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

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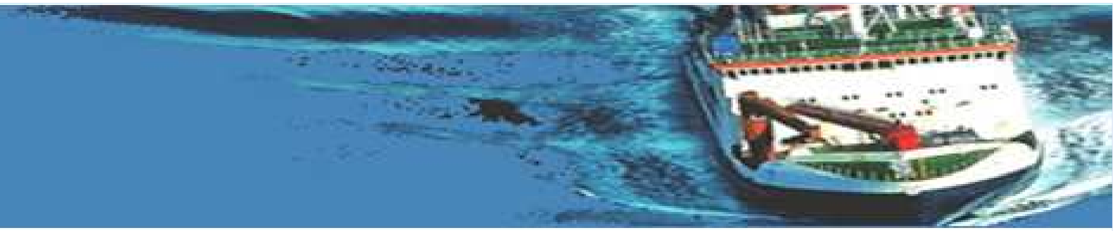
St Petersburg, FL September 20, 2011

Outline

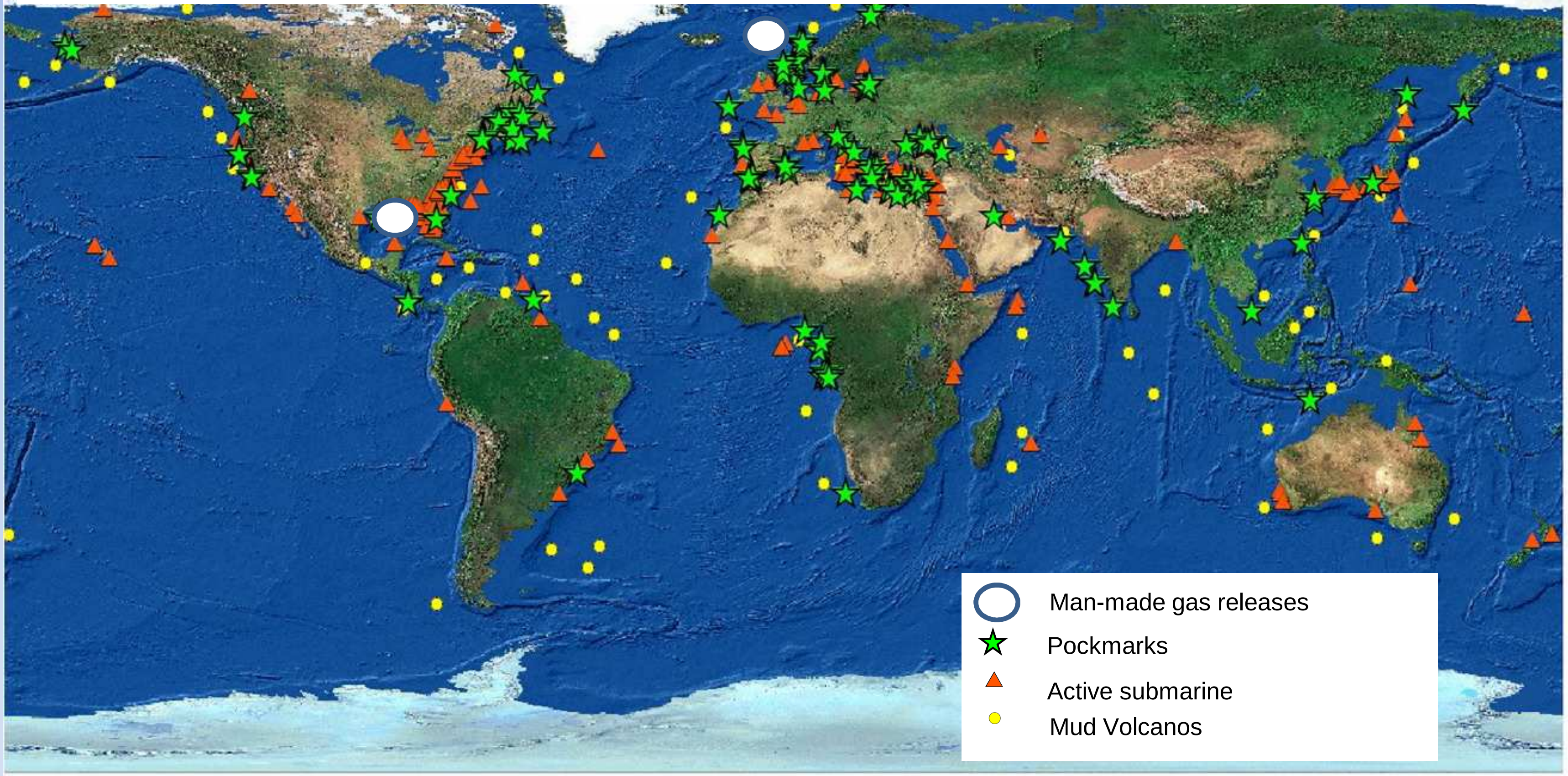


- Background — Why high resolution measurements?
- Motivation — Improving detection limit and security system.
- Design of the Cryotrap — Peltier element and stirling cooler.
- Redesign of the sample inlet compartment

  Mass spectrometer, cryotrap, under water pump
- Field applications — 3D-measurements at gas flares
- Summary

Background

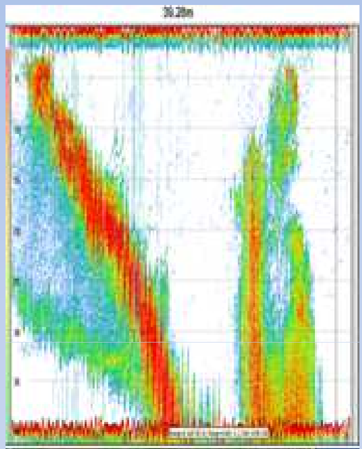
Worldwide distribution of gas flares and seepages.



