



# Development of Technology and Associated Platforms for In-situ Sensing of Physicochemical and Biological Parameters in Extreme Environments

Prepared for: 9th Annual Polar Technology Conference (PCT 2013)
April 2, 2013

Prepared by: Andres M Cardenas-Valencia, PhD

With Contributions from: Michelle Cardenas, Eric Kaltenbacher, John Kloske, Timothy Short, Libby Tyner, Scott Williams

# Outline

- SRI International
  - Space and Marine Technology Program
- Space and Marine Sensing (FL Office)
  - Portable Mass Spectrometry
    - Principle
    - Applications, including Polar-like Regions
  - Optical Sensors
    - Microorganism Properties Characterization: Algae Enumeration
    - Optical-based Chemical Mapping
    - Refractive Index Sensor: Salinity, Density, and Reagentless Transducers
- Other SRI St Petersburg Capabilities: Marine Operations Group

# Introduction to SRI International

*SRI is a world-leading R&D organization*

- An independent, nonprofit corporation
  - Founded by Stanford University in 1946
  - Independent in 1970; changed name from Stanford Research Institute to SRI International in 1977
  - Sarnoff (RCA Labs) acquired as a subsidiary in 1987; integrated into SRI in 2011
- 2011 revenues: approximately $585 million
- More than 2,500 employees
- More than 20 locations worldwide

Silicon Valley - Headquarters

Washington, D.C.

Princeton, New Jersey

Harrisonburg, Virginia

St. Petersburg, Florida

State College, Pennsylvania

Arecibo, Puerto Rico

Tokyo, Japan

# SRI's Impact on Society

*More than 60 years of technology breakthroughs*

### Banking


**Magnetic ink character recognition enabled automatic check processing (1950s)**

### Computer Mouse

**SRI invented this and other foundations of personal computing (1968)**

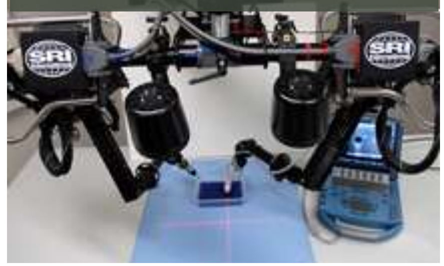
### Internet

**SRI received the first logon to the ARPANET (1969); made the first TCP-based Internet transmission over three dissimilar networks (1977)**

### Health

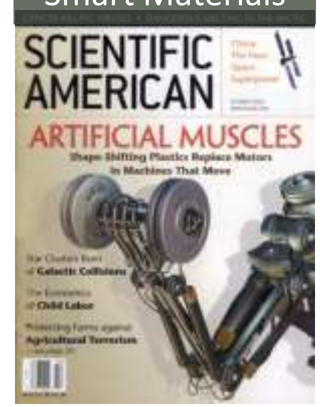
**SRI made ultrasound practical for medical diagnostics (1980s).**

### Telerobotic Surgery




**SRI technology allows surgeons to remotely perform minimally invasive surgical procedures. (1990s)**

### Smart Materials




**Electroactive polymers for sensing, actuation, and energy harvesting (1990's)**

### Speech Recognition

**SRI's natural language platform automates delivery of customer support (1996)**

### Bioinformatics

**Genomic databases combined with artificial intelligence and symbolic computing techniques accelerate research (2000s)**

### Intelligent Computing

**Decision support software helps the Internet be your personal assistant (2000s)**

# SRI Focus Areas

*Combining discovery, engineering with disciplined innovation processes*

*"To promote and foster the application of science in the development of commerce, trade, and industry … the improvement of the general standard of living… and the peace and prosperity of mankind"*

1946 Charter

# Marine and Space Sensing (MSS)

*Office located in St. Petersburg, FL, part of SRI's ER&D*

**Part of the Space and Marine Technology Program:**

- Space Technology Integration – Menlo Park, CA
- Marine and Space Sensing – St. Petersburg, FL

## Goals

- Create **new paradigms for technology innovation** in marine environments
- Enable rapid and low-cost technology driven demonstrations and missions
- Generate new opportunities for SRI technologies and innovations

## Focus Areas

- Sensing for Extreme Environments
- Communications & Operations
- Missions & Demonstrations

Multidisciplinary group at the MSS

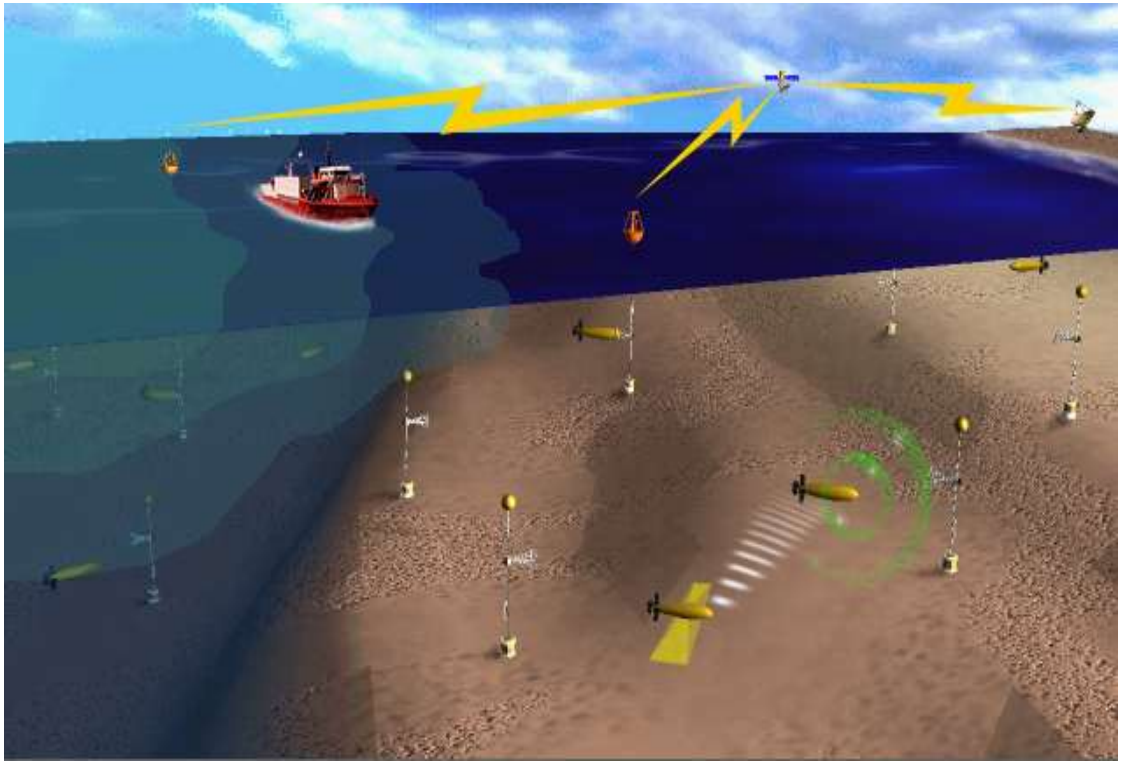
St. Petersburg, Florida

# Need for In-water Chemical Monitoring and Profiling

- Oceans and coastal regions
  - Biogeochemical studies
  - Hydrothermal vent analysis
  - Pollution monitoring and tracking
  - Bloom and plume diagnostics
  - Ecosystem health (global climate change)
  - Energy source discovery
    - Methane and natural gas
    - Oil reservoirs
- Harbors and internal waterways
  - Port safety and security
    - Inadvertent chemical release
    - Deliberate chemical release
  - Water supply monitoring

