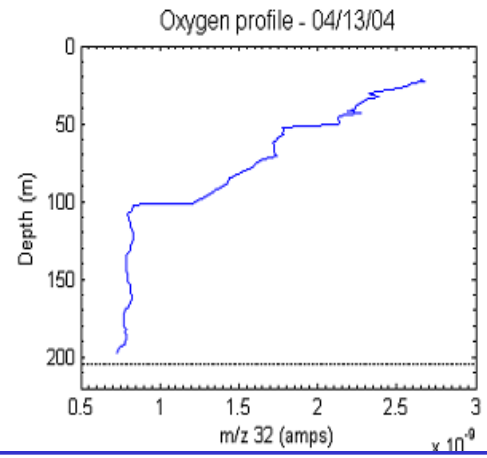
Simultaneous Depth Profiles Obtained

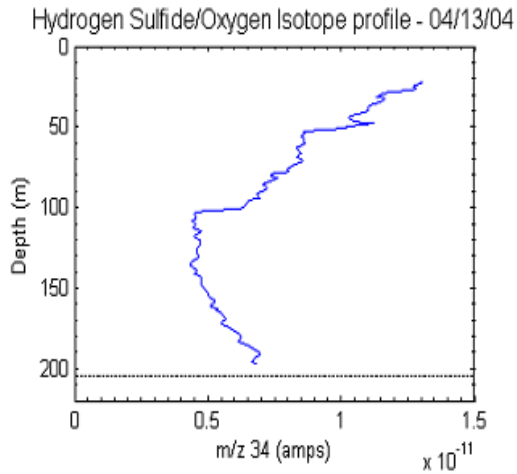






- Sharp increase m/z 44,15
- Sharp decrease m/z 32
- Thermocline 100 m

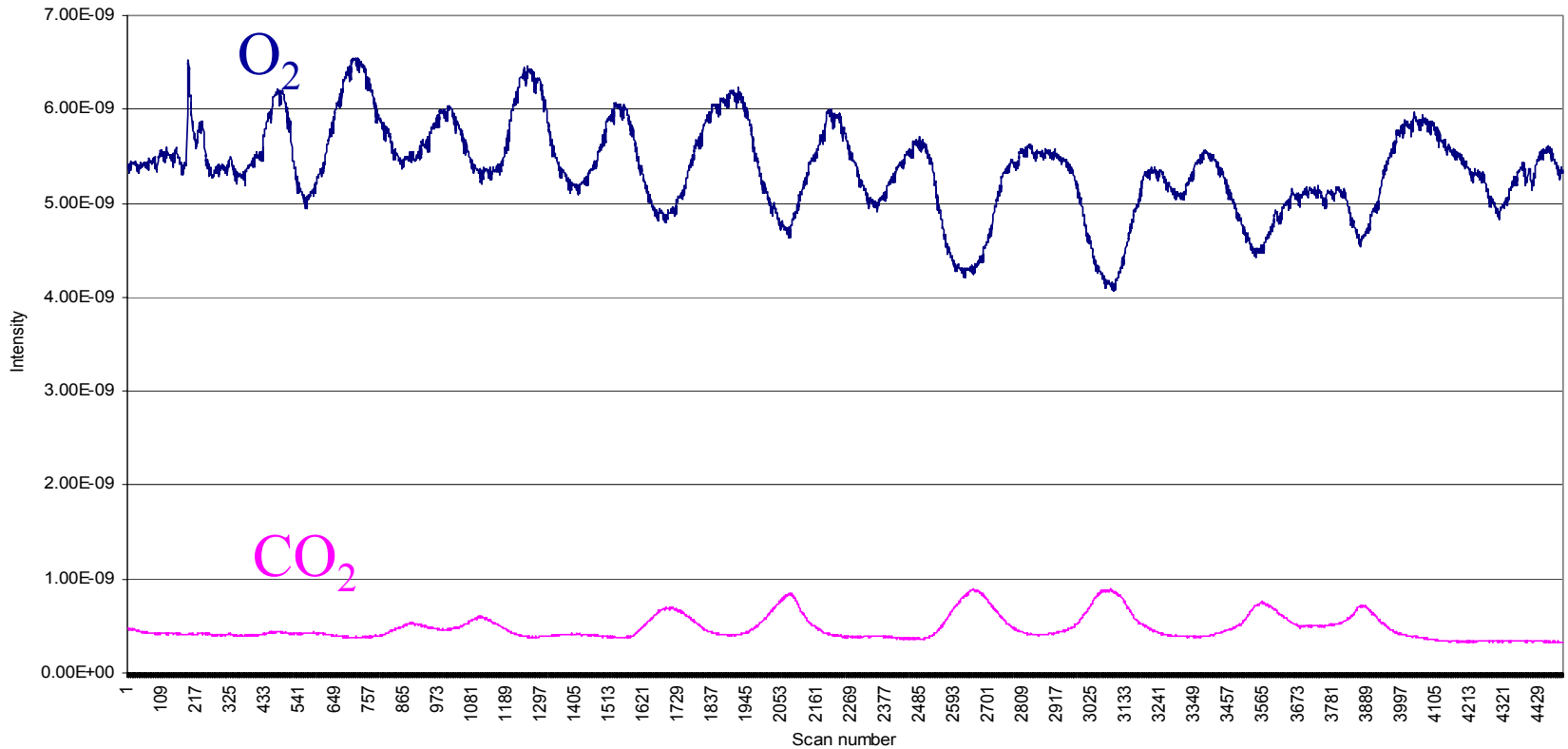




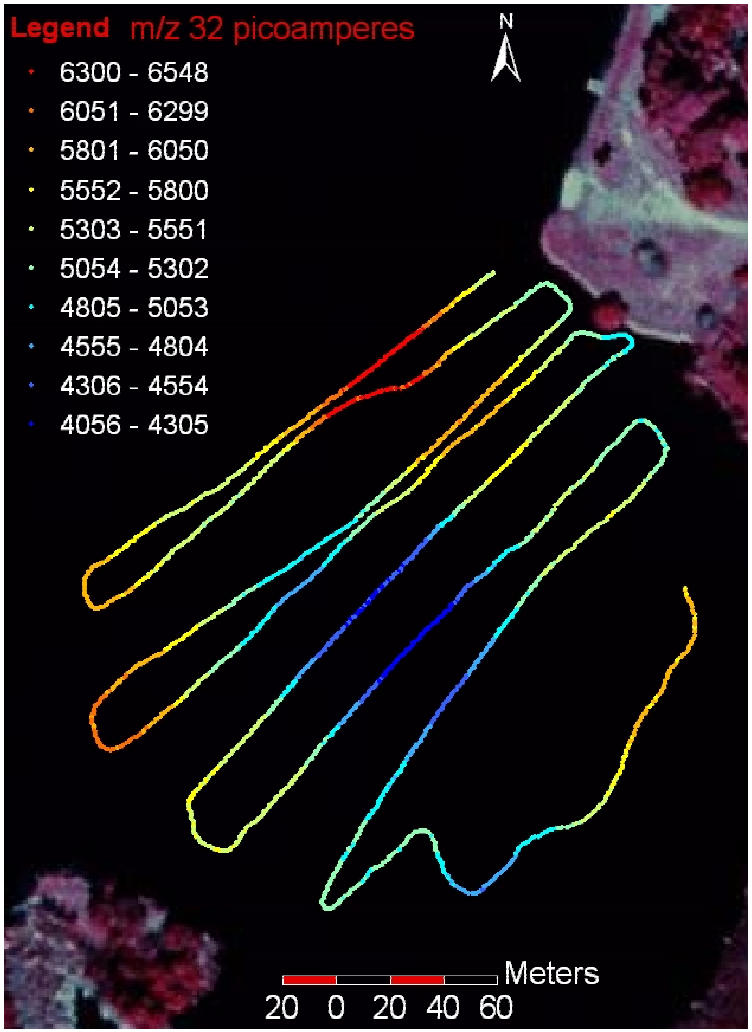
Lake Maggiore Chemical Surveys

- Mass spectrometer deployed aboard a guided surface vehicle
- Mapping variation of dissolved gas ion intensities
- Develop surface contour maps based on gas ion intensity data
- Carbon Dioxide, Oxygen and Methane as examples