Improved online and onside methods are required for the detection of gas flares, seepages as well as the calculation of mass fluxes of methane released from the seafloor.

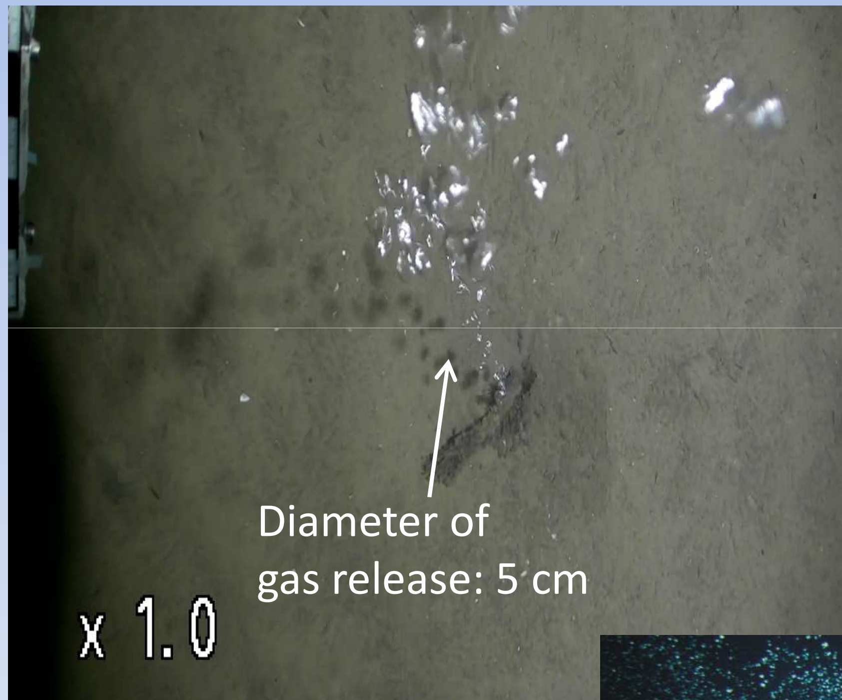
Hydroacoustic and visual detection of gas release

Hugh, colourfull impression



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

Small source area with steep gas gradients



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

Gas analysis by gas chromatography

Problems:
-time consuming,
-coarse spatial and temporal resolution

Need for new methods

Mono-parameter instruments

HydroC, Contros

Mets, Franatech

Poly-parameter instruments

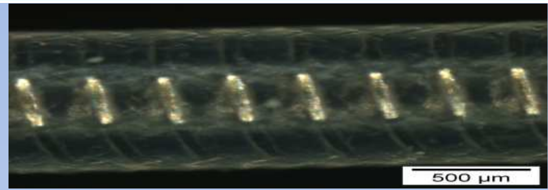
Inspectr200-200, AML,
by T. Short and G. Kibelka

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

R. Camilli, H. Hemond, Trends Anal. Chem. 23 (2004) 307.
Short, R. T. and others, J Am Soc Mass Spectr **12** (2001). : 676-682.

Motivation: getting rite of the water vapor

70 times magnification



320 times magnification

Water vapor

is the main gas that permeates through this membrane?

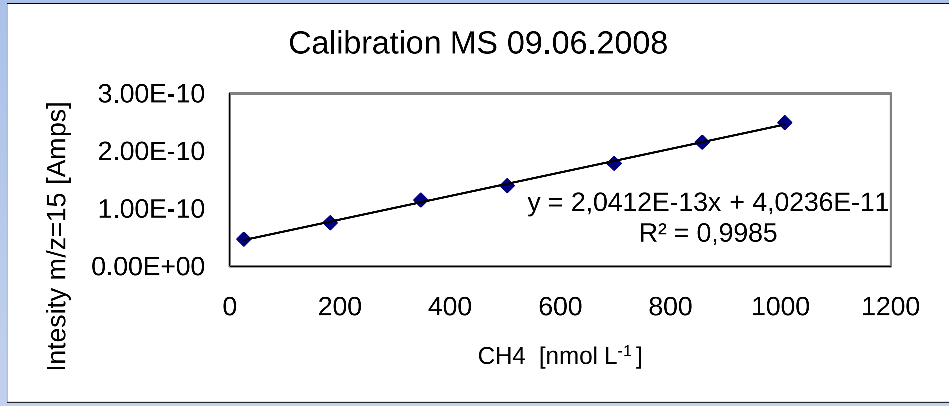
- Downgrades the detection limit
- Affects on the ionization effency
- Could cause condensation in the analytical line
- Downgrades the life time of the filament
- Indicate a high pressure in the analytical line

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 effency
High emission at the ion source

Improved detection limit:
From > 100nmol L^{-1} to 16 nmol L^{-1} CH_4

Schlueter, M., and T. Gentz. 2008.
Application of Membrane Inlet Mass Spectrometry for Online and In Situ Analysis of Methane in Aquatic Environments.
J Am Soc Mass Spectr **19:** 1395-1402.

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

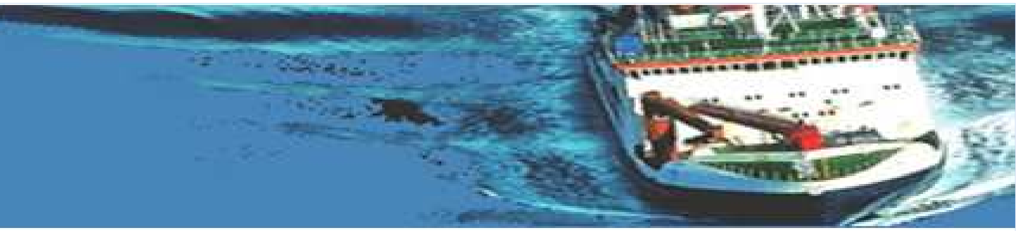
(5) service life time of more than 10 hours is favorable

(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.