# Autonomous Ocean Sampling Network Concept

- Distributed network cells
  - Sensors, power, communication, intelligence and mobility
  - Data management, near-real time actionable data, integrated information sharing
- Benefits of *in situ* analysis
  - Reduced sample contamination
  - Increased sampling speed/density
  - Measurements in harsh environments
  - Real-time feedback
    - Rapid response
    - Adaptive sampling
    - Gradient mapping
  - Self-directed sensors

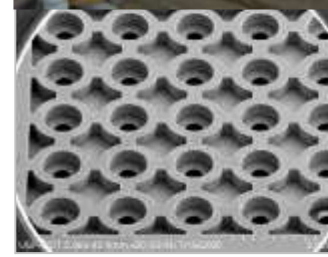


# Parallel Development Projects at MSS

- Portable underwater mass spectrometry
- Miniaturization and microfabrication of charged particle traps for mass spectrometry and other applications
- Optical sensors, reagentless transducers
- Advanced projects
- Power and fuel sources
- Antifouling and Biomarkers
- Data management and visualization software

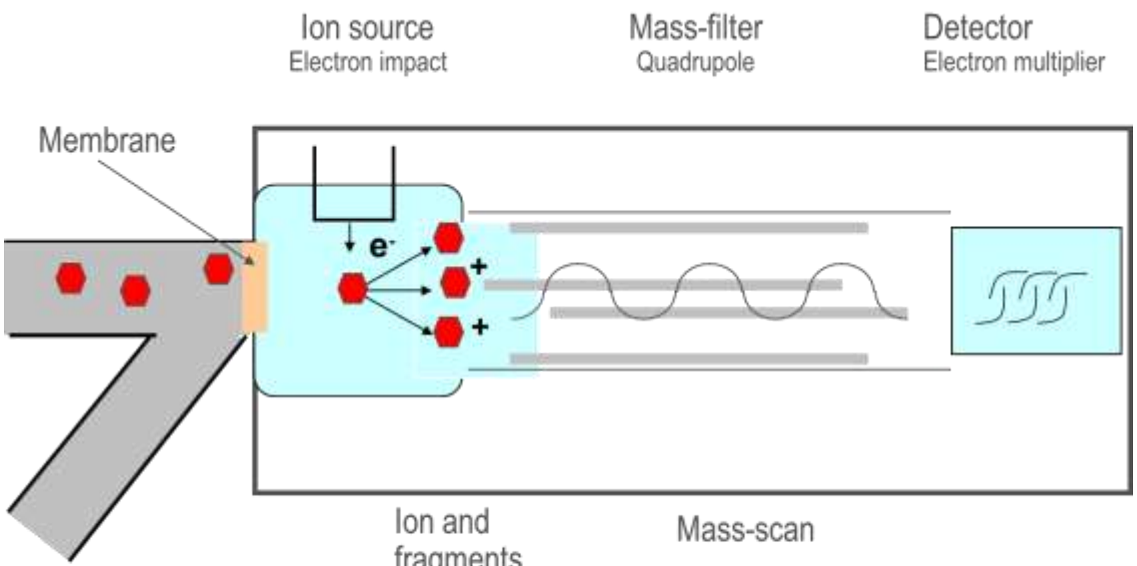
→ *Networks of unattended high-performance marine chemical analyzers.*

*Use of these analyzers in marine vehicles*



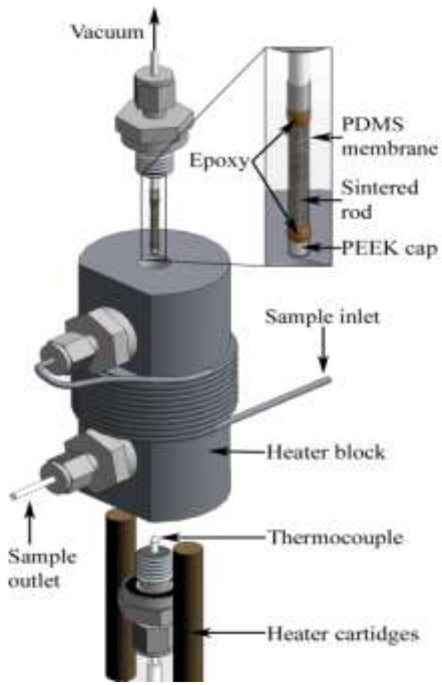
# Portable Mass Spectrometry

- Membrane Introduction Mass Spectrometry is ideal
  - Passive (except for sample pumping and heating, if desired)
  - Polydimethylsiloxane (PDMS) or Teflon are most common choices (hydrophobic)
  - Provides sensitive detection of dissolved gases and volatile organic compounds
- Need to mechanically support membrane (hydrostatic pressure)
  - Porous metal or ceramic frit

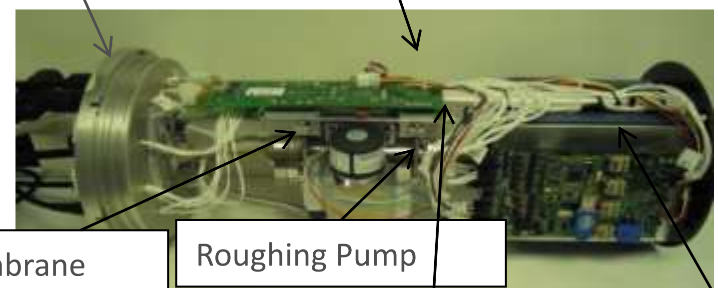


# New, Smaller SRI MIMS Instrument

High pressure membrane interface



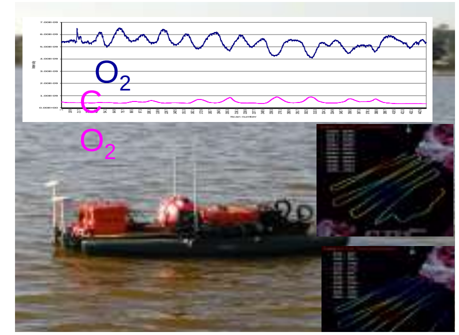

- Flow-over membrane interface design
- Temperature regulated
- Pressure tested to 200 bar (2000 m depth)