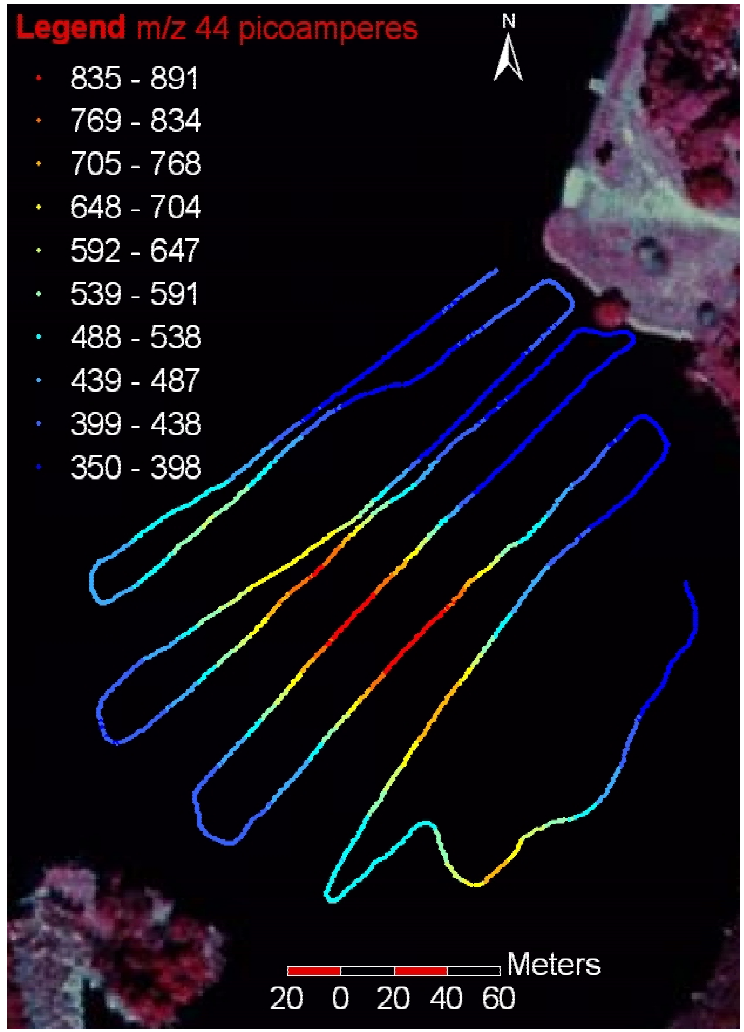
MS Data from Survey of Lake Maggiore