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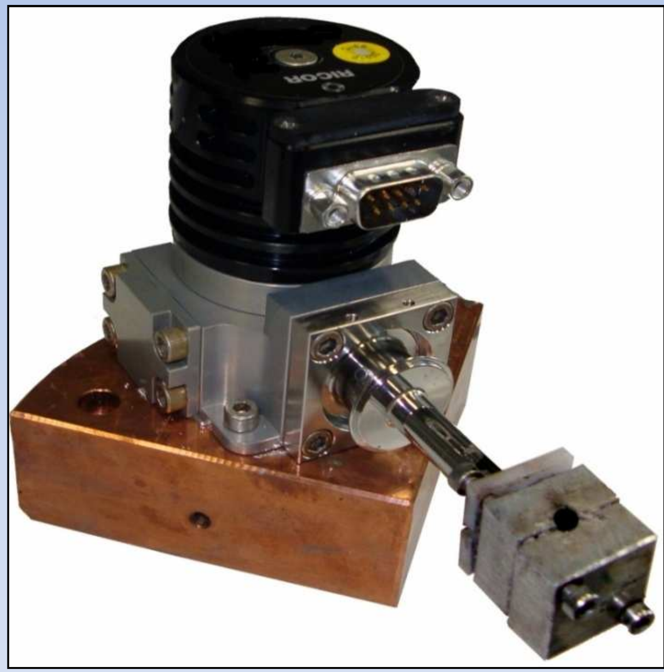
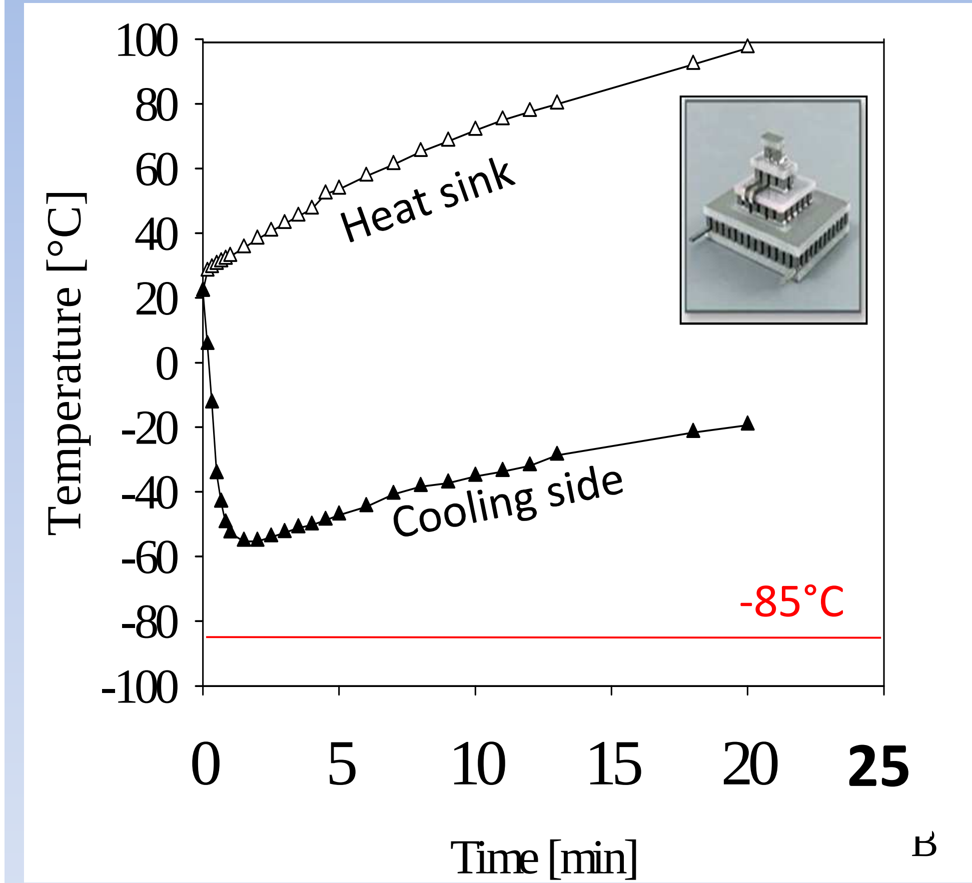
Peltier element, Whatson Marlow, MI4040