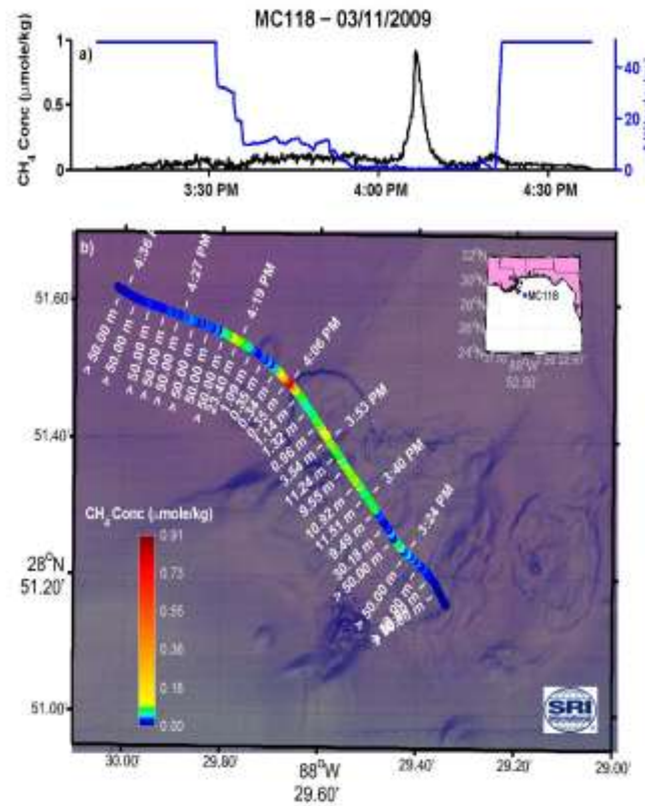


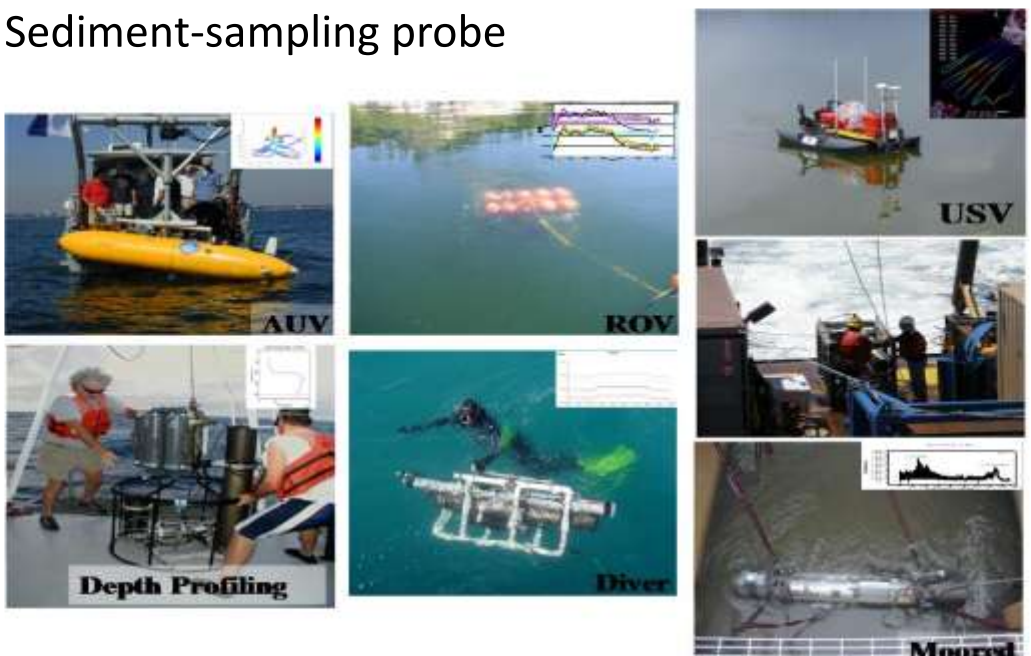

- Specifications
  - Power: 50-70 Watts
  - Voltage: 24 VDC
  - Dimensions:
    - Length: 64 cm
    - Diameter: 24 cm
  - Weight:
    - In air: 25 kg
    - In water: 5 kg neg.
  - Depth rating: 2000 m

# Simultaneous Detection of Multiple Analytes

- Dissolved gases
  - e.g. nitrogen, oxygen, argon, carbon dioxide, methane, hydrogen sulfide
  - In the water column or in porewaters (sediment)
- Volatile organic compounds
  - e.g. toluene, benzene, dimethyl sulfide, chloroform
- Larger MW compounds with modification
  - e.g. PCBs, pesticides, drugs, toxins
  - Sediment-sampling probe

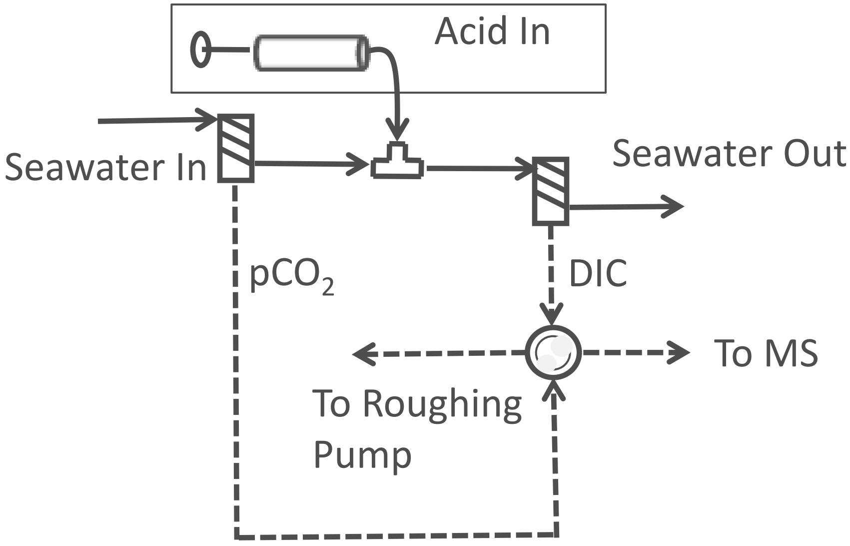


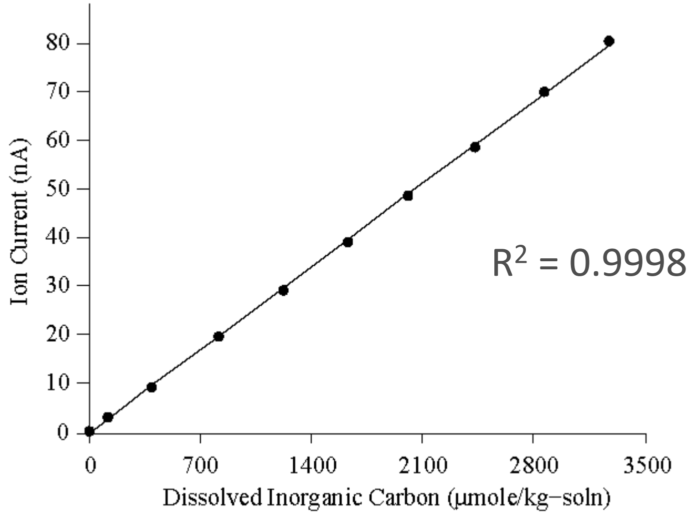



# Oceanic Carbon System Measurements via UMS

- Method for measuring gaseous dissolved carbon dioxide ($pCO_2$) and total dissolved inorganic carbon (DIC) with UMS
  - Calculate total alkalinity and pH
- Dual membrane probe system
- Switching valve for rapid changing between acidified and non-acidified samples (DIC/ $pCO_2$)



