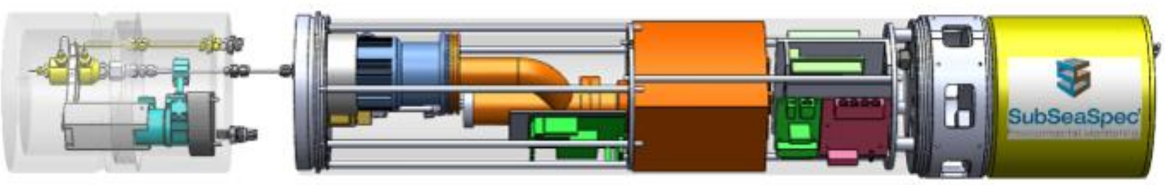
Improvements in Under Water Mass Spectrometry



Torben Gentz

Postdoc, Marine Geochemistry

Alfred-Wegener-Institute for Polar and Marine Research, Bremerhaven, Germany

Baltimore; September 15, 2015

ALFRED-WEGENER-INSTITUT
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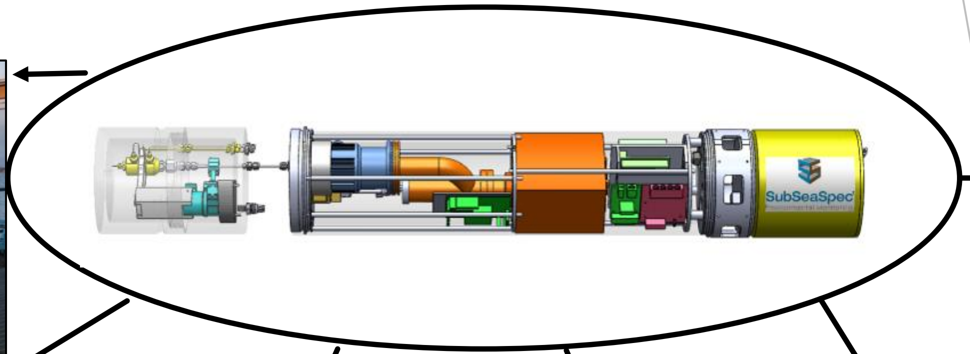
UND MEERESFORSCHUNG

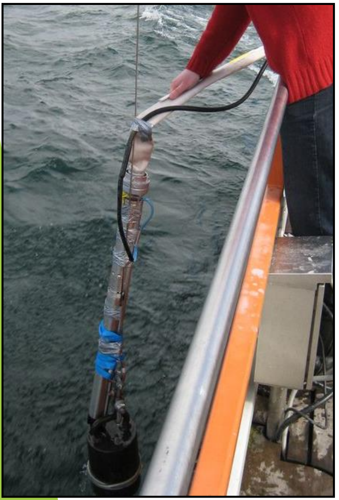
Mode of operation in industry and science