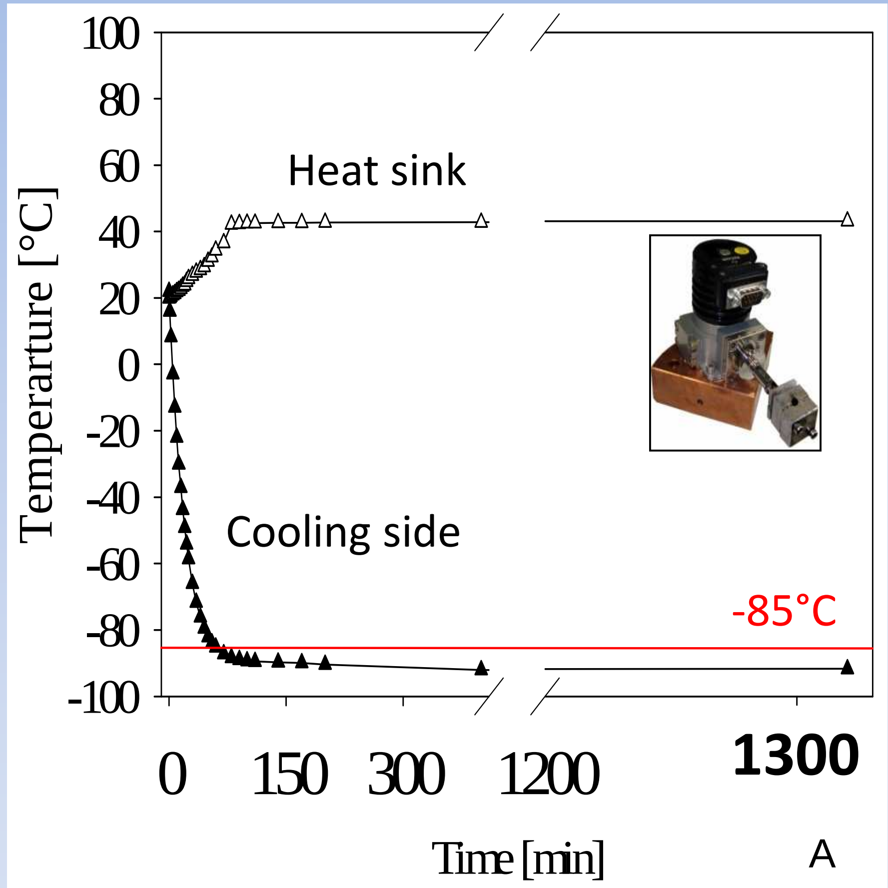


Micro Stirling Cooler, Ricor K508

Comparison…



Peltier element, Whatson Marlow, MI4040



Micro Stirling Cooler, Ricor K508

Peltier element: 80 W at 6.8 V.

Stirling cooler: 6 W at 24 V

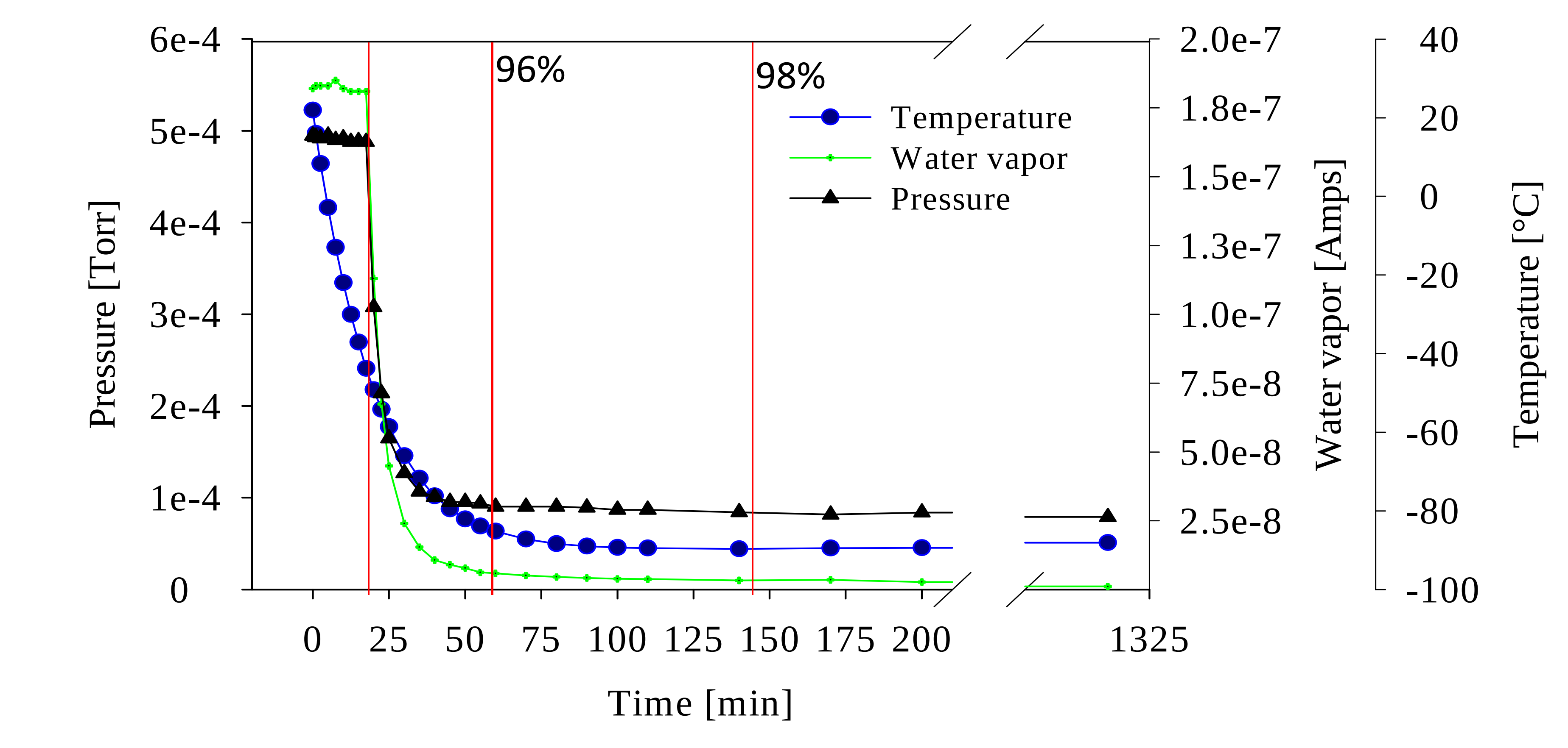
Performance of the cryo-trap

Requirements:

(4) large quantity of water vapor need to be trapped

(5) service life time of more than 10 hours is favorable

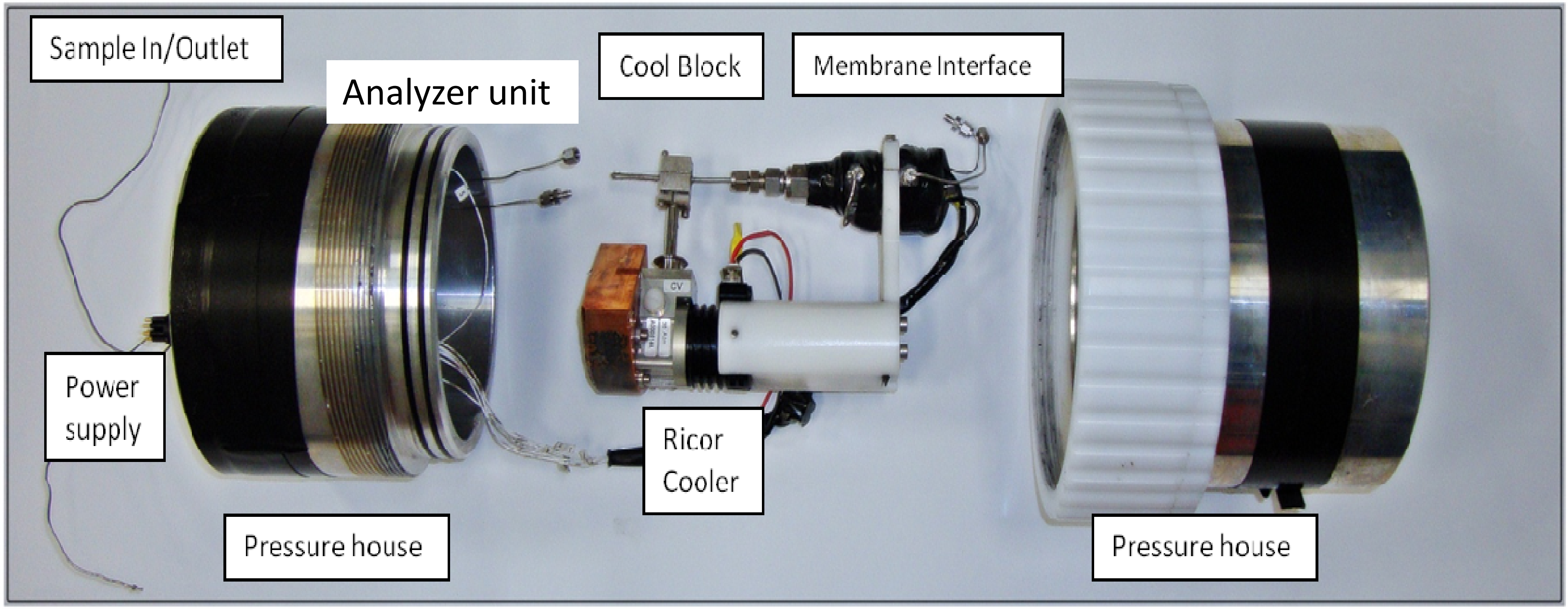
(6) a short cool down time below 60 min is necessary



Under water Cryo-Trap

Requirements:

(7) The system should be robust, of small dimensions and low weight



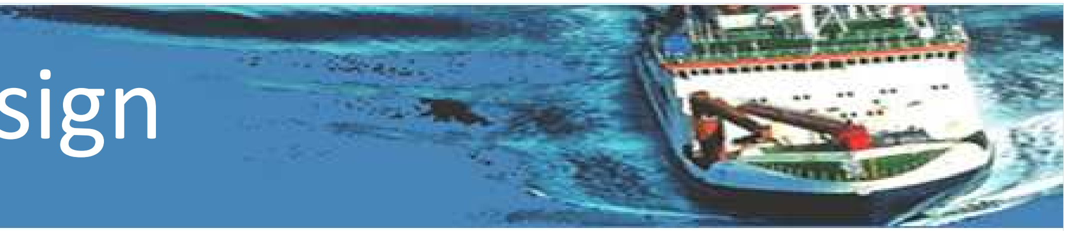
Connection to the sensor unit   Cooler unit   Membrane unit

Specifications:

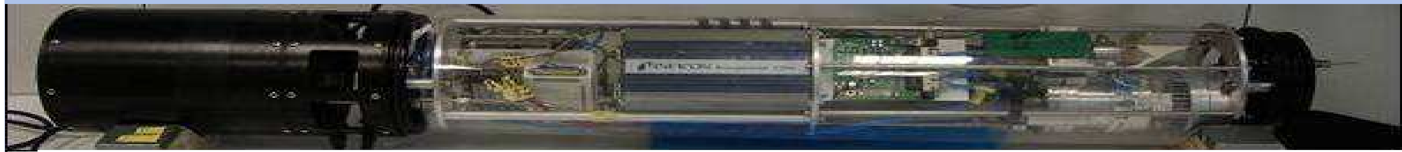
Length: 290mm   Max depth: 200m   Weight: 5.1 kg   Cooling area: 20mm

Outer diameter: 190mm   Inner diameter: 180mm   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

1/8“ Capillary
Heater control
Power supply

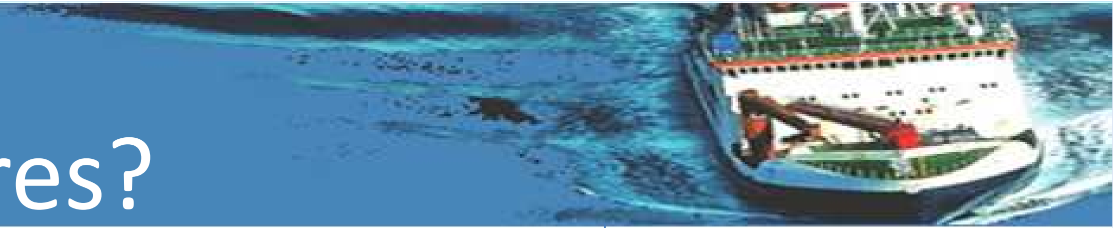
Sensor unit (dry)

CT-MIS (sample unit)