Mapping of Dissolved Gases

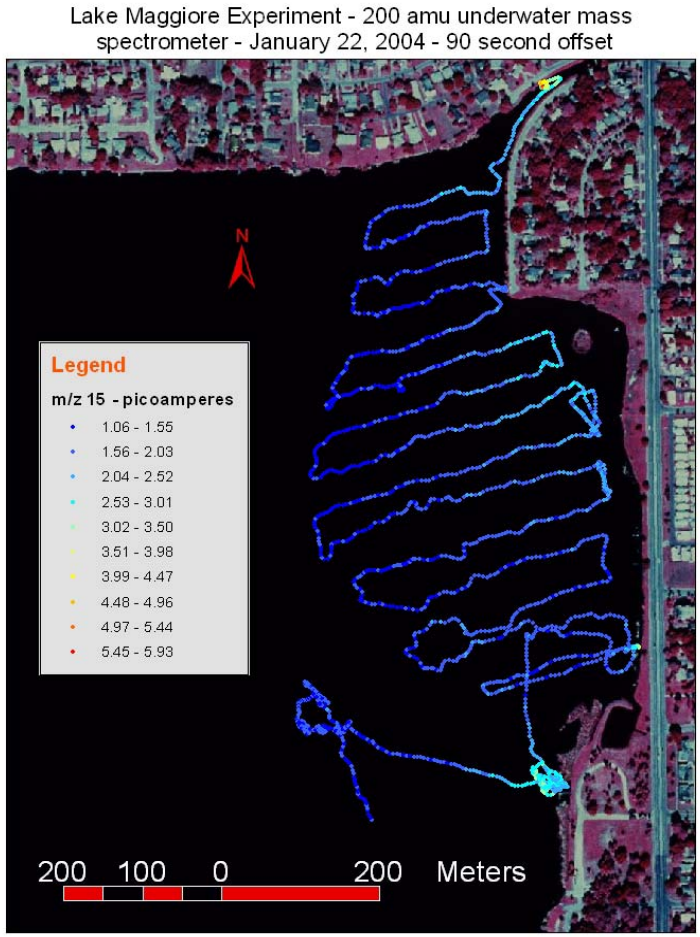


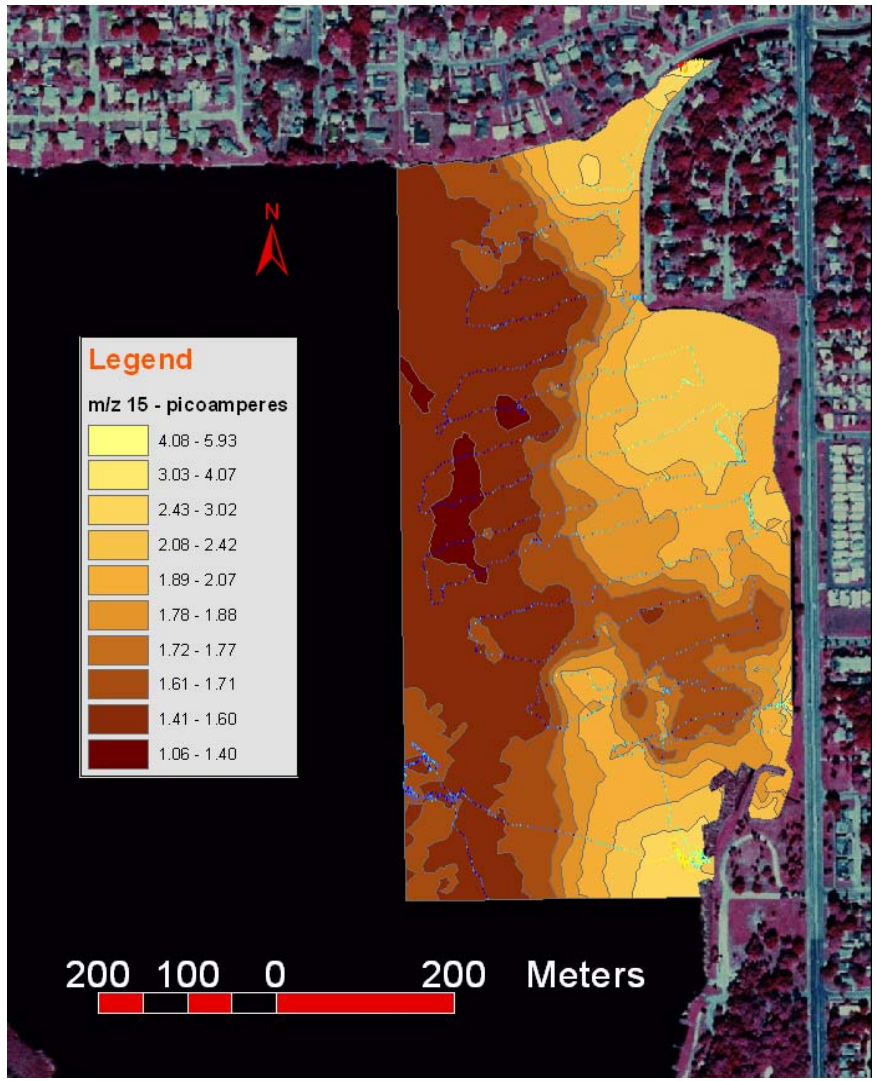