Detection of the greenhouse gas methane and other hydrocarbons



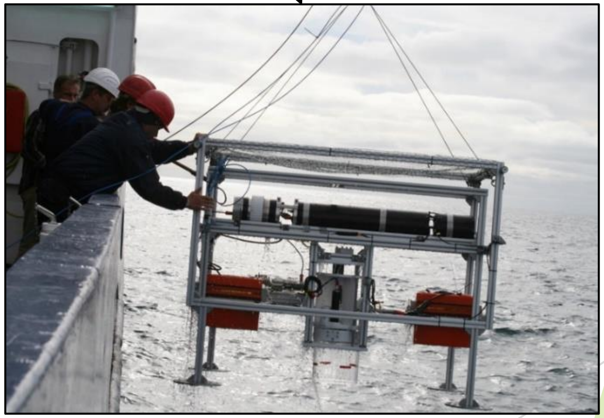
Saab Saabertooth AUV

Laboratory measurements



Ex situ

AUV

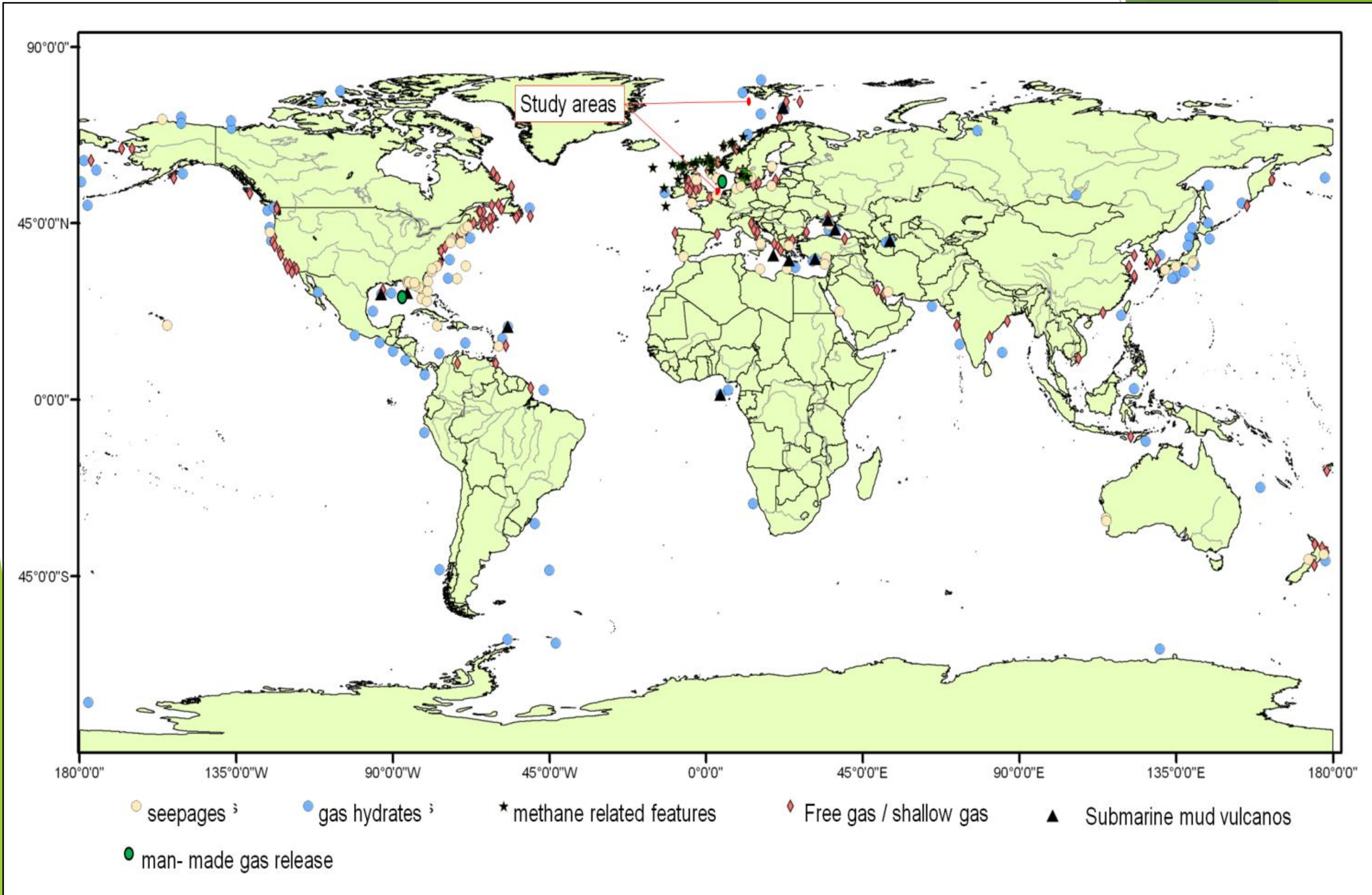


In situ in a frame
including benthic chamber

In situ at sediment-
water-transition-zone

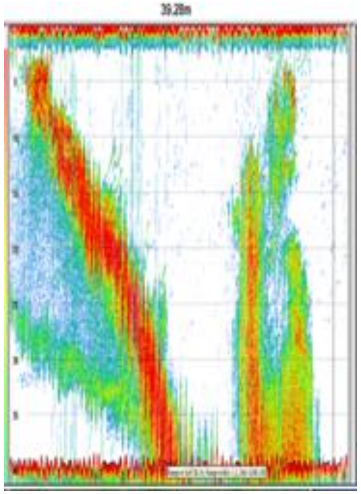
CONTRIBUTION OF UWMS TO SCIENTIFIC QUESTIONS

WORLDWIDE DISTRIBUTION OF SUBMARINE METHANE RELEASE



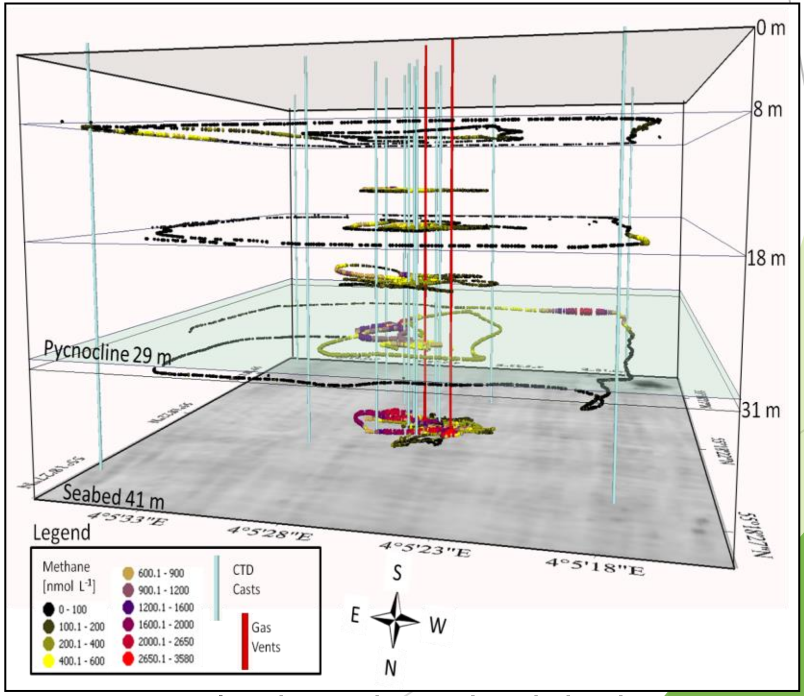
Worldwide distribution of submarine mud volcanos (Milkov 2000), gas hydrates (Kvenvolden et al. 2001), free gas occurrence (Fleischer et al. 2001), and pockmarks (Hovland et al. 2002).