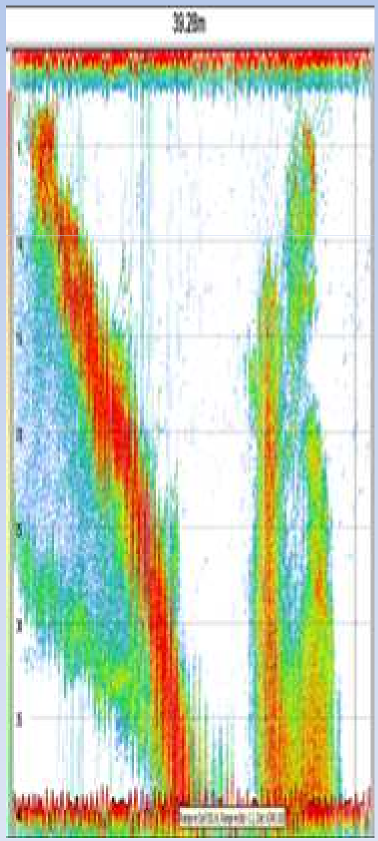
Application in harsh environments

Deployment of the under water gas analyser system

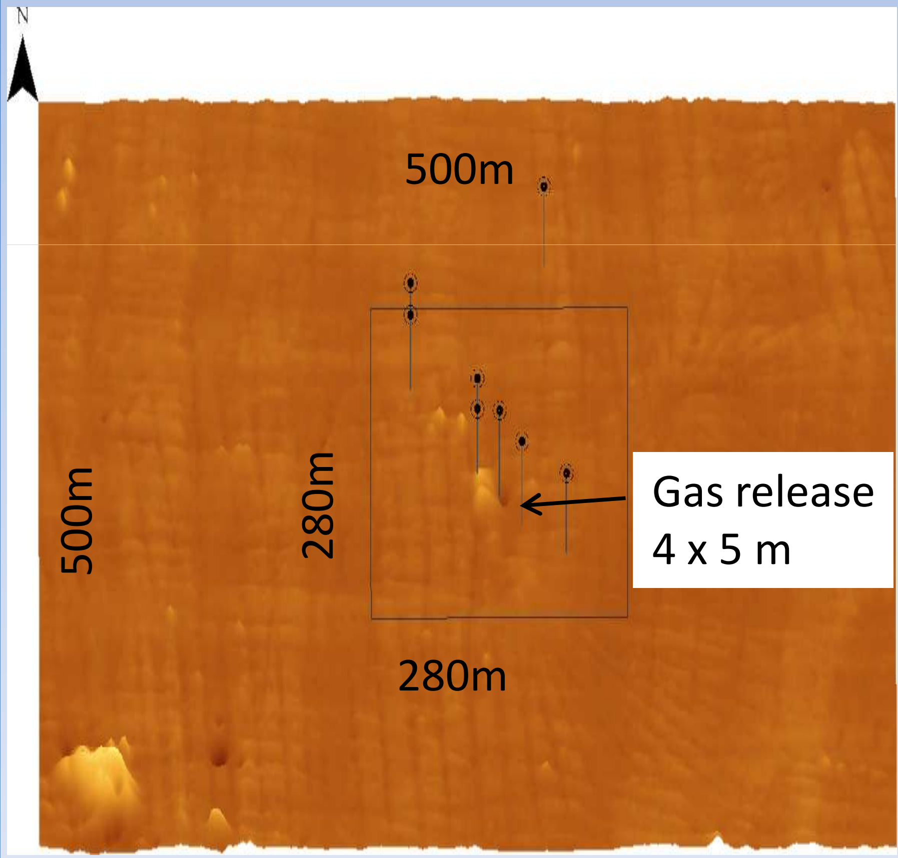
How to find and investigate gas flares?