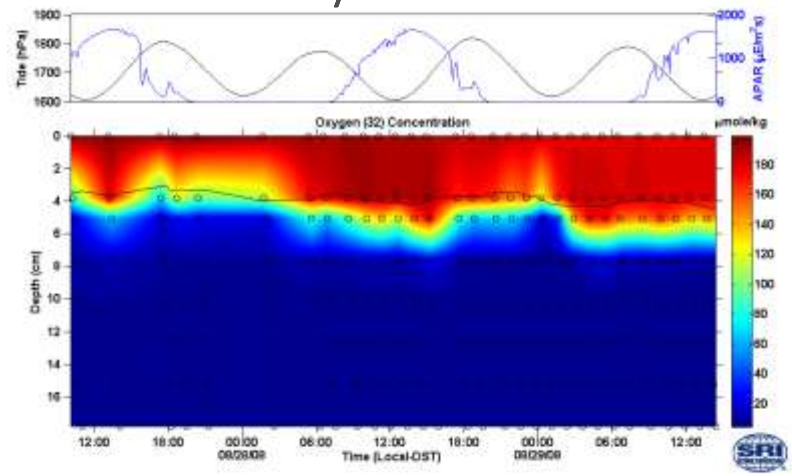

Cardenas-Valencia, A.M., L. Adornato, R. Bell, R.H. Byrne, and R.T. Short. Rapid Comms. In Mass Spec., In press, 2013

# Time-dependent Vertical Dissolved Gas Profiles in Sediment Pore Water

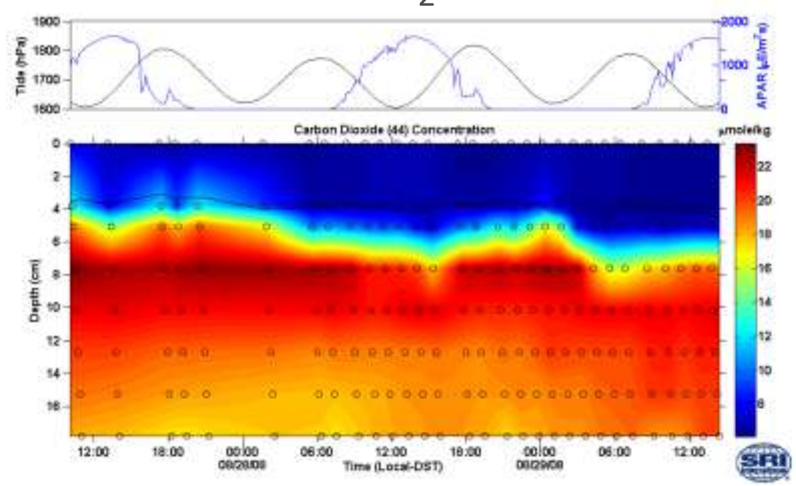
- Programmable sediment probe
- Water column/sediment profiles

- Coarse sediments
- Steep gradients

2-day time series




$O_2$

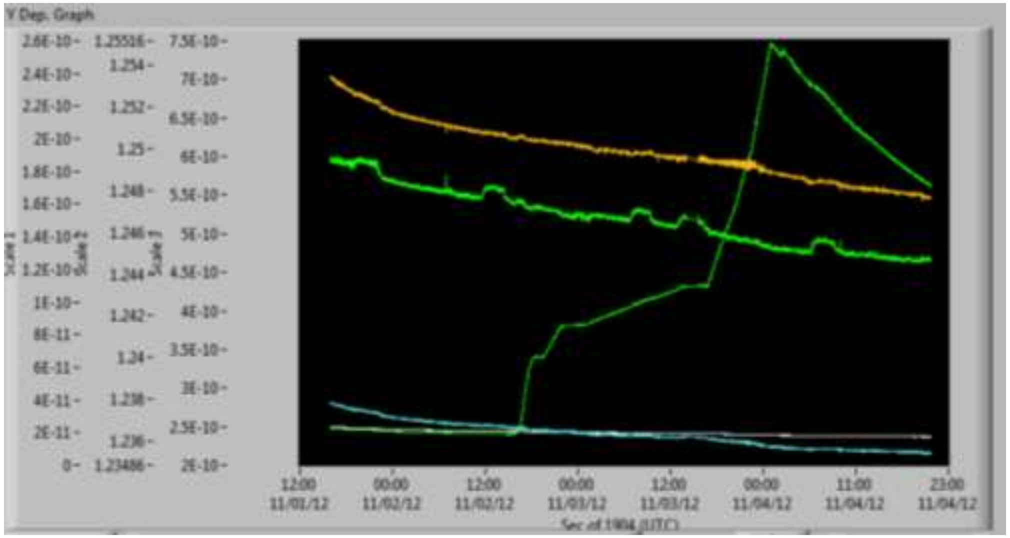



$CO_2$

# MIMS deployment in Polar-Like Region

*Simulated Sea Ice Conditions*

- Brice Loose's (URI) NSF Project "Gas transfer through polar sea ice (GAPS)"
- Performed at the Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, NH
- MIMS in Ice Engineering Test Basin for 1 week (-1.4 deg C)
- Monitored dissolved gas concentrations (basin water spiked with $CO_2$)



*>3 days of MIMS data*

m/z 18 – green
m/z 28 – orange
m/z 32 – blue
m/z 40 – white
m/z 44 – green (strong variation)

