Underwater Membrane Mass Spectrometry: Developments and Calibration

Ryan J. Bell, R. Timothy Short, Strawn K. Toler, Friso H.W. van Amerom, Peter G. Wenner, and Robert H. Byrne

> SRI International & University of South Florida College of Marine Science





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- Google Maps

In Situ Underwater Membrane Introduction Mass Spectrometry at USF & SRI International

1. Description of Underwater Membrane Introduction MS

2. Calibration Methodology

3. Surface Contour Deployments

4. Depth Profile Deployments

5. Benthic Moored Deployments

MS: Versatile Chemical Sensor

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



No configuration valid for all analytes

Membrane Introduction Mass Spectrometry (MIMS)

Ion source Electron impact Mass-filter Quadrupole Detector Electron multplier



Simultaneous Detection of Multiple Analytes

Dissolved Gases

- e.g. Nitrogen, Oxygen, Argon, Carbon Dioxide, Methane, Hydrogen Sulfide
- Volatile Organic Compounds

 e.g. Toluene, Benzene, Dimethyl Sulfide, Chloroform
- Larger MW Compounds with Modification
 e.g. PCBs, Pesticides, Drugs, Toxins

Principle Features of UMS



Туре	Linear quadrupole mass filter
Mass range	200 amu
Inlet System	Membrane introduction system
Power consumption	100 Watts
Voltage of operation	24 VDC or 110 VAC
Deployment time	Configuration dependent
Dimensions	Ø 19 cm (7.5")
	L 105 cm (41'')
Weight	33 kg (72.7 Lb)
Depth	>1000 m
DSL tether range	~1600 m (1 mile)

New 200 amu In Situ Mass Spectrometer



Microcontroller Embedded PC

MS electronics box

200 amu linear quadrupole in vacuum housing w/ heating jacket

Turbo pump MIMS probe

Roughing pump

Membrane Assembly



Calibration - Instrument Parameters

• Physical parameters that affect instrument response:

- Detector settings
- Filament settings
- Membrane geometry
- Residual gas
- Membrane temperature
- Sample velocity

– Hydrostatic pressure

Constant during deployment

Variable during deployment

Laboratory Calibration - Pressure and Concentration



• An HPLC pump and back pressure regulator allow control of hydrostatic pressure for pressure calibrations

• Two solutions with known gas concentrations are mixed at various ratios to allow for intermediate concentrations and *in situ automated* calibration



Calibration Results



Calibration Results - Pressure



Field Calibration

• Three or more field samples are sparged at constant temperature with gas standards of various concentrations.

• Each standard is sampled prior to deployment

Field Baseline Determinations

• Oxygen baseline is determined by the addition of sodium sulfite to solution.

• Carbon dioxide baseline is determined by the addition of sodium carbonate to solution.

Field Baseline Determination

 Baselines for nitrogen, argon, and methane, are determined by stopping the sample pump, whereupon sample in contact with the membrane is completely degassed



• Pump stop method is compared to sampling of boiling water for baseline determination.

Stopping Sample Pump

• Comsol Multiphysics (finite element) model of sample degassing during stopped sample flow at the membrane surface



Pre-Deployment Calibration



Deployment Methods



Lake Maggiore Chemical Surveys



Mass spectrometer deployed aboard an unmanned surface vehicle

 Mapping variation of dissolved gas ion intensities

• Develop surface contour maps based on gas ion intensity data

 Carbon dioxide & oxygen data displayed

Lake Maggiore, St Petersburg, FL O_2 and CO_2 are inversely correlated in areas of active photosynthesis and respiration



Hillsborough River, February 2007



Hillsborough Deployment Method



Hillsborough Deployment Method



Oxygen Time Series



300

YSI Dissolved Oxygen Sensor MS m/z 32 MS m/z 32 - Argon Corrected

0 2:24 PM 3:21 PM 4:19 PM 5:16 PM 6:14 PM Time



Oxygen at Sulfur Springs



Carbon Dioxide



Methane



Depth Profiles in The Gulf of Mexico



- Vertical profiles of dissolved gases with underwater mass spectrometer in Gulf of Mexico
- Mount instrument on custom frame along with CTD, DO and pH Sensors
- Communicate with instrument through standard UNOLS CTD tether using Seabird Modem
- Determine dissolved gas concentrations from mass spec data with the aid of a portable calibration unit

Depth Profiles in The Gulf of Mexico



Depth Profile Data (Florida Shelf)



Profile obtained while sampling the water column Profile obtained while sampling a standard solution

Correction Method: • Normalized m/z 17

- Normalized standard solution cast
- Corrected using to laboratory data



Alternative Techniques:



Depth Profile Data (Miss. Coast)





R/V Savannah





• Benthic Chamber (30m)

• R2 Navy Tower

















Future Plans for Underwater MS

Continued Deployments

Alternative Sampling Interfaces
 Wider range of analytes

Unattended Operation/ Full Ocean Depths
 – Ocean Observatories

Extreme MS Miniaturization
 MEMS Microfabrication

Questions, mateys?





Ahoy there landlubbers -- it's time to talk pirate Tue Sep 18, 2007 10:11am BSTEmail This Article |Print This Article | RSS [-] Text [+] Begin: Story Text By Paul Majendie

LONDON (Reuters) - Put a parrot on your shoulder, strap on a peg leg, hit the rum and start bellowing "Shiver me Timbers" -- Wednesday is International Talk Like A Pirate Day.

"Pirates of the Caribbean" star Johnny Depp is not the only over-the-top buccaneer allowed to have fun.

September 19 is your once-a-year chance to don an eye patch, sport a ridiculously large hat and keep on saying "Arrrr.

The basics

Ahoy! Avast! Aye! Aye aye! **Arrr!** Beauty **Bilge rat Bung hole** Grog Hornpipe Lubber **Smartly**

Argon Time Series