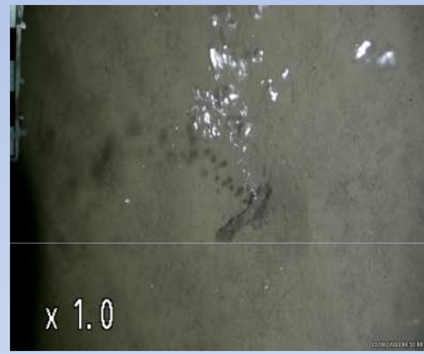
Hydroacoustic in the water column

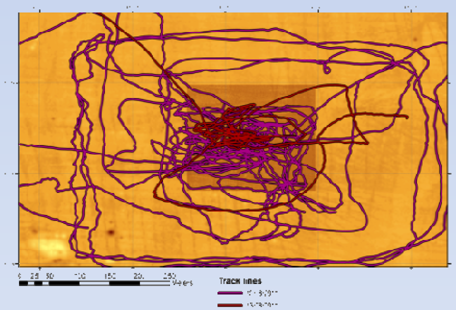


Multibeam echosounding:
High resolution bathymetrie of the seafloor

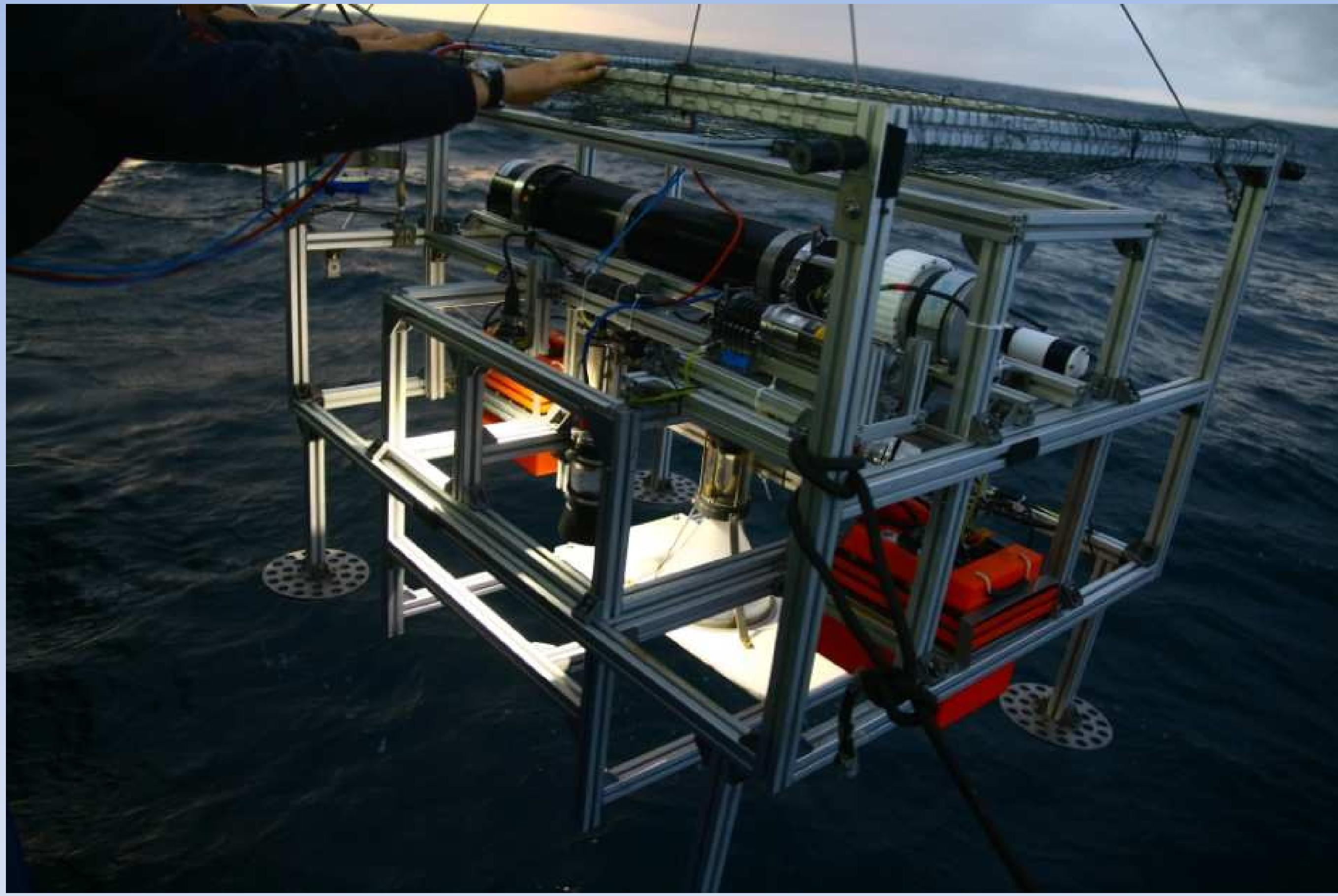


Under water observation and measurements





Under water gas analyser, sampler and observing system



Mode of deployment:

