University of Southampton

National Oceanography Centre

Royal Academy of Engineering

INTEGRATED PHOTONICS FOR OIL SPILLS MONITORING

Rand Ismaeel
Marine Photonics
(RAEng)

National Oceanography Centre

FROM SOUTHAMPTON

ONLY AT SOUTHAMPTON..

NOC

ORC

OTE

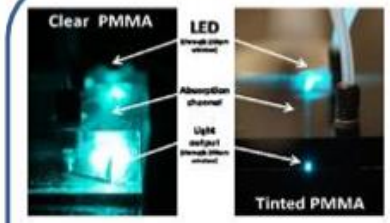
NOC: research, technology

Ocean Technology and Engineering Group (OTEG)

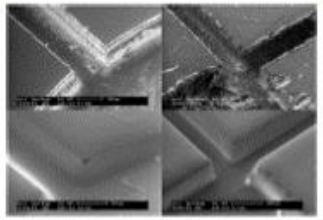
Mission (***"To develop novel technology and engineering resulting in the greatest impact for environmental and marine science"***)

OTEG sensors expertise

electronics



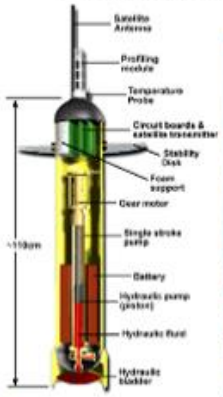
optics



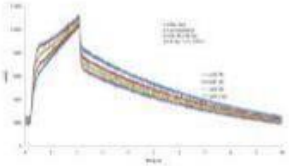
manufacturing

Integrated systems

Platforms & comms