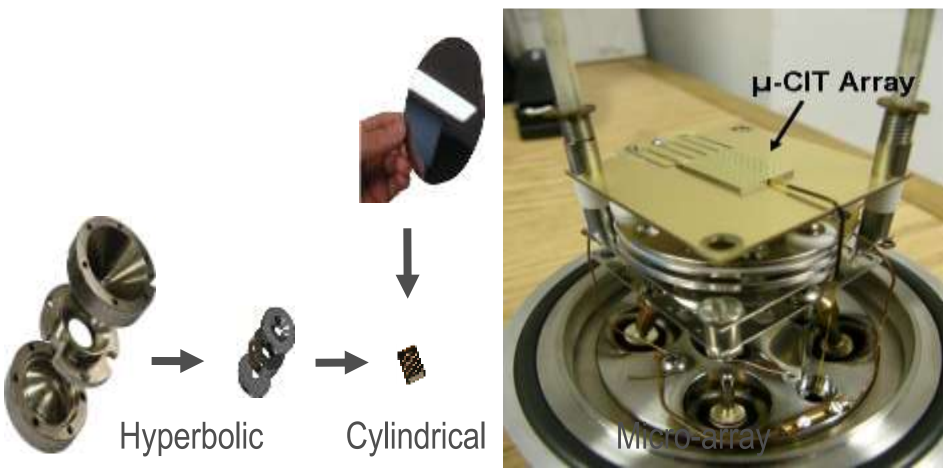
# Next Steps- Lower Cost, Smaller MSs

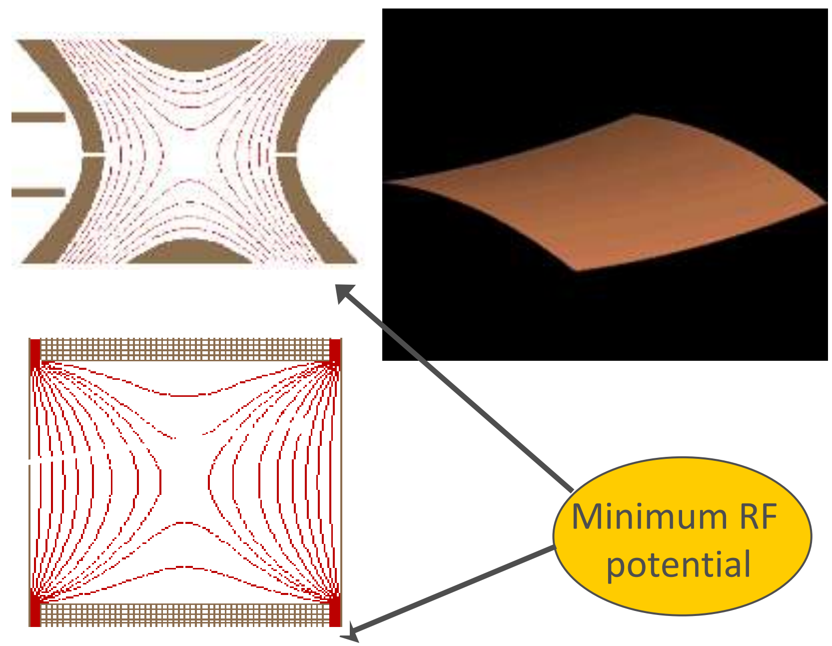
*Miniaturization and Microfabrication of Mass Spectrometers*

RF voltage is applied to the ring electrode (cylindrical in this case) to generate an oscillating electric field to trap ions. RF voltage is ramped up to eject ions

$$V_{rf} = (q_z r_0^2 \Omega^2 m) / (4A_2 e)$$

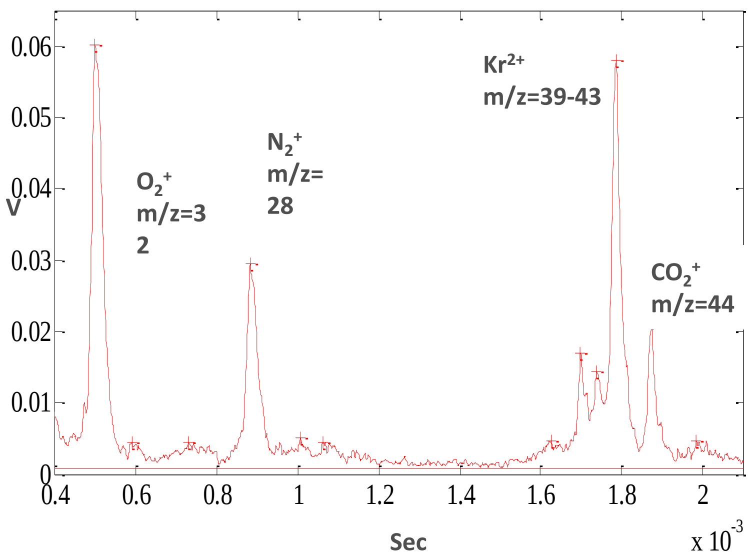
**Quadrupole Ion Trap Geometry**

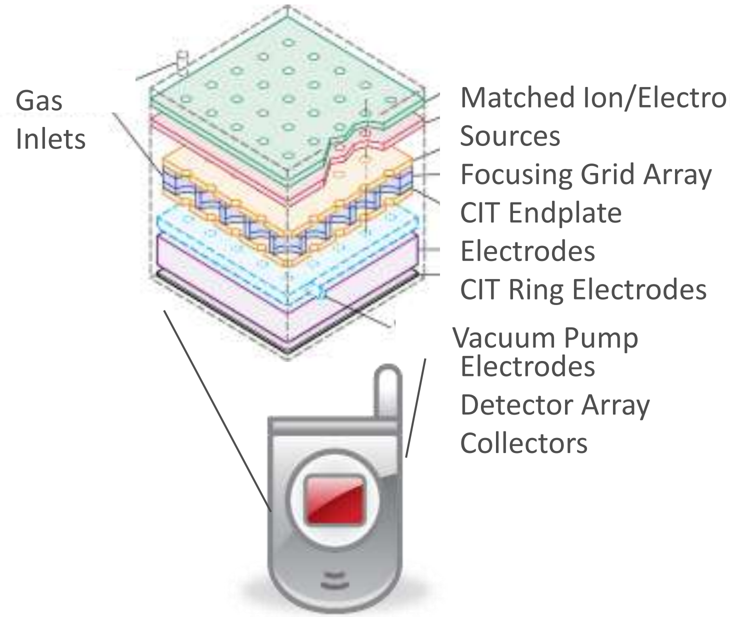


# Potential: Unit Mass Resolution and Looking Ahead

| Total pressure | RF voltage frequency | Axial modulation frequency | Axial modulation amplitude |
| --- | --- | --- | --- |
| 6.5 $10^{-6}$ Torr. | 7.65000 MHz | 1.98360 MHz | 25 mV0-p |