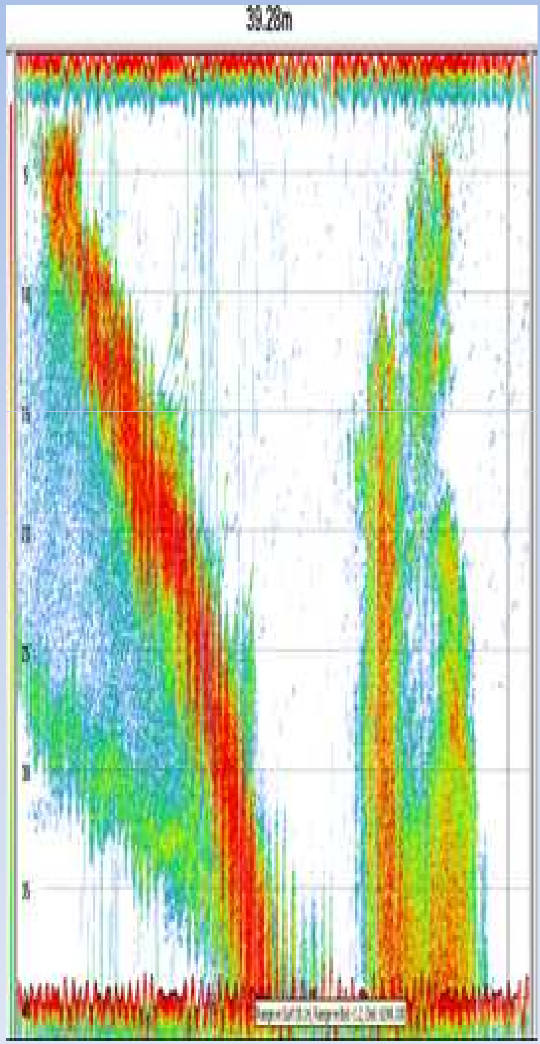
Towed system by research vessel

Mobile underwater platforms

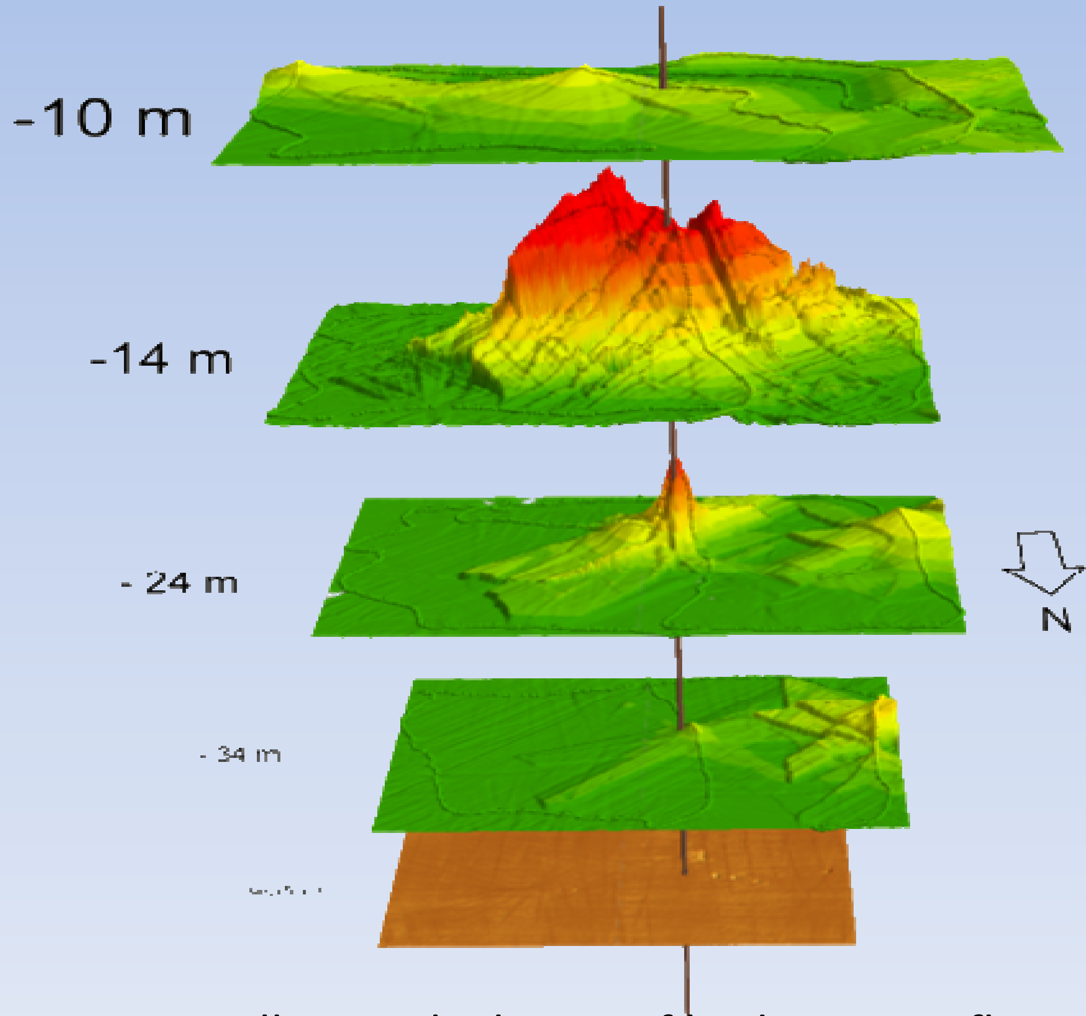
- CT-UWMS
- CTD
- Oxygen optode
- Turbity sensor
- Camera / Spot light
- Syringe sampler
- Energy supply
- Bubble counter

3D-concentration field of CH_4

Gas Bubbles

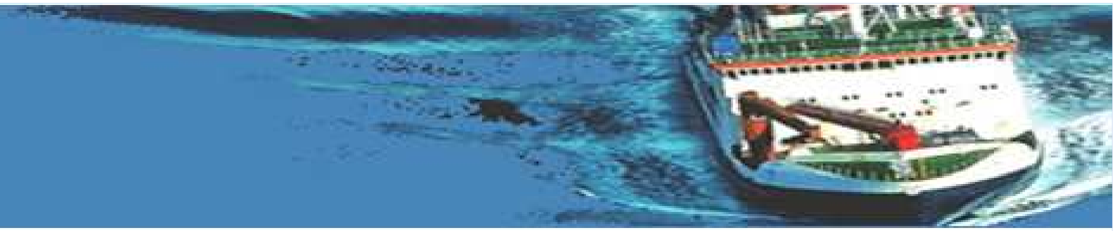


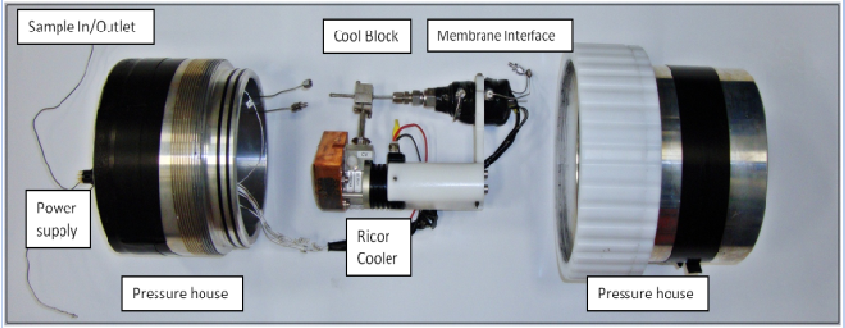
$CH_{4(Dissolved)}$ [nM/L]



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

Summary

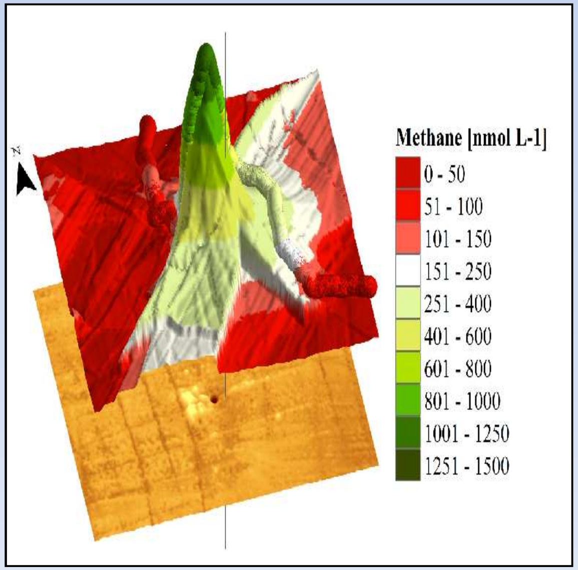




Under water cryo trap membrane inlet system for underwater and other harsh environment:

- 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

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