Microfluidics



Assay optimisation

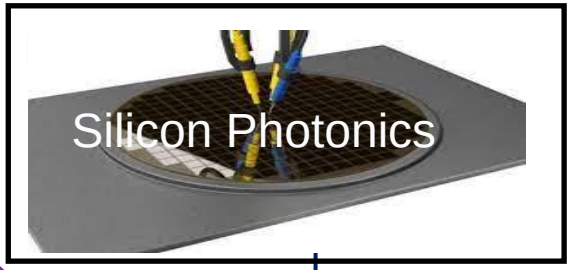
Lab on a chip

Biofouling mitigation

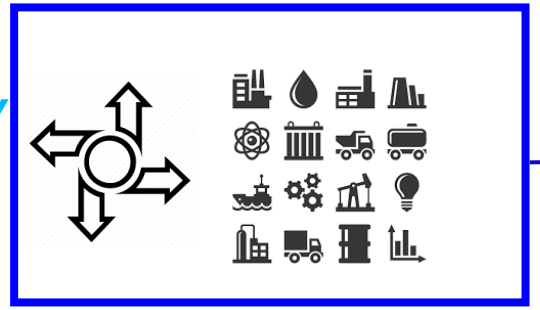
ORC

October 2005

Today

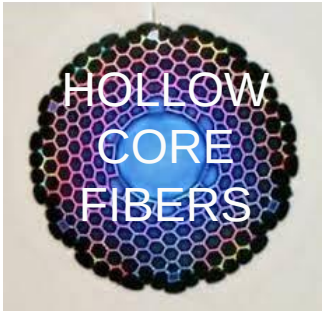


INDUSTRY AND SPINOUT

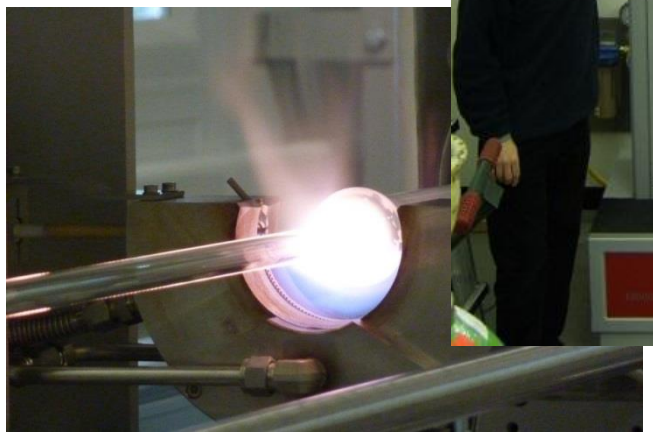


ORC capabilities

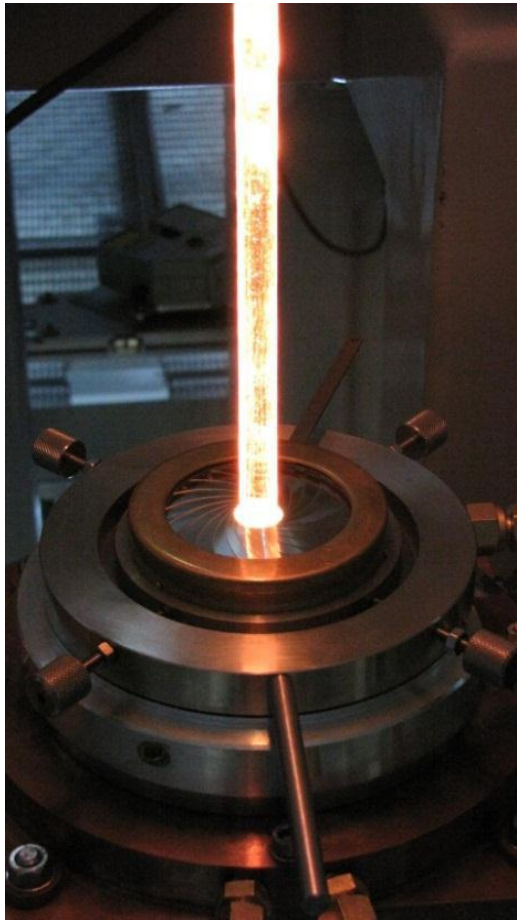
SCIENTIFIC RESEARCH



RESEARCH FACILITIES: PREFORM FAB



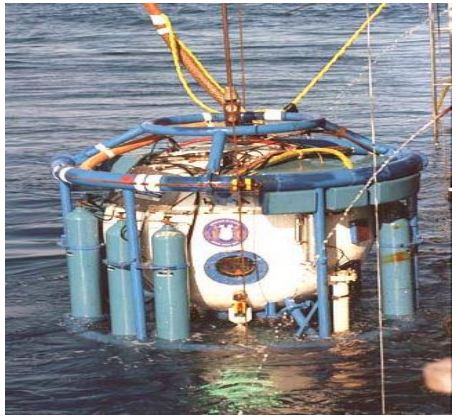
RESEARCH FACILITIES: FIBRE FAB

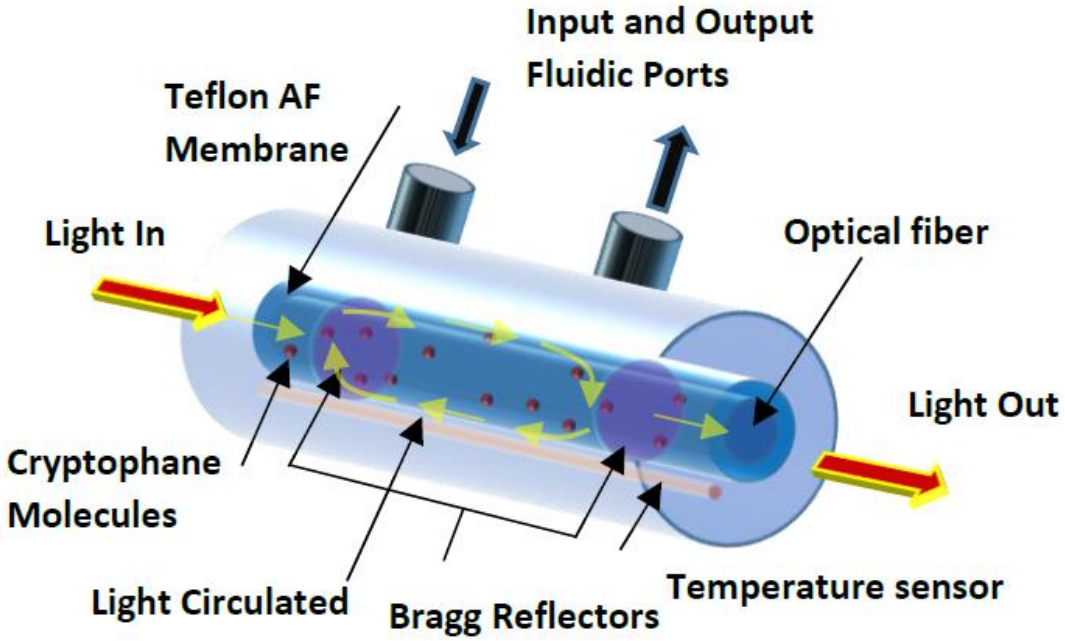


Royal Academy of Engineering Fellowship:

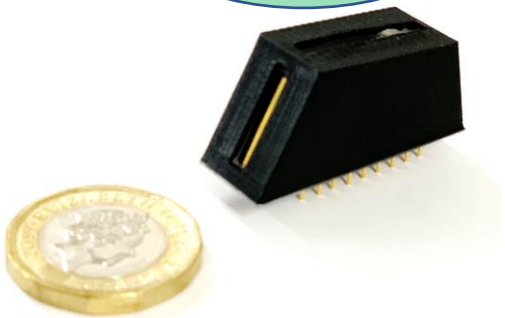
Transform ocean sensing methodology <u>to the next generation</u>

Current methods





The Future



Methane SPR Sensor

