Towards *in situ* monitoring of submarine gas hydrate fields with the Deep-Ocean Mass Spectrometer (DOMS)

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Location of Ulleung Basin Gas Hydrate Fields, East Sea, Korea

From: Bahk et al. (2013)
Goals of Research

- *In situ* analysis of a variety of dissolved gases and volatile organic compounds, using Membrane Inlet Mass Spectrometry (MIMS)

- An extended presence in the deep ocean for monitoring long-term seafloor processes, with several months to a year deployment, using battery power

- High sensitivity, simultaneous chemical analysis with only modest power consumption

- Reasonably high precision and accuracy via lab MIMS calibration and *in situ* T, P corrections

- Make instrument as compact, low-power, and light as possible without compromising analytical capability

- Investigate volcanic gas monitoring with similar instrumental approach
Mass Spectrometer Pros & Cons

**Pros**

- Multi-molecular, quasi-simultaneous analysis possible
- High sensitivity analysis (ppb to ppt)
- Reasonably compact & robust MS now available
- Promise of isotopic analysis
- Applications are diverse and growing

**Cons**

- Usually a large lab instrument with high power consumption
- Most MS require high vacuum \((10^{-5} \text{ Torr or better} \Rightarrow \text{power})\)
- What to do with waste gas in a pressure housing?
- High precision requires frequent calibration
- Expensive, unless self-made or mass-produced
Legacy DOMS Instrument

On Deck - R/V Atlantis
-Costa Rica Pacific Margin
-June, 2005

On Seafloor - 1000 m
-Mound 12, Costa Rica Margin
-Four months deployment
Deployment Options

Option 1: Mass spec has a circulating pump

Option 2: No pump on mass spec - just uses the natural flow from the seep
Deployment Options

option 1: mass spec has a circulating pump

flux meter → collection chamber → mass spec

option 2: no pump on mass spec - just uses the natural flow from the seep

flux meter → mass spec → collection chamber
Scientific/Technical Description

- **Scientific Details:** Improve System Mass Spectrometer

- **Technical advancement sought:**
  - Compact size
  - High-speed analysis
  - Higher sensitivity of analysis
  - Greater mass range

- **How it will be achieved**
  
  Replace existing SRS-200 Quadrupole MS with new MKS Granville-Phillips “ART” Ion Trap MS
MKS Granville-Phillips “ART” MS

ART Ion Trap MS (in 2.75” Conflat Housing)

All MS Electronics, 3” x 6” card!

Detached ART-MS Electronics in NIM-standard rack box

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Scientific/Technical Description

**Scientific Details:** Reduce Size and Weight of Existing DOMS Underwater Mass Spectrometer System

**Technical advancement sought:**

Compact size, to **6.6 in. (17 cm) OD** and **35.4 in. (90 cm) length**

Weight reduction, to **95 lbs. (43 kg) in air** and **49 lbs. (22 kg) in water**

**How it will be achieved:**

- Compact MS
- Simple, compact 2-card electronics
- (1 MS card, 1 Controller card)
- Add NEG-Ion pump, or
- New compact turbo pump
- Reduce size of roughing pump
- Reduce size of waste vacuum

Schematic diagram of the proposed Mini-DOMS instrument
Scientific/Technical Description

High-Vacuum Assembly – NEG-ion
**Scientific/Technical Description**

- **Scientific Details:** Increase sensitivity of Membrane Inlet MS (MIMS) analysis

- **Technical advancement sought:**
  Take current VOC low-ppb sensitivity to low-ppt sensitivity, or even lower, to ppq?

**How it will be achieved:**
- Heat, constant temperature
- Flow rate, turbulence increases
- Membrane thickness
- Water vapor load removal
- Soft and selective ionization
- Capillary selective loading – gas chromatography

From: Hernandez (2005)
Scientific/Technical Description

* MIMS = Membrane Inlet Mass Spectrometry
Results of Flow Rate & Repeated Solution-Water Cycles—

Chloroform @ 1 ppm; Temp. = 25° C
Tube Silicone @ 250 µm wall

Faster flow increases signal!

Two consecutive days running as sample /DI H₂O rinse.

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Heating experiments

Instrument Response vs. Time under different membrane temperatures (22°, 100°, 120°, 140°, 160°C)

- **Chloroform**
  - 3-5% left over

- **Toluene**
  - 5-12% left over

- **Benzene**
  - 15-25% left over

- **Chlorobenzene**
  - 20-45% left over
Heating experiments

**Pressure in MS vs Temp. of Membrane**

- X-axis: Temperature of Membrane
- Y-axis: Pressure x10^-5 torr

**Signal of volatile vs Membrane temper.**

- X-axis: Membrane temperature C
- Y-axis: Analytical signal x 10^5 counts

**Signal of volatile vs solution Temper.**

- X-axis: Solution temperature C
- Y-axis: Analytical signal x 10^5 counts

**Instruments Response (counts x 10^5)**

- **Chloroform**
  - Pumping pure water
  - Left over ~5%
- **Toluene**
  - Pumping water
  - Left over ~5%
- **Chlorobenzene**
  - Pumping water
  - Left over ~5%

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DOMS Ti Pressure cases

Main Instrument case

External Battery case
New DOMS Deck Box

Combines many deck functions into a compact, splash-proof box with internal status lights.