Cruise Vessel Heincke



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

- Online up to 100 m water depth
- Offline up to 200 m water depth
- In situ benthic chamber measurements
- Cruise vessel needed

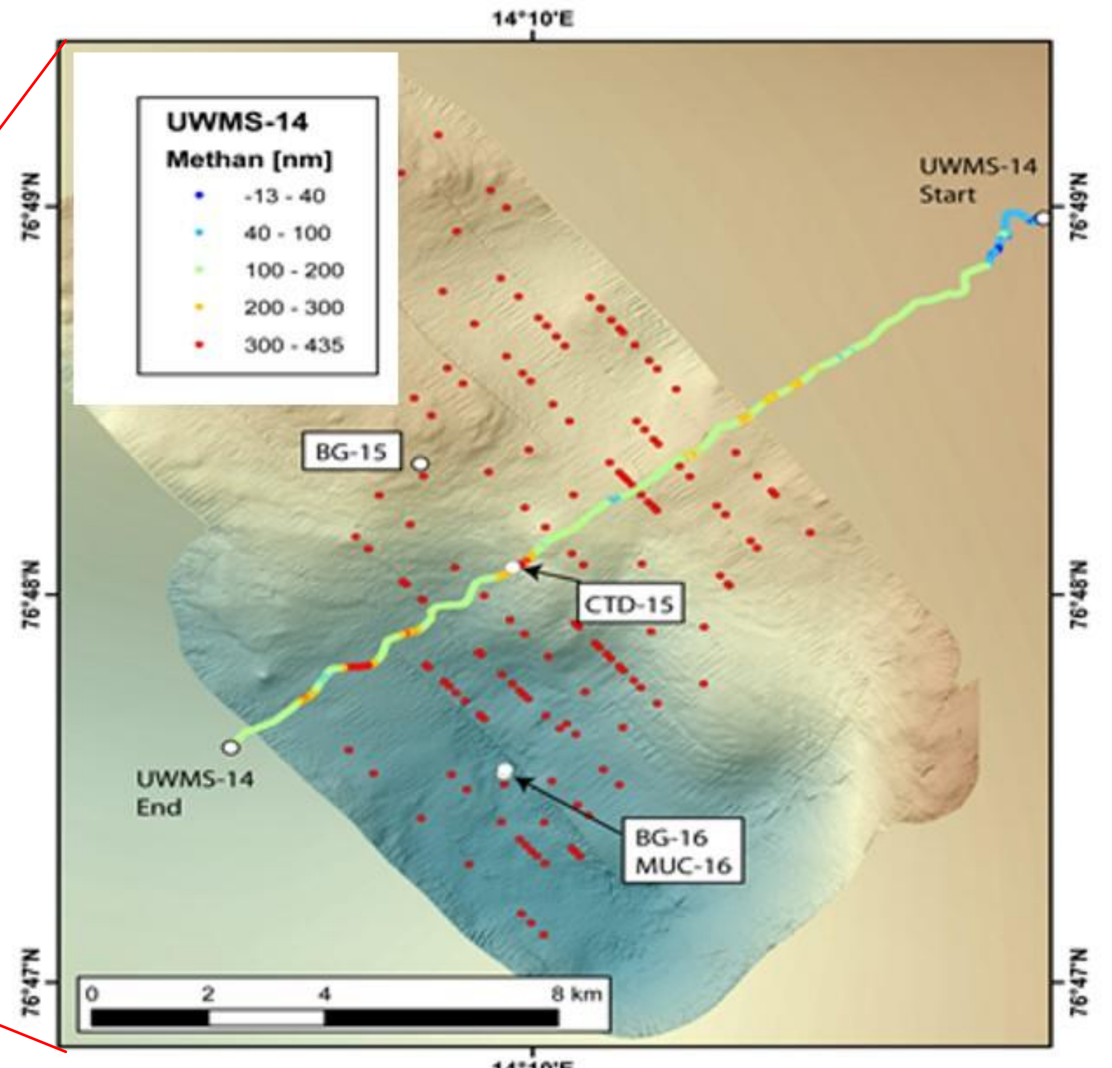


11900 samples in various depth in between 24 hours
(Gentz et al.; in internal review)