Expand the technology to monitor other unexplored organic and inorganic analytes in the marine environment.

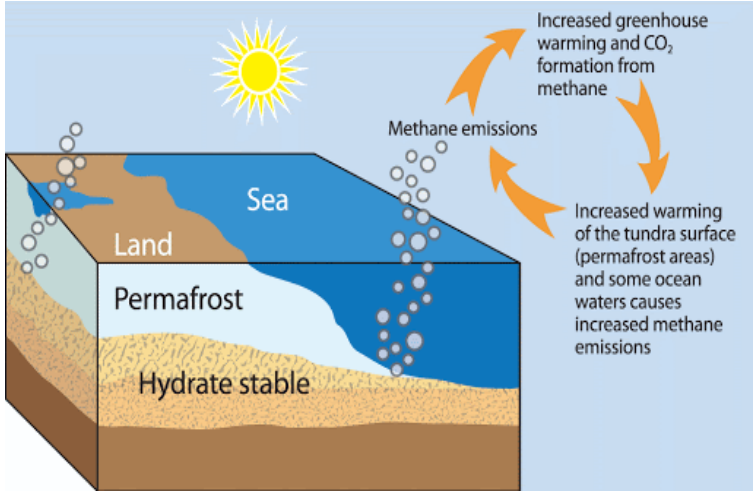
National Oceanography Centre

Why the need for in situ Dissolved methane sensor?

- ***Methane is a potent greenhouse gas pollutant, its ability to absorb energy is 81 times greater than the same mass of carbon dioxide. (Methane 20-years Global Warming Potential 'GWP' is 81-83[1]).***
- ***Pipeline leakage***: cost £1,000,000,000s in repair and loss of product.
- ***Understanding of ocean's methane contribution to the global warming***: the methane bomb, unquantified threat to the marine biota.
- ***Assessments:*** before construction or decommissioning of offshore infrastructure.