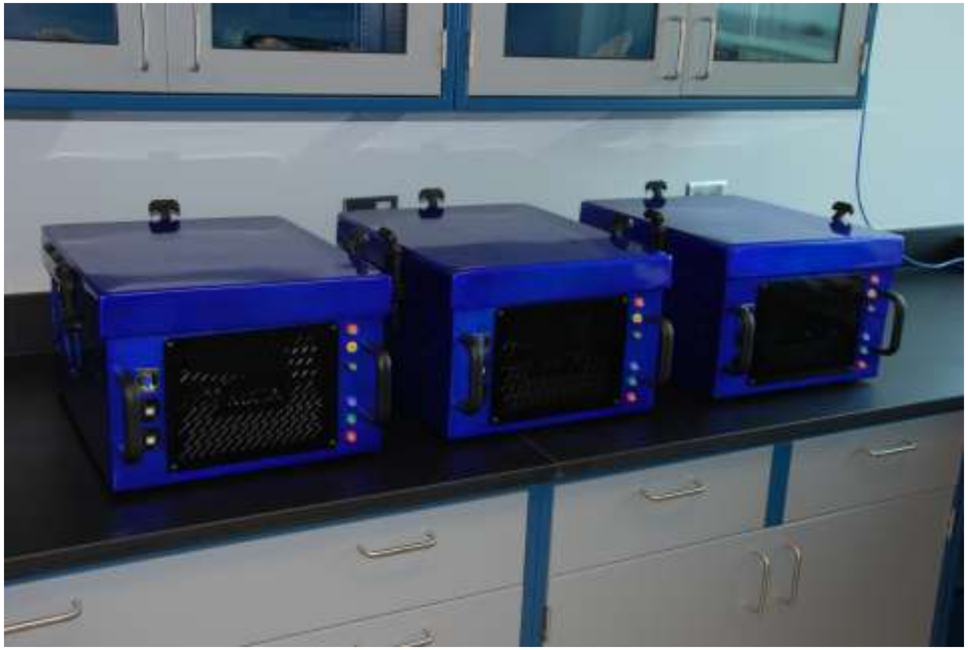




- Requires microfabrication and integration of all components
- High-density CIT arrays for increased sensitivity
- Matched ionization sources
- Fast high-gain detector for poor vacuum
- Micro vacuum pumps
- Integration into small package

# Optical Sensors

## Studying Ocean Acidification

Innovative instrument development provides researchers with the tools needed to make accurate and repeatable measurements



The multi-parameter inorganic carbon analyzer (MICA)

## Current or Recent Projects

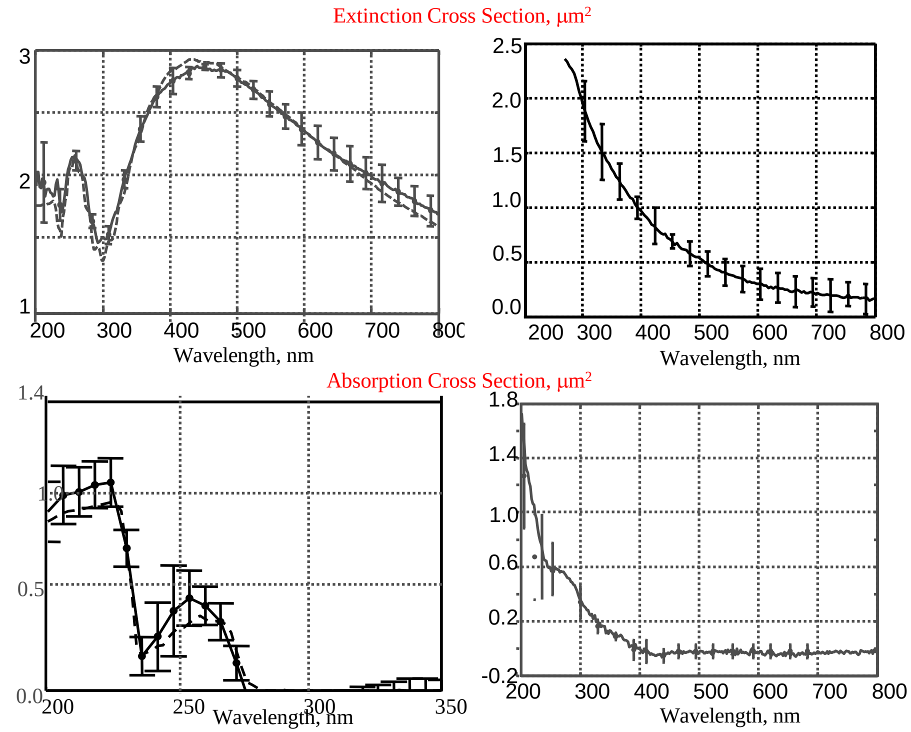
- **Sensor development**
- **Thermodynamic parameter determination in a high $CO_2$ world**
- **Direct measurement methods**

## Impact and Opportunities

- Enable global observations
- Improve understanding and awareness by general public and policy makers
- Provide standardized approach for uniformity and data consistency

# Determining Intrinsic Properties of Microorganisms

Develop methods to determine intrinsic properties (dielectric and optical) of algae and bacteria to permit enhanced cytometric and characterization of such microorganisms




**Optical signatures of a standard and of bacteria properties**

## Current or Recent Projects

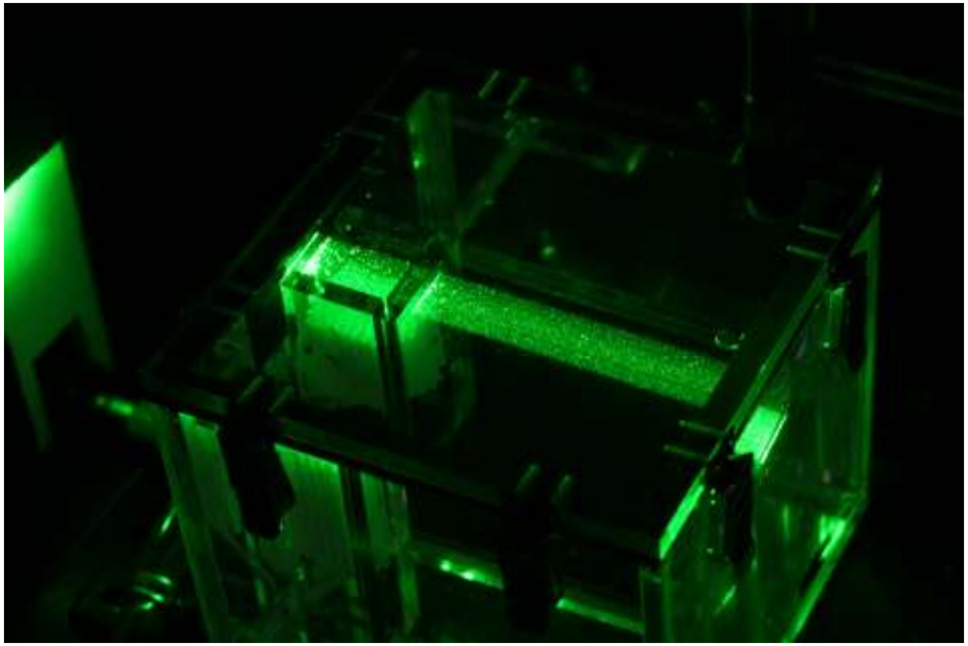
- **Lab bench proof-of-concept demonstration**
- **Modeling and inversion of optical properties of colloidal dispersions: i.e. standards, bacteria, and algae (Gymnodinium Breve, Karlodnium micrum, Heterosigma akashiwo)**