NEW RESULTS IN OCEAN RESEARCH

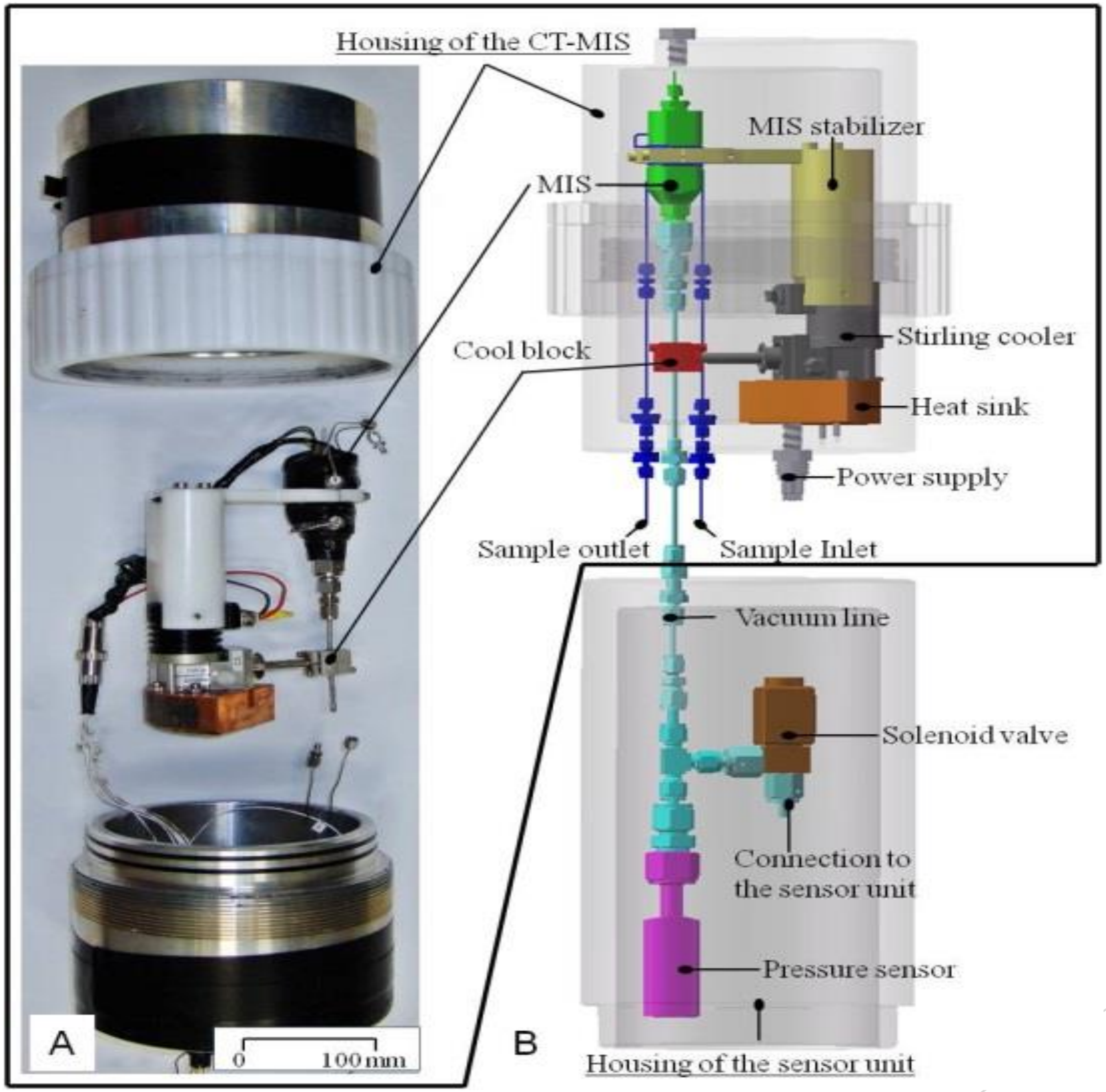
HE 449; August 2015

Map of Svalbard



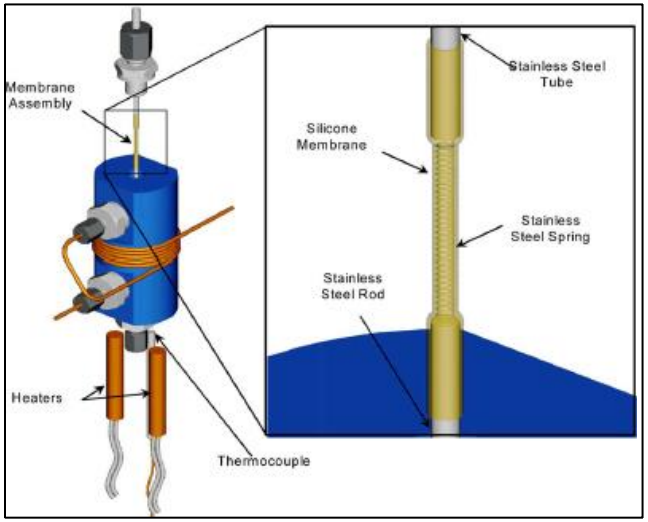
Methane distribution above gas seeps

Cryotrap: Improvement of the detection limit (e.g. methane) by factor 5

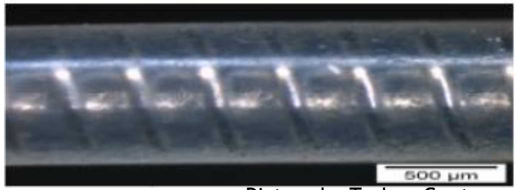


Gentz Torben , Schlüter Michael , *(*2012*)*, Underwater cryotrap-membrane inlet system (CT-MIS) for improved in situ analysis of gases, Limnol. Oceanogr. Methods, 10*, doi:10.4319/lom.2012.10.317.*