Pipeline Leak

Methane Hydrate

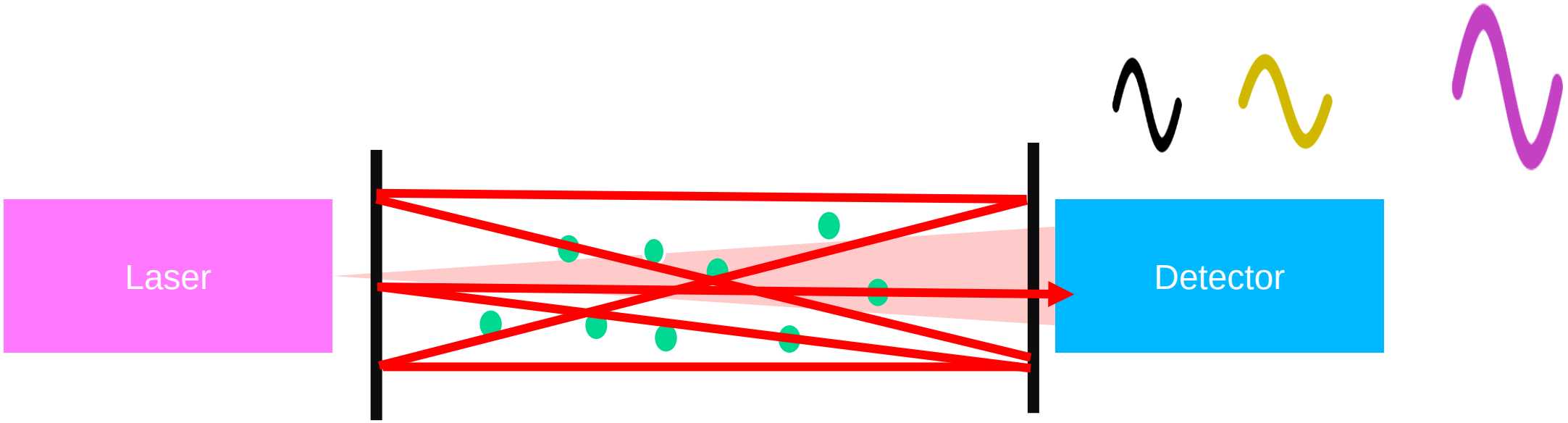


The Big Problem

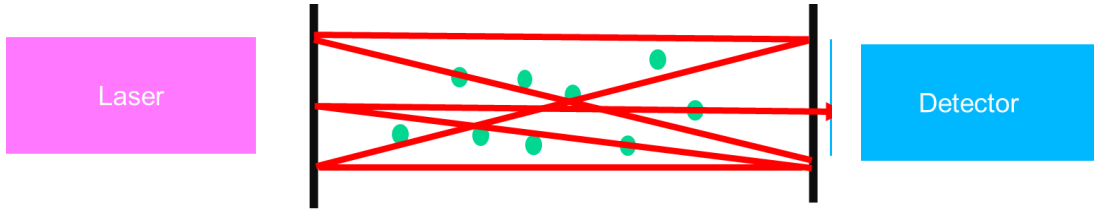
An urgent need for 3D mapping ocean methane and methane isotopes

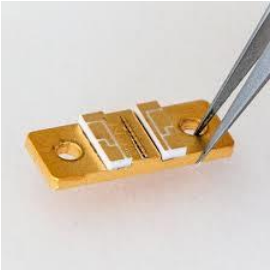
[1] From EPA, U.S. Environmental Protection Agency

STATE OF ART TECH FOR HYDROCARBON DETECTION

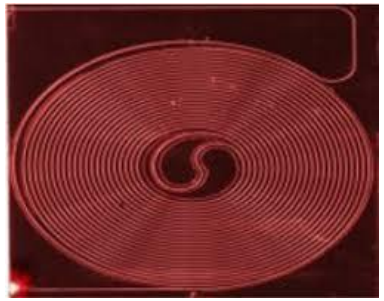


WHAT THE FUTURE WILL LOOK LIKE?



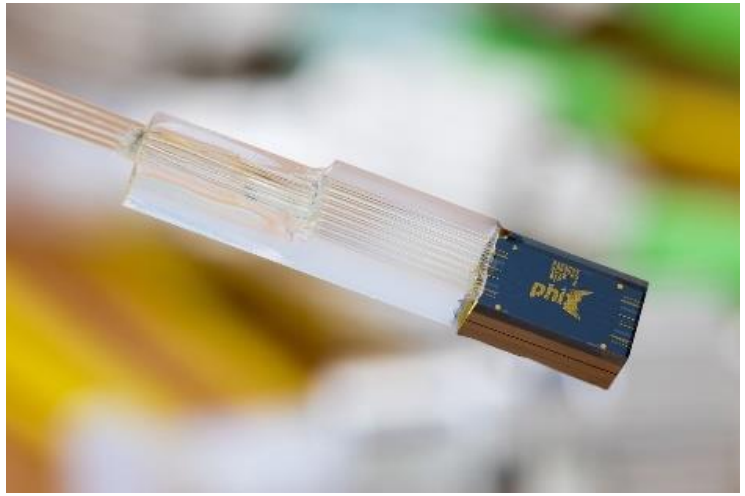


QCL



Optical waveguide

MCT detector



Optical **dissolved** Gases Sensors

Which Band is more suitable?