Internal view of electronics

Top exterior view
Lab Calibration Set Up--Gases
 Calibration results--
Methane

Temp. = 24° C
Flow Rate = 35 – 50 ml/min.
by Peristaltic Pumping
Calibration results—pCO$_2$

$y = -247030x^2 + 9593.7x + 3.7973$

$R^2 = 0.998$

pCO$_2$ by acid titration of NaHCO$_3$ solution

Temp. = 24° C
Flow Rate = 35 – 50 ml/min. by Peristaltic Pumping
KISOS
DOMS
Deployment

May, 2014
KISOS Dive results

MS Spectrum Stack

Samples vs. Date-time

Power Connector Pin burn

Yellow = background noise
DOMS Surface Seawater Experiment

Sampling setup on back deck

MS Spectrum stack

All gases vs. sampling number (time)
Surface Seawater Experiment—Dissolved CH4

Diss CH4 (ppb)

Run 1

Run 2

Ship Event?

Diss. Conc. (ppb)

Range of Modern Atmospheric CH4

Range of Surface Ocean CH4

Elapsed Time (sample no.)

Diss. Conc. (ppb)

Range of Surface Ocean CH4 in Ulleung Basin (Ahn et al., 2014)

Range of Surface Ocean CH4 in Bay of Bengal (Berner et al., 2003)
Conclusions

• The MKS G-P “ART” ion trap mass spectrometer adds speed, compact size and low power to the mini-DOMS. Detachable MS electronics assist in sizing.

• Use of a NEG-Ion High Vacuum further reduces overall power consumption by 50% over the legacy DOMS, to about 25 W in the present mini-DOMS.

• High-pressure MIMS has been achieved, to >400 bars, in an internal fluid circulation, heater, flat-membrane design.

• Use of high fluid flow rates, heat, and thin PDMS membranes increases the sensitivity and speed of MIMS analysis. Molecular water reduction also increases signal sensitivity, but remains a challenge at low power.

• The ART ion trap approaches quadrupole MS sensitivity, but spectrum noise reduction is important, by signal averaging, electronic filtering and statistically smoothing the acquired spectra.

• Calibration of the DOMS instrument response requires fluid flow, temperature, and perhaps pressure and ionic strength corrections.
Spare Slides
Scientific/Technical Description

NEG-Ion Mini-DOMS (V-CAFÉ version)
Bench Test

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Scientific/Technical Description

High-Vacuum Assembly – Turbo Pump
Shallow-water Mini-DOMS Pressure Housing

All-titanium housing human-rated to >1000-m water depth.

Case is 6.625 in. OD by 33.4 in. L and displaces 42 pounds.
Deep-Ocean Mini-DOMS Pressure Housing

All-titanium housing human-rated to >4000-m water depth.

Case is 6.625 in. OD by 35.4 in. L and displaces 46 pounds.
"Hammerhead" Plenum

Goal: using two Seabird impeller pumps and passive valves, re-circulate ~500 ml of sample fluid while heating internal MIMS assembly. Delrin block (red) acts as insulator, minimizing heat loss from fluid.
Scientific/Technical Description

- **Scientific Details:** Improve DOMS System Software

- **Technical advancement sought:**
  - Simpler, faster, user-friendly analysis
  - Flexible spectral analysis & display

**How it will be achieved:**

Write new code in Windows format to accommodate new GUI and spreadsheet functionality in one program, test.
System Software Improvements
Comparison of Brooks ART with SRS Quadrupole Mass Spectrometer - on Bench

Note: PCs not in views.
Effect of Noise Reduction by Spectrum Smoothing: a 40-ppm chloroform solution

Quadrupole mass spectrum

ART mass spectrum – raw

ART mass spectrum - smoothed
Comparison of Brooks ART with SRS Quadrupole Mass Spectrometer: Mass Spectral Response

Solution concentrations in ppm
Field Tests

Mini-DOMS on basket of HURL Pisces 4

HURL Pisces 4 launch off R/V K-o-K, Sand Island Outfall, Mamala Bay, Oahu

Mini-DOMS on deployment frame for Makai Research Pier test, 48-hours

48-hour Pool Test
Field Tests

Results of 48-hour Pool Test

Normalized Rel. Intensity

Mass/charge

Background concentrations, normalized

Sample concentrations, normalized

Normalized Rel. Intensity

Mass/charge
Scientific/Technical Description

High-Pressure, Heated MIMS Assembly (internal mount)

25W Heaters ($n = 4$)

HP Water Intake

HP Water Outflow

Thermistor Ports

Vacuum Line to MS
Custom, evacuated, compact Nafion™ Dryer Unit
(removes 80% water vapor @ zero power overhead)
DOMS Internal Components

***Vacuum Components Only***
From: Pace Tech DOMS User’s Manual
Surface Seawater Experiment—Dissolved Methane

Plots of Methane at mass-13 (CH+) versus mass-15 (CH$_3$+) indicate the anomalously high value is not analytically spurious.