Steel springs



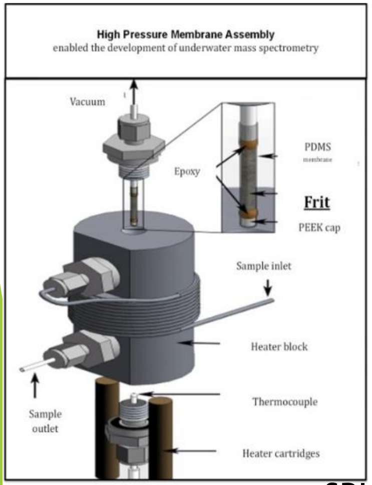
SRI



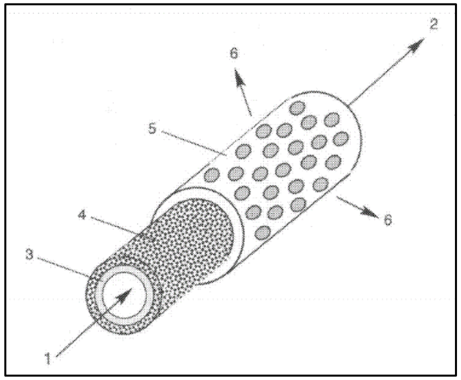
Picture by Torben Gentz

Steel spring
High porosity
Low pressure stability
Great reproducibility

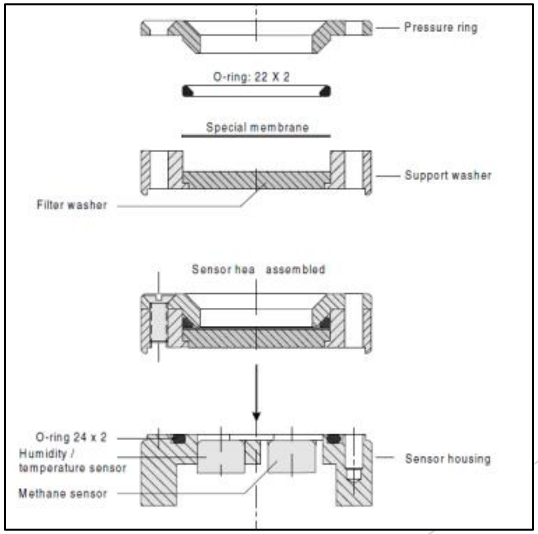
Etched and sintered material



SRI



Mcmurtry

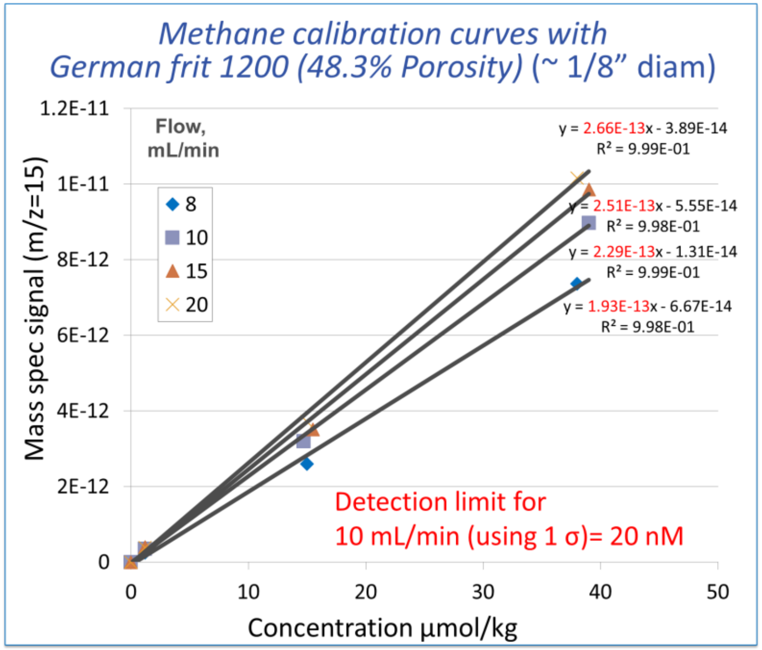


Contros

Hastalloy C frits:
Low porosity
High pressure stability
Bad reproducibility

- www.Contros.de
- Mcmurtry Patentnumber: US 2014/0283626 A1; http://www.freepatentsonline.com/20140283626.pdf
- Bell, R.J., et al. (2011), *Limnol. Oceanogr.-Meth.* 9: pp. 164-175
- P.G Wenner et al., Environmental chemical mapping using an underwater mass spectrometer, TrAC Trends in Analytical Chemistry,
- Volume 23, Issue 4, April 2004, Pages 288-295, ISSN

The Fraunhofer Institute in Dresden, Germany, used powder metallurgical processes to manufacture frits.