Near IR	Mid IR
Weaker absorption for green house molecules	High absorption for green house molecules (1000 times better than NIR
Low water absorption Measurement can be in liquid phase	High water absorption Needs Gas separation (slow response)
Mature Technology Low loss, can be tailored to cavity	100 times lower TRL than NIR Progressing rapidly

Which to Choose?

Optical **dissolved** Gases Sensors

Both! **For now…**

Near IR	Mid IR
Refractive Index change sensors	Compact waveguide sensors With
Resonance spectroscopy	
Spectroscopy-Long waveguides with pre-concentrators	

Future dominant technology

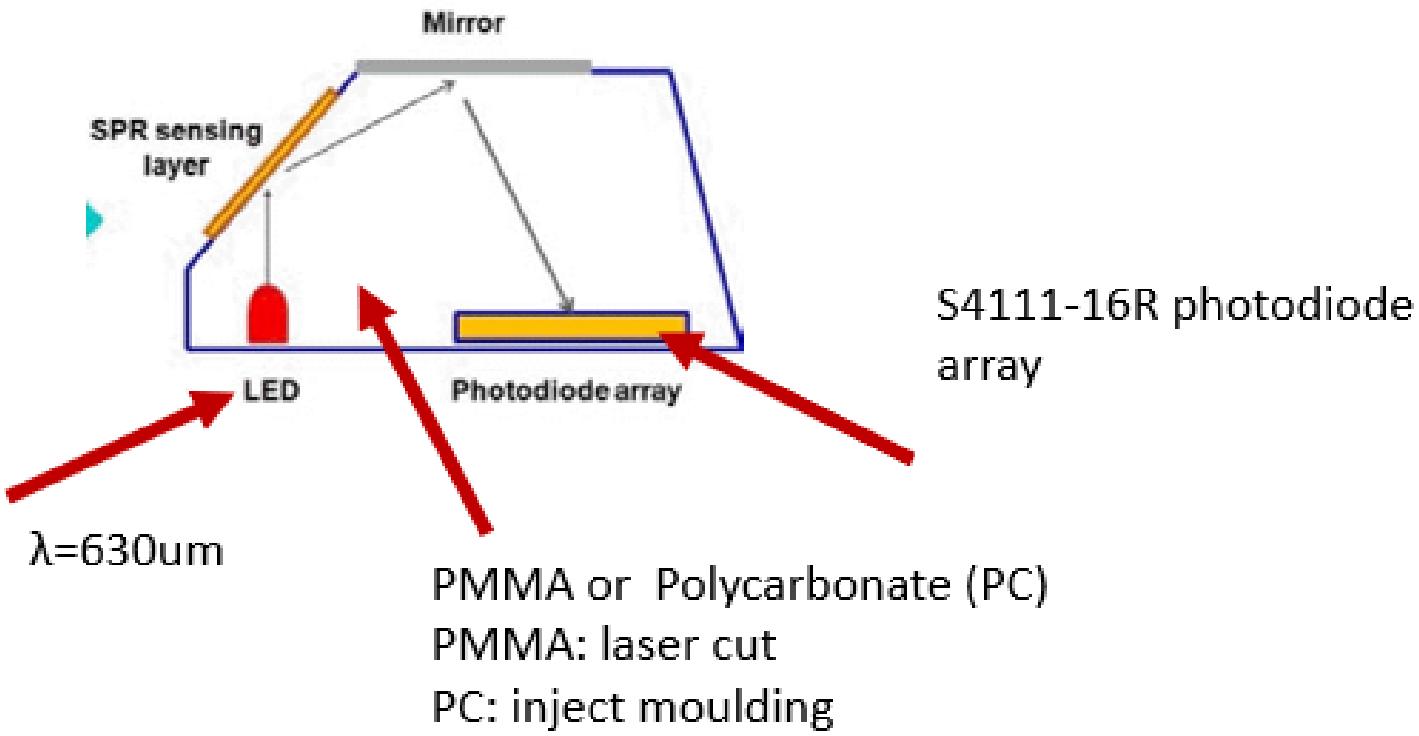
10-20 years span

National Oceanography Centre

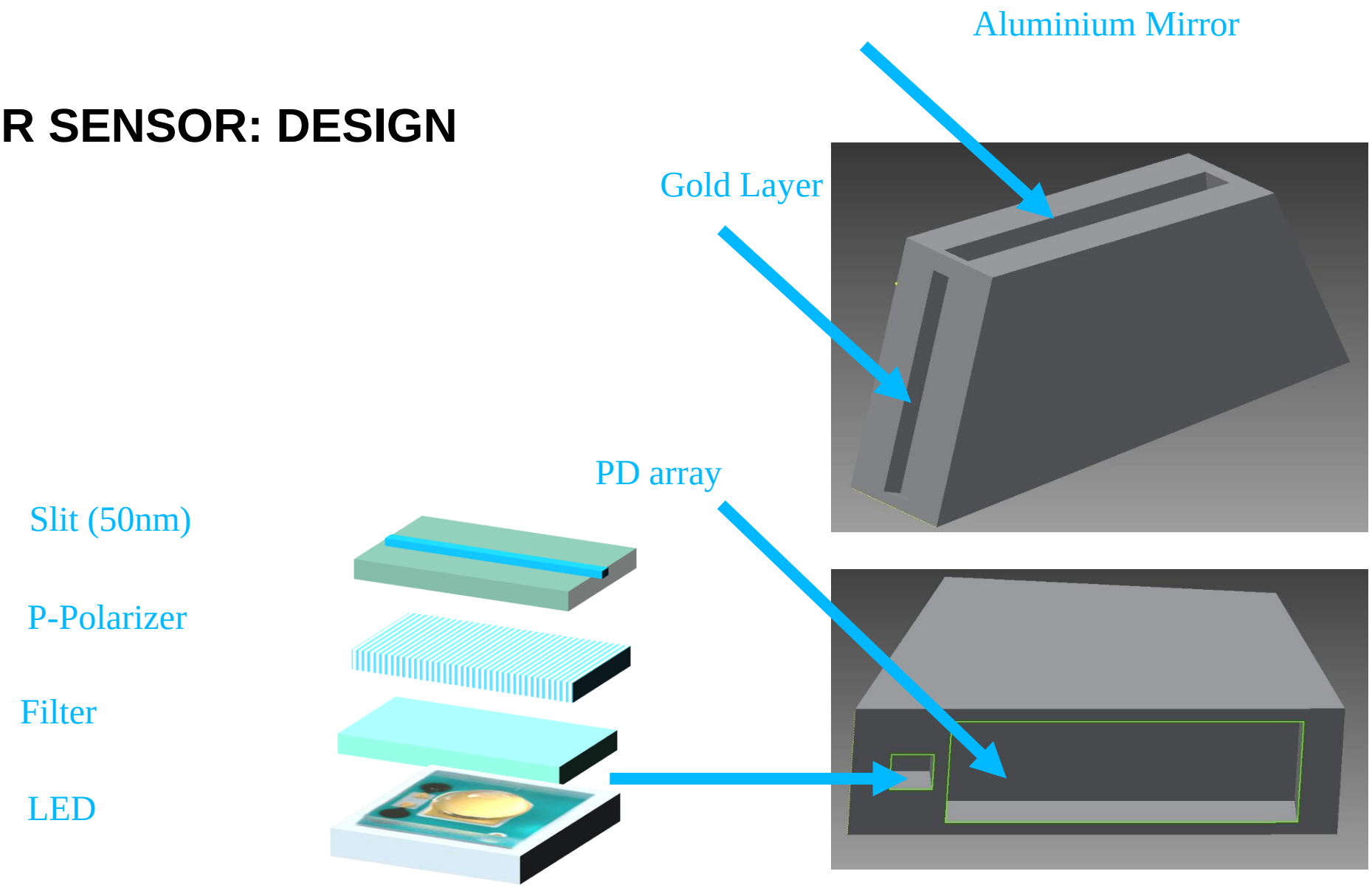
Part 1: Refractive index sensors

SPR METHANE SENSOR

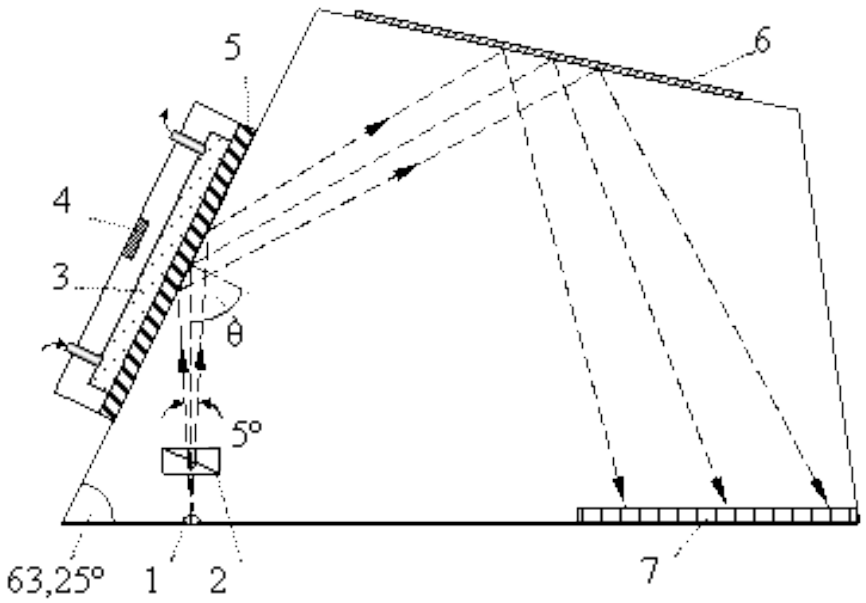
SPR METHANE SENSOR: DESIGN



SPR SENSOR: DESIGN

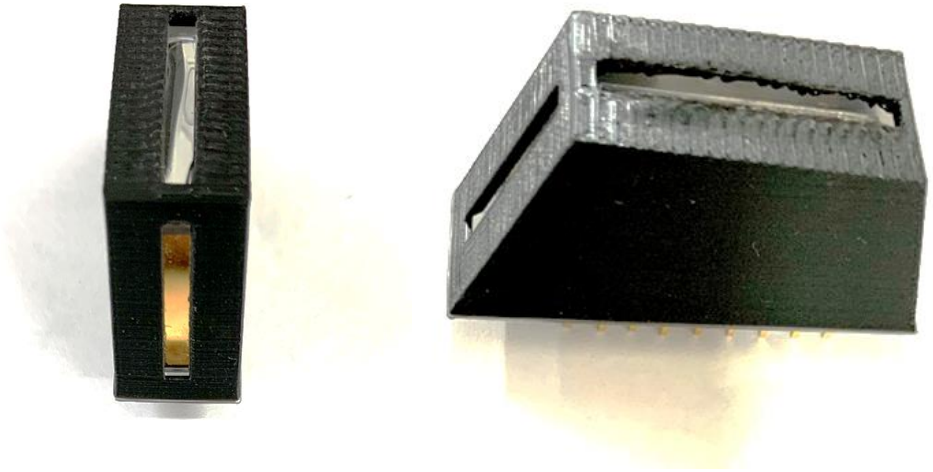


