Underwater cryotrap - membrane inlet system (CT-MIS) for improved in situ analysis of gases by mass spectrometry.

Torben Gentz & Michael Schlüter

Alfred Wegener Institute for Polar and Marine Research
Bremerhaven, Germany

Presented at the 8th Workshop on Harsh Environment Mass Spectrometry, St Petersburg, FL September 20, 2011
Outline

• Background
  Why high resolution measurements?

• Motivation
  Improving detection limit and security system.

• Design of the Cryotrap
  Peltier element and stirling cooler.

• Redesign of the sample inlet compartment
  Mass spectrometer, cryotrap, under water pump

• Field applications
  3D-measurements at gas flares

• Summary
Improved online and onboard methods are required for the detection of gas flares, seepages as well as the calculation of mass fluxes of methane released from the seafloor.
Hydroacoustic and visual detection of gas release

Hugh, colourful impression

Small source area with steep gas gradients

Acoustic “image” of gas bubble plumes in the water column.

Diameter of gas release: 5 cm

Gas release in the North Sea

Gas release at the Hakon Mosby Mud Volcano, Barent Sea continental slope
Gas analysis: State of the art

Water column and sediment sampling

Phase separation (gas phase from aqueous phase):
- Headspace technique for analysis of discrete samples

Problems:
- Time consuming,
- Coarse spatial and temporal resolution

Gas analysis by gas chromatography
Need for new methods

Mono-parameter instruments

HydroC, Contros

Mets, Franatech

Poly-parameter instruments

Inspectr200-200, AML,
by T. Short and G. Kibelka

Nereus/Kemonaut,
by R. Camilli, H.F. Hemond

Motivation: getting rite of the water vapor

Water vapor is the main gas that permeates through this membrane?

- Downgrades the detection limit
- Affects on the ionization efficiency
- Could cause condensation in the analytical line
- Downgrades the lifetime of the filament
- Indicate a high pressure in the analytical line

For several applications including investigations of natural as well as manmade gas seepages there is a strong demand for:
1. Improve detection limit
2. “Security System” in case of membrane rupture
First step: Shipboard Cryo-Trap coupled to the Inspectr200-200

**Inspectr200-200**
External membrane inlet system
Cryo-trap: Dewar flask with -100 °C ethanol
Cooling Thermostats or liquid nitrogen

**Improved signal noise ratio at m/z 15**
Higher ionisation efficiency
High emission at the ion source

**Improved detection limit:**
From > 100nmol L\(^{-1}\) to 16 nmol L\(^{-1}\) CH\(_4\)

Application of Membrane Inlet Mass Spectrometry for Online and In Situ Analysis of Methane in Aquatic Environments.
How to get a Cryo-Trap System to operate under water?

Requirements for under water applications:
(1) temperatures below -85°C have to be reached,
(2) a small waste-heat production is required,
(3) the energy consumption has to be below 10 W,
(4) large quantity of water vapor need to be trapped
(5) service life time of more than 10 hours is favorable
(6) a short cool down time below 60 min is necessary, and
(7) the system should be robust, of small dimensions and low weight

The system was intended to be designed for application with different sensor systems (IR,MS) and for “non lab” environments.
Peltier element and stirling cooler.

Requirements:
(1) temperatures below -85°C have to be reached,
(2) a small waste-heat production is required,
(3) the energy consumption has to be below 10 W,
Comparison...

Peltier element: 80 W at 6.8 V.
Stirling cooler: 6 W at 24 V
Performance of the cryo-trap

Requirements:
(4) large quantity of water vapor need to be trapped
(5) service life time of more than 10 hours is favorable
(6) a short cool down time below 60 min is necessary
**Under water Cryo-Trap**

**Requirements:**
(7) The system should be robust, of small dimensions and low weight.

**Specifications:**
- Length: 290mm
- Max depth: 200m
- Inner diameter: 180mm
- Weight: 5.1 kg
- Cooling area: 20mm
- Material: Aluminum
Cryo-Trap and redesign

Design of the Inspectr200-200 (AML)

Analyzer unit  MIS & Gear pump  Sample inlet

Redesign of the Cryo trap & UWMS

"Simulation of membrane failure: Frozen water plug"

1/8" Capillary Heater control Power supply

Sensor unit (dry)  CT-MIS (sample unit)
Application in harsh environments

Deployment of the under water gas analyser system
How to find and investigate gas flares?

Hydroacoustic in the water column

Multibeam echosounding: High resolution bathymetry of the seafloor

Under water observation and measurements
Under water gas analyser, sampler and observing system

Mode of deployment:
Towed system by research vessel
Mobile underwater platforms

- CT-UWMS
- Camera / Spot light
- CTD
- Syringe sampler
- Oxygen optode
- Energy supply
- Turbidity sensor
- Bubble counter
3D-concentration field of CH$_4$

This 24000 points allows calculation of budgets, gas fluxes etc.
Summary

Under water cryo trap membrane inlet system for underwater and other harsh environment:
- improves detection limits
- reduce the internal pressure significantly
- expand the lifetime of the analyser
- secure the analyser for inflowing water
- is easily to adapt to other sensors

The improved detection limit of the UWMS by the CT enhanced the computation of mass budgets as well as the search for gas flares, since small CH$_4$ concentration gradients are guiding to the gas flares.
Thank you for your attention

www.awi.de

Torben.Gentz@awi.de