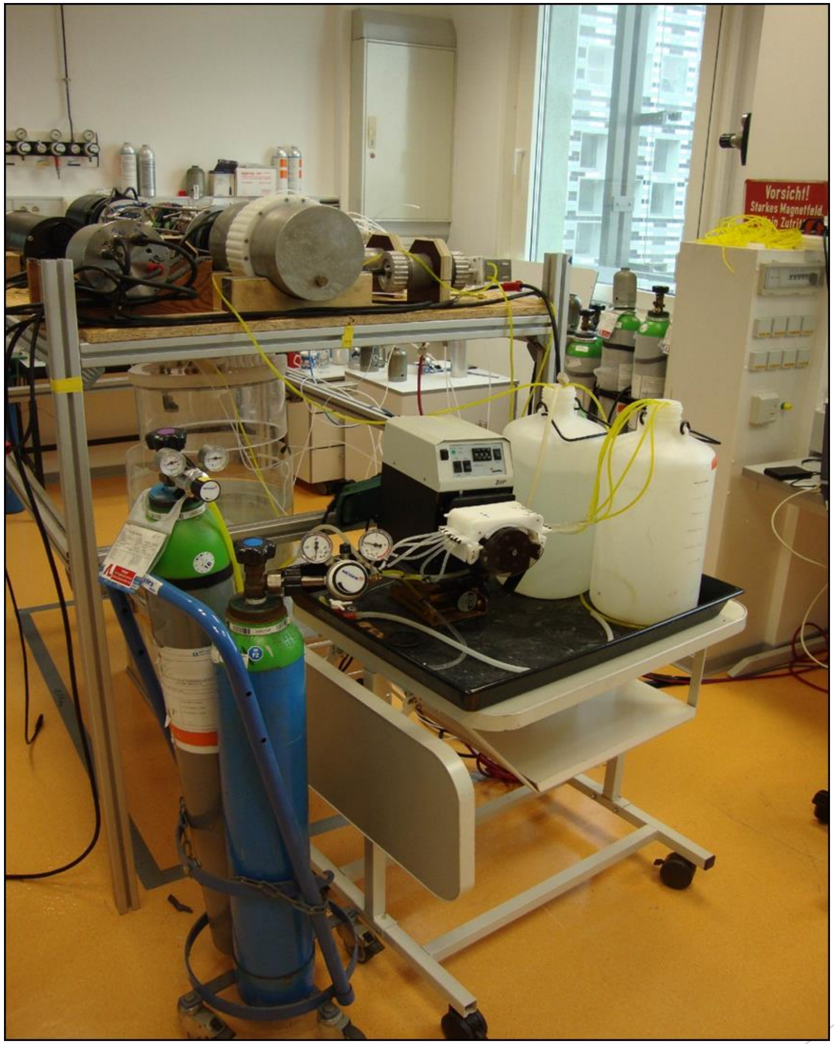
Temperatur of sintering	1150 °C	1200 °C
	Porosität	Porosität
sample 1	48,6 %	33,8 %
sample 2	47,1 %	32,5 %
sample 3	49,1%	31,3%
Average	**48,3%**	**32,5%**

German frits
Low porosity
High pressure stability
Better reproducibility
but not good enough

New way to get frits with high pressure stability **and** high porosity!

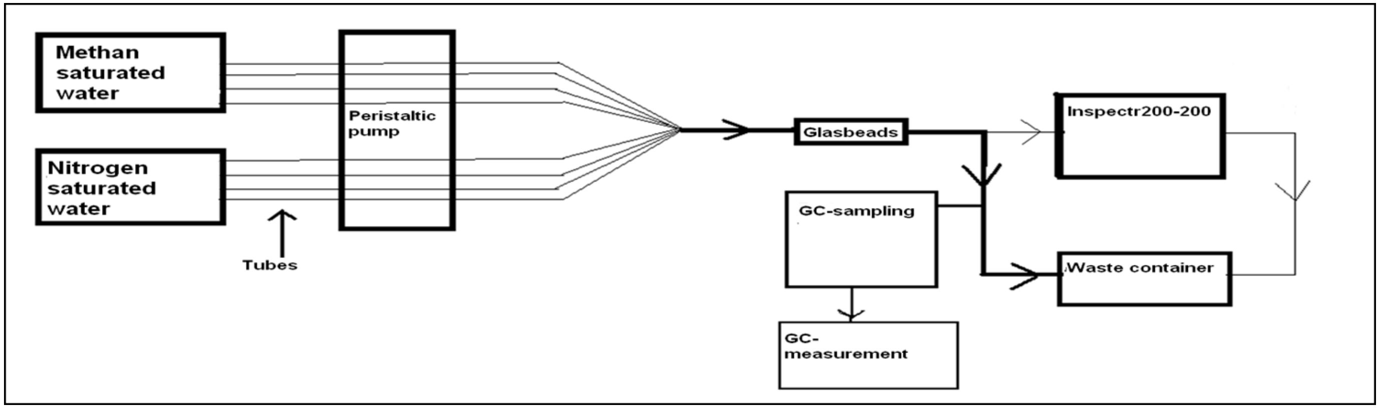
Need of known gas solutions in water

- Not on the market available -



Lab calibration of UWMS prior field campaigns

Laboratory calibration



+ High accuracy
- Time consuming
- Transport in between

Field calibration prior and after each deployment

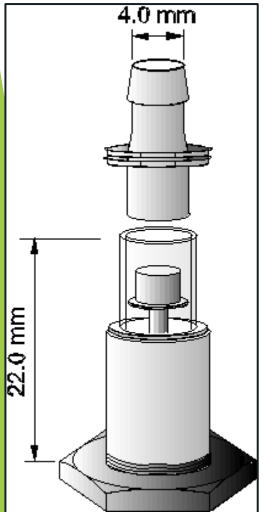
Gas in water standards filled in 120 ml glass bottles and crimped tight

+ Good accuracy (depending of the number of standards)
+ calibration in less than 30 min
+ calibration directly on board
- Each bottle only on time usable
- No certified concentration for each bottle