m/z 32



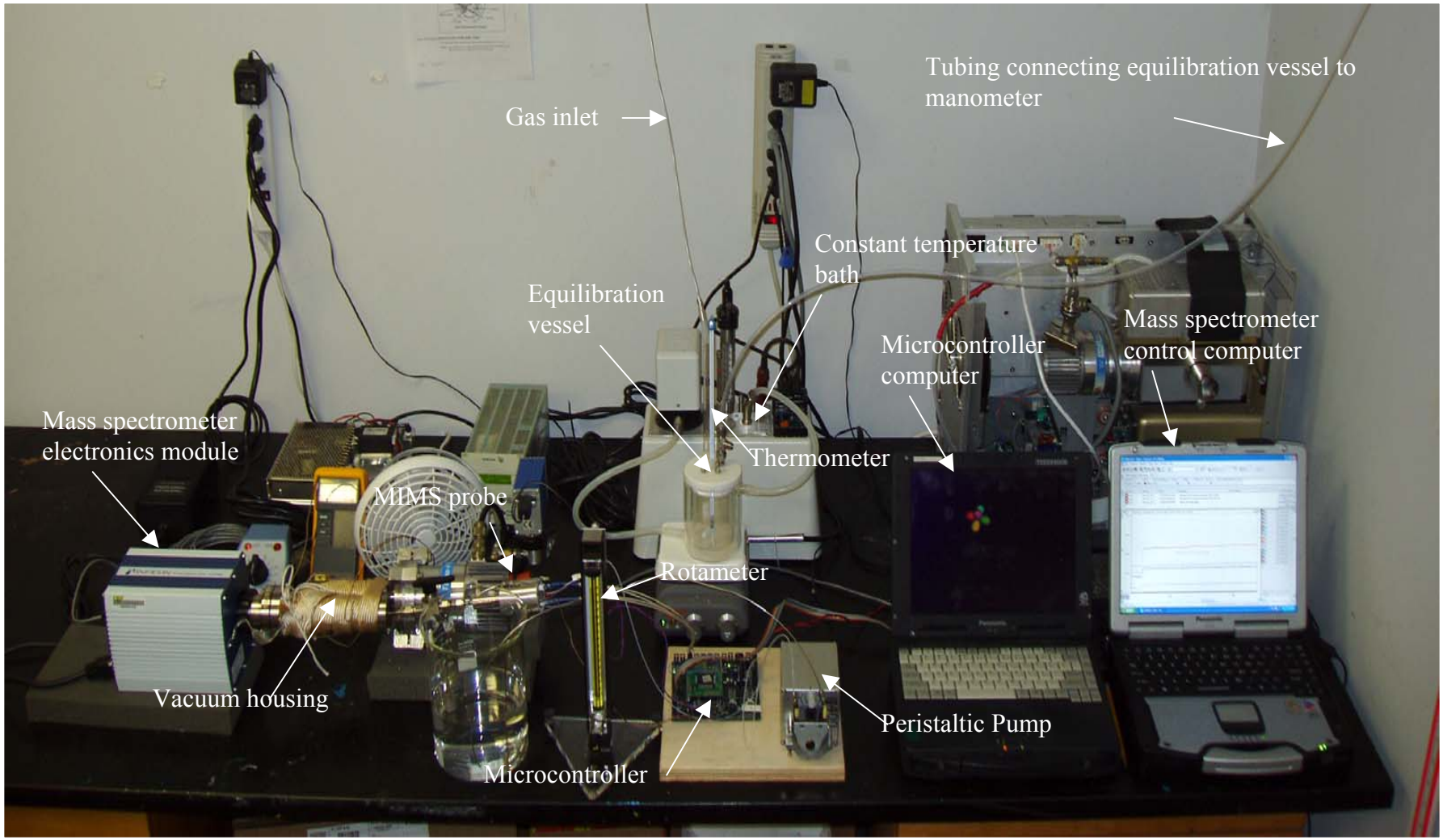
m/z 44

Mapping of Methane (m/z 15)