## Impact and Opportunities

- Increase database of available properties for analysis of suspended particle populations
- Identification and quantification of organisms in mixed populations
- Can be used to determine properties of colloidal systems with traditional optical techniques

# Enumerating Harmful Algae

SRI is working to create new technology that will enable the identification and enumeration of harmful algae before bloom conditions



Laboratory investigation of algae optical properties

## Current or Recent Projects

- **Proof-of-concept demonstration**
- **Mapping optical properties**
  - **Pigments**
  - **Scattering functions**

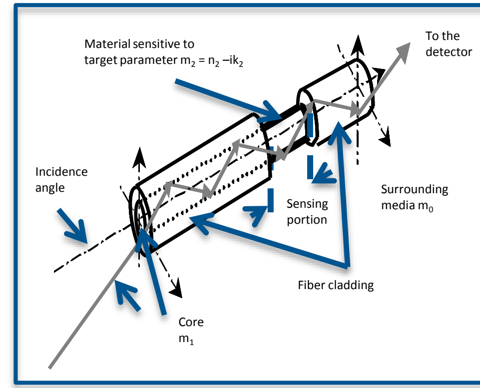
## Impact and Opportunities

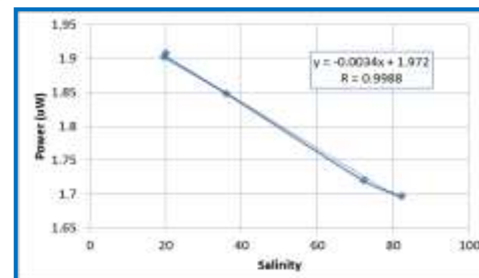
- Protecting populations through prediction of harmful algae blooms
- Identifying organisms in ballast water
- Increasing the sampled volume over that in traditional techniques

# Optical Sensors and Reagentless Transducers

*Develop novel optical interrogation platforms and demonstrate advantages of optical vs. conductivity for salinity determination*

- Conductivity: - Highly dependent on temperature
  - Non-electrolytes not (i.e. $NO_2$ and $CO_2$)[1]
- Refractive index: - n(T) is 10 times smaller than conductivity[1]
  - Direct measure of the density of the solution




## Current or Recent Project

- Lab bench proof-of-concept demonstration of waveguide approach enabling high sensitive optical property determination
  - $1x10^{-6}$ RI is desired (0.005 salinity)
- Current working on a deployable improved prototype (T)
- Develop algorithms to deconvolve salinity, density[2,3] and other chemical targets (attachment of transduction molecules)

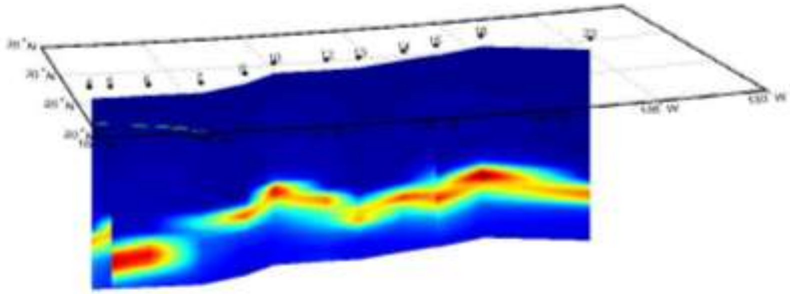
## Impact and Opportunities

- Miniature (2X OoM), low-power (1x OoM), low-cost sensors (1xOM) can be configured in several form factors
- Increase temporal/spatial resolution of physicochemical parameters ivia the distribution of more sensing nodes


[1] Grosso, P., M. L. Menn, et al. (2010). Deep Sea Research Part I: Oceanographic Research Papers 57(1): 151-156.
[2] Cardenas-Valencia, A.M., R.H. Byrne, and E.T. Steimle. Sensors and Actuators B-Chemical, 2006. **115**(1): p. 178-188.
[3] Cardenas-Valencia, A.M., et al. Sensors and Actuators B: Chemical, 2007. **122**(2): p. 410-418.

# High-Sensitivity Optical-based Chemical Mapping

SRI develops and deploys instrumentation for in situ chemical analysis in both freshwater and marine environments



Nitrite concentration in the North Pacific

SRI's instruments deployed to monitor a barrel sponge

## Current or Recent Projects

- **Reef studies**
- **Agricultural run-off**
- **Deep water studies**

## Impact and Opportunities

- Novel technology provides part-per-trillion sensitivity
- Analysis of drinking water for contaminants
- Highly flexible and adaptable for a wide variety of analytes

# Marine Operations Group

Space and Marine Technology Program

SRI International

## Bluefin 12-inch AUV

- **Depth Rating:** 600m w/1000m option
- **Payload:** Up to 36” long, free flooding
- **Power:** Up to 8 hrs runtime; 100W of power for sensors
- **Speed:** 3 kts cruise (1.5 m/s); 5kts max (2.5 m/s)

**Weight:**

- **Air**: Up to 550lb with payload
- **Salt water:** Neutral

**Dimensions:** 12-¾”D x 132” L

## Deep Sea Systems Sea Max ROV

- **Depth Rating:**300 meters with 1000-meter option
- **Payload:** up to 150 lbs
- **Sub Sea Power:** 800W of 12 or 24 VDC with 120AC available
- **Comms:** Fiber to surface; Ethernet and RS232/485 subsea
- **Navigation:** INS-Kearfott T16; USBL- and DVL-aided
- **Weight:** 1100 lbs in air
- **Dimensions:** 66” L x 35” W x 45” H
- **Launch and Recovery System:** Crane or A-frame

# Control Van

- Designed as a vehicle shipping container and operations support center
- Separate operations section and work space
- Theater-style seating
- Dimensions: 8’W x 20’L x 9.5’H
- Climate controlled
- Built-in automated, plumbed coffeemaker

# Facilities

## SRI's Tampa Bay harbor-side facility accommodates a variety of operations and testing requirements

**450-ft. Wharf**

- 20' alongside depth
- 2-ton capacity crane
- 3-phase 220/480 vac power
- Dockside Ethernet and water
- Dock is accessible for large truck deliveries
- Compressed air

**Marine Operations Building**

- 34' x 54' air conditioned operations support shop w/direct wharf access
- 5-ton hoist
- Internet access
- Compressed air
- 3-phase 220/480 power
- Generator backed-up single phase 110 VAC
- Conference/training room 1000 $ft^2$ (36+ person capacity)
- Additional office space, conference, and training rooms