Field calibration prior and after each deployment

These bags made by a special production process (US Patent) and contain five different layers of materials:

- Polyester (outside)
- Polyvinylidene Chloride
- Aluminium Foil
- Polyamide
- High Density Polyethylene (inside)



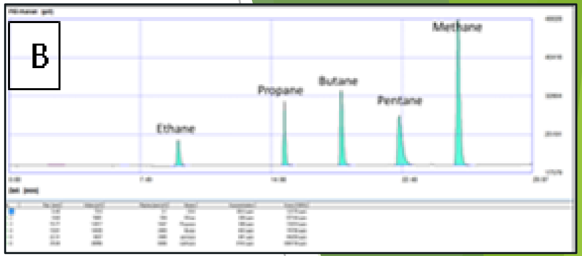
\+ Good accuracy (depending of the number of standards)
\+ calibration in less than 30 min
\+ directly on board
\+ usable more than once
\+ each bag is certified in concentration

Luer-taper Quik-Mate™ Connector

CALIBRATION OF THE UWMS

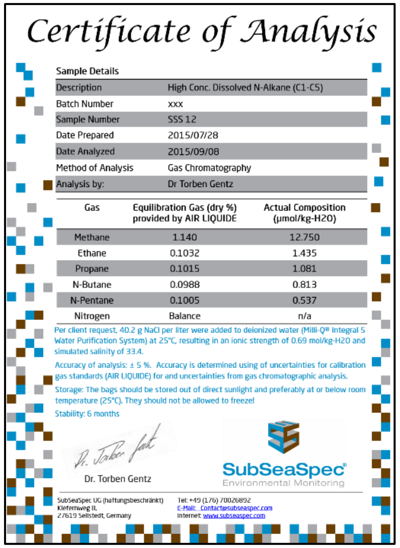
Certification of each bag

Headspace sampling



Analysis by GC

Calculation of the gas composition for each bag



Certificate of Analysis

Sample Details

Description	High Conc. Dissolved N-Alkane (C1-C5)
Batch Number	xxx
Sample Number	SSS 12
Date Prepared	2015/07/28
Date Analyzed	2015/09/08
Method of Analysis	Gas Chromatography
Analysis by:	Dr Torben Gentz

Gas	Equilibration Gas (dry %) provided by AIR LIQUIDE	Actual Composition (µmol/kg-H2O)
Methane	1.140	12.750
Ethane	0.1032	1.435
Propane	0.1015	1.081
N-Butane	0.0988	0.813
N-Pentane	0.1005	0.537
Nitrogen	Balance	n/a

Per client request, 40.2 g NaCl per liter were added to deionized water (Milli-Q® Integral 5 Water Purification System) at 25°C, resulting in an ionic strength of 0.69 mol/kg-H2O and simulated salinity of 33.4.

Accuracy of analysis: ± 5 %. Accuracy is determined using of uncertainties for calibration gas standards (AIR LIQUIDE) for and uncertainties from gas chromatographic analysis.

Storage: The bags should be stored out of direct sunlight and preferably at or below room temperature (25°C). They should not be allowed to freeze!