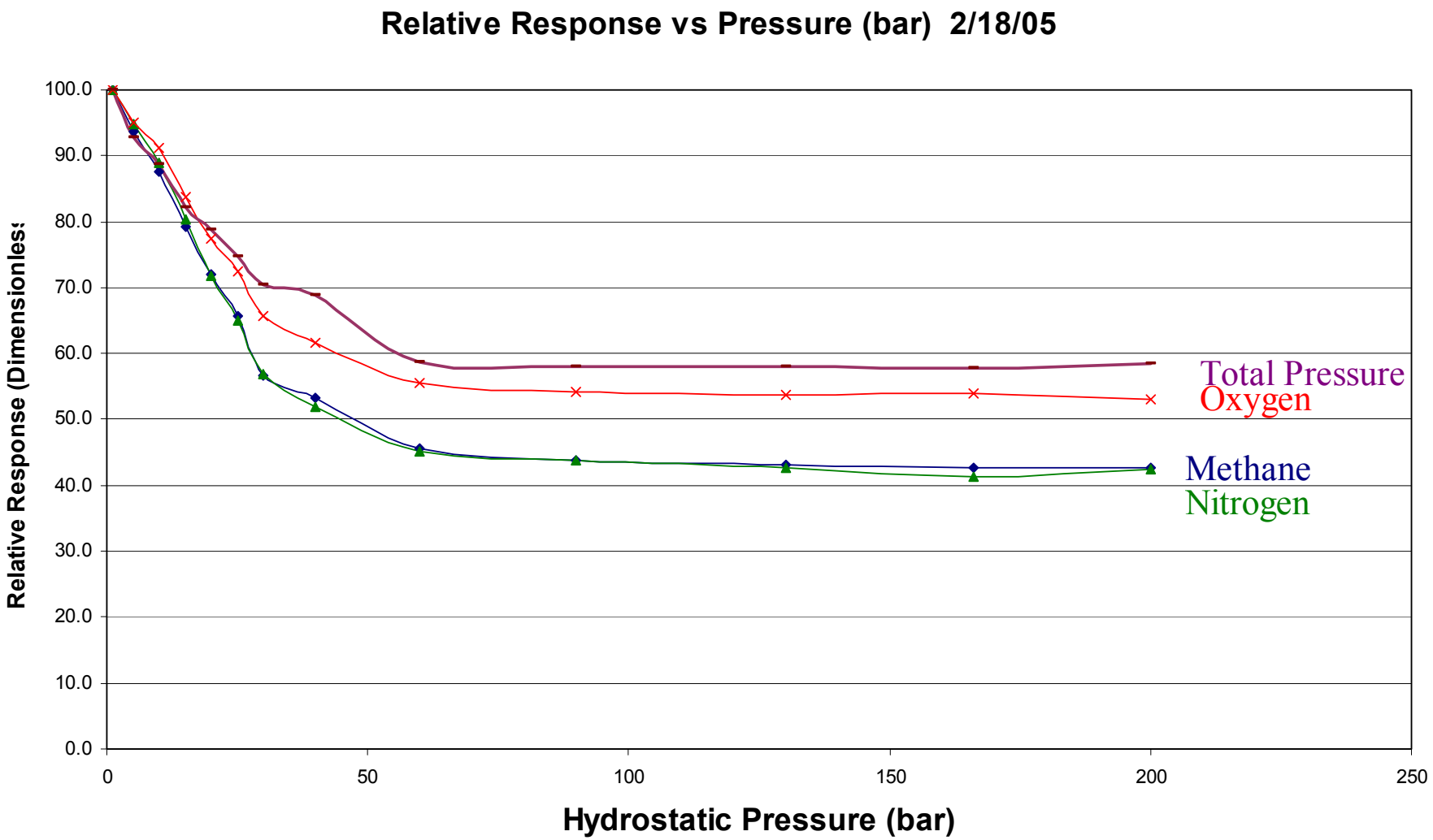




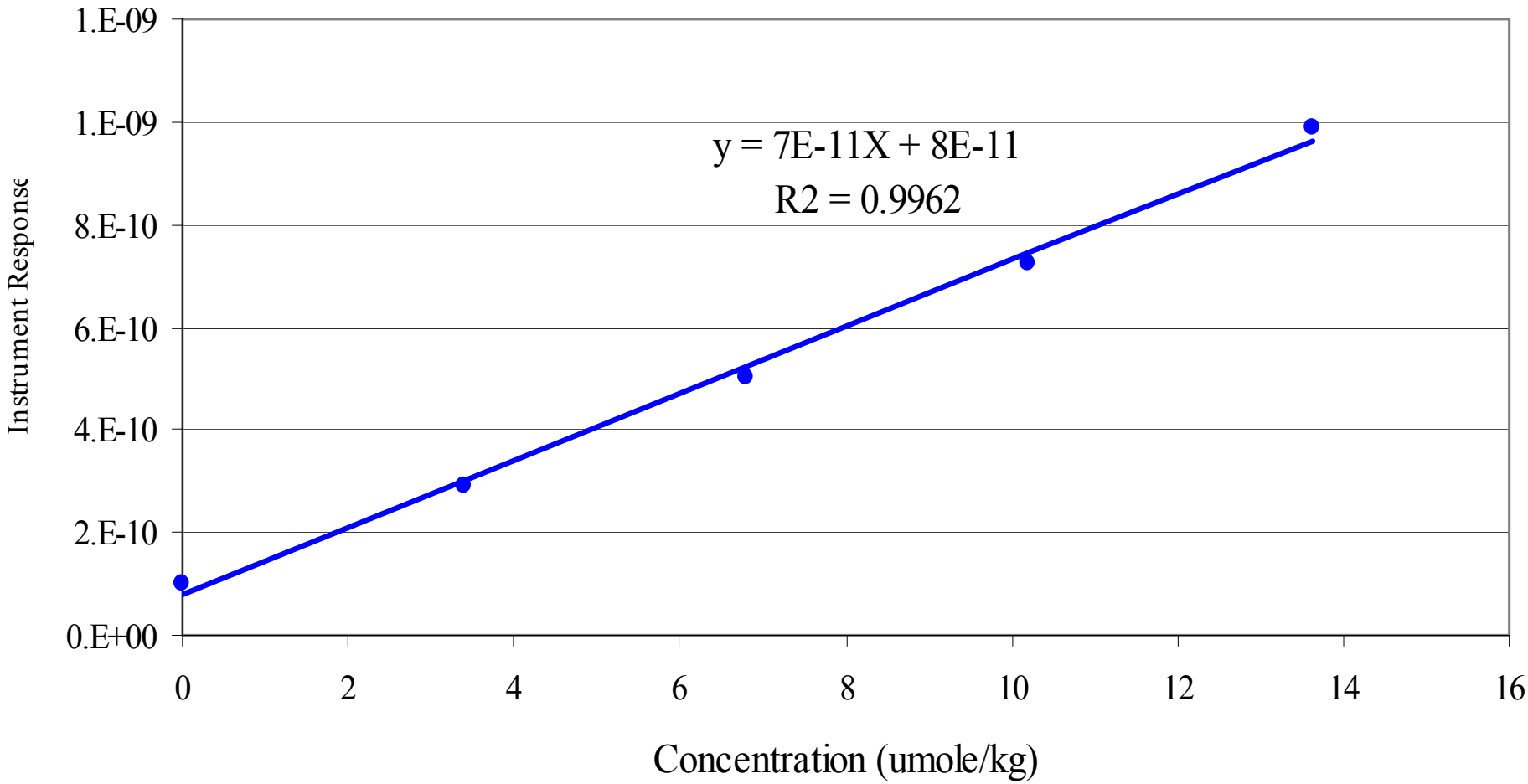
Benchtop Calibration Apparatus for Dissolved Gases



Pressurized Sample Data



Methane Calibration at 200 bar



Future Development Plans

- Laboratory Calibration
  - Directly correlate UMS intensities to dissolved gas concentrations
- Alternative Sampling Interfaces
  - Wider range of analytes
- Unattended Operation/ Full Ocean Depths
  - Ocean Observatories
- Automated Chemical Mapping
  - Track Gradients $\Rightarrow$ Self-directed sensors

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