# Contact of SRI Marine Operations

**SRI Marine Operations**:

**John Kloske**

**SRI International**

**450 8th Avenue SE**

**St Petersburg, FL 33701**

**john.kloske@sri.com**

**Shop: 727.498-6765**

**Cell: 727.252-6477**

# Contact Space and Marine Sensing

**SRI International**

**Andres M. Cardenas-Valencia, PhD**

**SRI International**

**450 8th Avenue SE**

**St Petersburg, FL 33701**

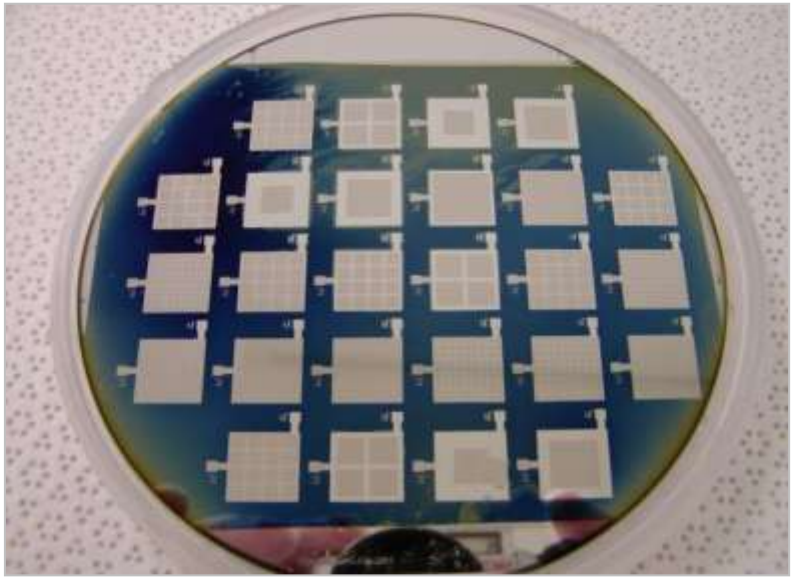
**andres.cardenas@sri.com**

**Office: 727.498-6721**

# Questions?

# Power and Fuel Sources

- Reserve-type micro-batteries
  - Microfluidic-actuated electrochemical sources
- Water-activated batteries
  - Application: High-power design
  - Valving manufacture
  - Novel developments (enabling technology)
- Semi-fuel cells
- Microbial fuel cells
- Other energy related projects:
  - Hydrogen production and storage
  - Water-energy link
  - Super capacitors
  - Fuel and energy production via sulfur wastes
  - Silane production



MEMS battery designs fabricated to verify the effects of cell configuration on the reagent utilization efficiency

J. Micromech. Microeng. 16 (2006) 1511-1518
Sensors and Actuators: Chem. B. 122(1) (2007), 328-336
J. Appl. Energy, Submitted (2012)

# Seawater-activated Batteries

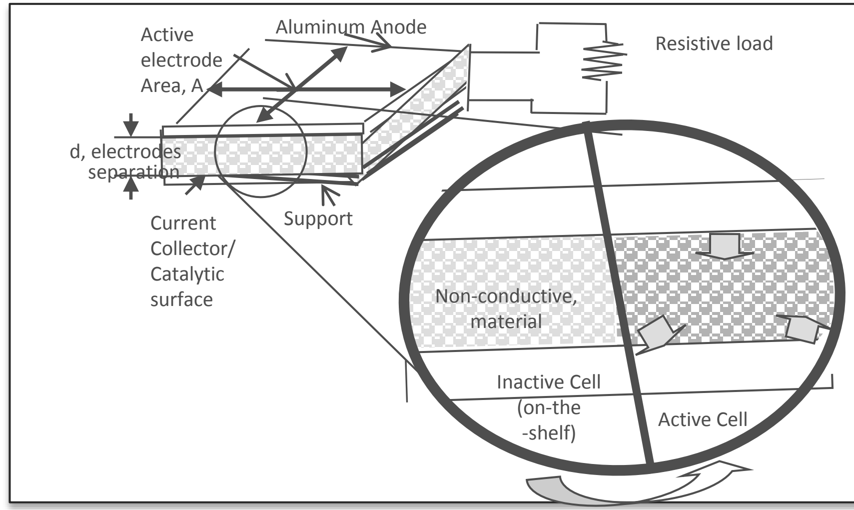
- Aluminum-anode, seawater-activated cells
  - No pressure vessel required
  - Immersion-activated designs
  - Organic halamines

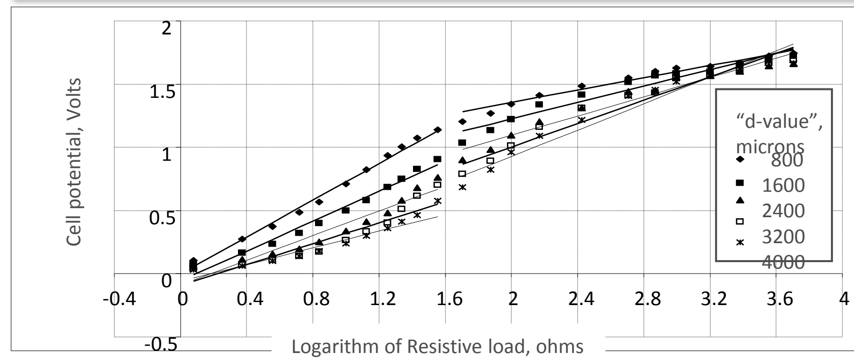
$$V_{load} = \left[ V_{oc} + \left( \frac{D}{\mu} \right) \ln \left( \frac{d}{\zeta e \mu A} \right) \right] - \left( \frac{D}{\mu} \right) \ln (R_{load})$$

Where D represents the ion diffusivity,
$\xi$ the ionic valence,
e the electron charge and
$\mu$ the ion mobility and
$R_{load}$ is the resistor representing the impedance to which the cells will be subjected.

- Commercially available baselines (2008)
  - Mg-Seawater: $1.5 to 10 / Wh (45 to 150 Wh/kg)
  - Alkaline–D type: $ 0.12 / Wh (160 Wh/kg)
- Low-cost and high-endurance cells
  - $ 0.16 / Wh (80 to 120 Wh/kg)
  - $ 2.5 to $ 5 / Wh (up to 200 Wh/kg)

*J. Power Sources* 166(1) (2007) 273-283.
*J. Power Sources* 184(1) (2008) 318-324.




High-endurance design

Potted terminals, low-cost design

# Antifouling and Biomarkers

*Photos courtesy Mickey Cook, SRI International*

Lawn of
*Escherichia coli*

Lawn of
*Staphylococcus aureus*

- Develop new natural and bioinspired antimicrobials from marine sources.
- Certain marine protists become susceptible to biofouling and predation at the onset of bleaching – a response to photo-oxidative stress
- SRI is investigating the chemicals associated with healthy an stressed organisms for:
  - Biofouling inhibition
  - Biomarker potential
  - Cell signaling and communication

- Taking advantage of current technologies available for antimicrobial drug discovery

- Initial results prove promising for inhibition of both a gram-positive and a gram-negative bacteria

- Potential for an environmentally-safe antifouling and antimicrobial coating developed for marine and medical use in the defense and commercial markets

# Additional Slides