Stability: 6 months

Dr. Torben Gentz

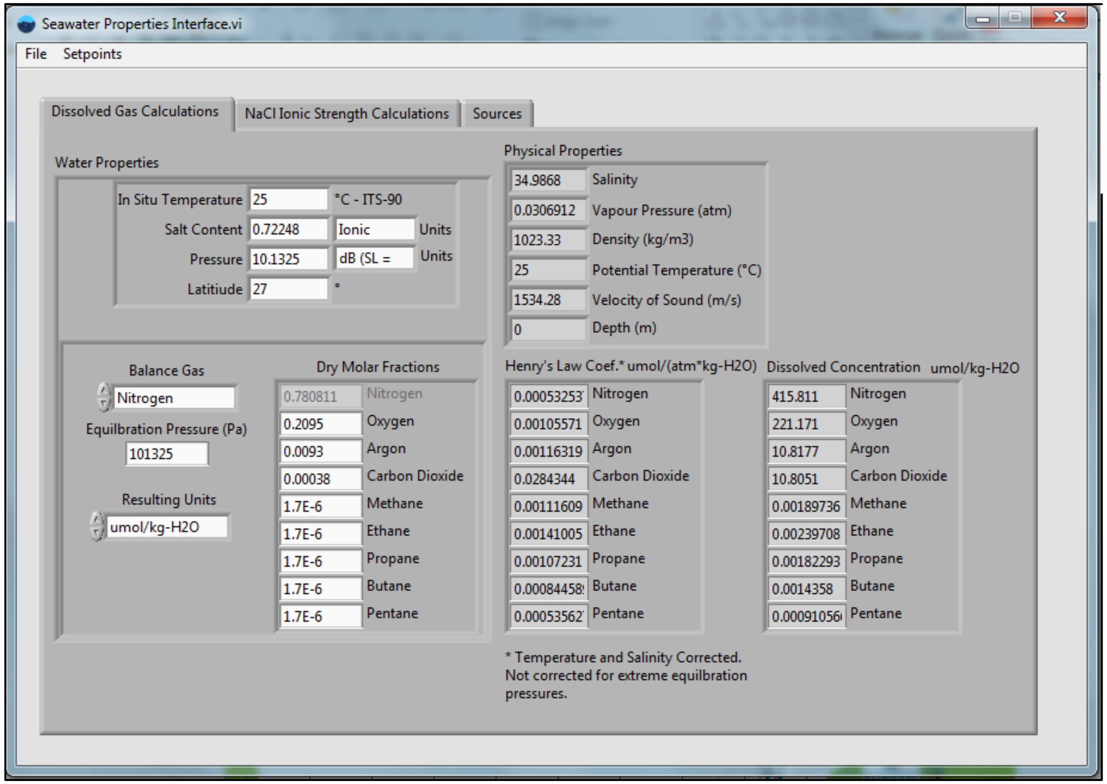
SubSeaSpec®
Environmental Monitoring

SubSeaSpec UG (haftungsbeschränkt)
Kiefernweg 8,
27619 Sellstedt, Germany

Tel: +49 (176) 70026892
E-Mail: Contact@subseaspec.com
Internet: www.subseaspec.com

Future work

Software developed by Ryan Bell



Beaver Creek Analytical LLC

http://www.bcanalytical.com/

- Henry law coefficients based on literature.
- Lab measurements to verify each coefficient (temp and salinity) to optimize the calculation

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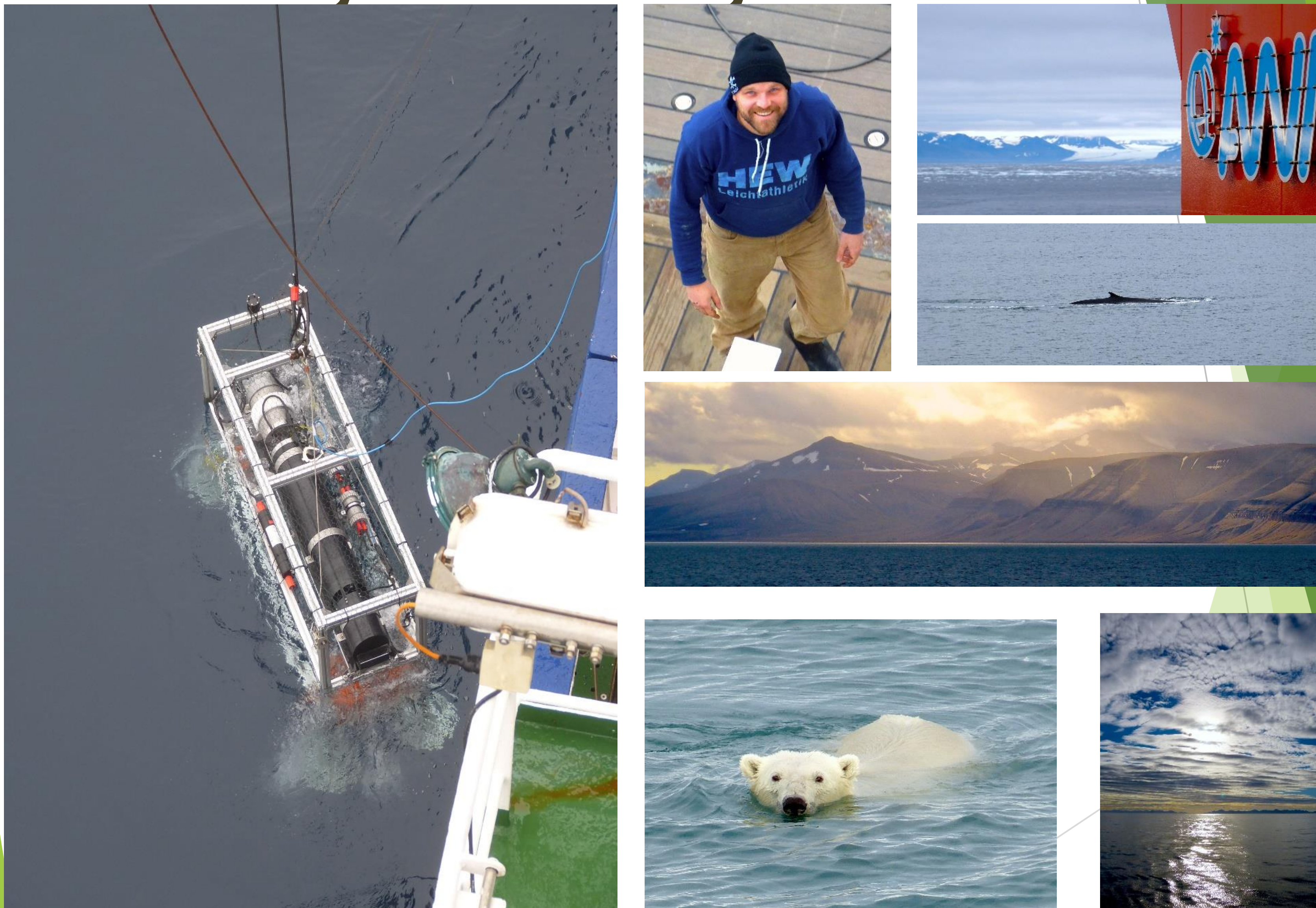
Environmental Monitoring

Thank you for your attention



Impressions of HE 449