SPR Sensor: Fabrication

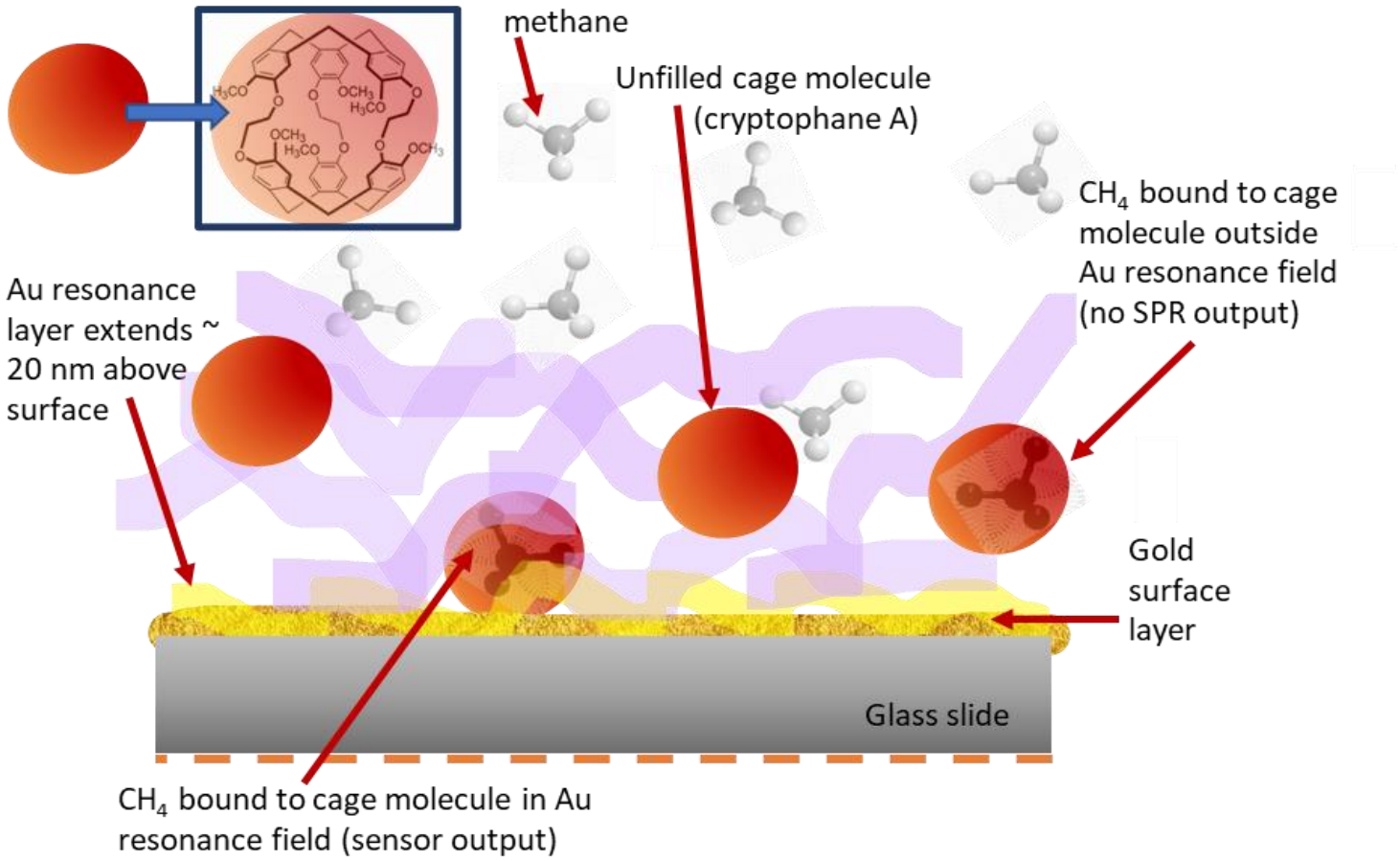


Optical design of the NOC methane sensor:

1 – LED
2 – polarizer
3 - flow cell
4 – Thermistor
5 – gold sensitive layer
6 - mirror reflective layer
7-photo detector array

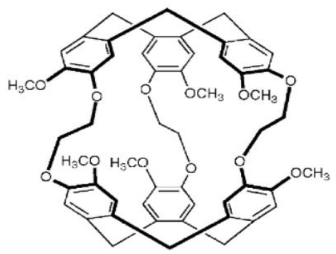


SPR SENSOR: SENSITIVE LAYER

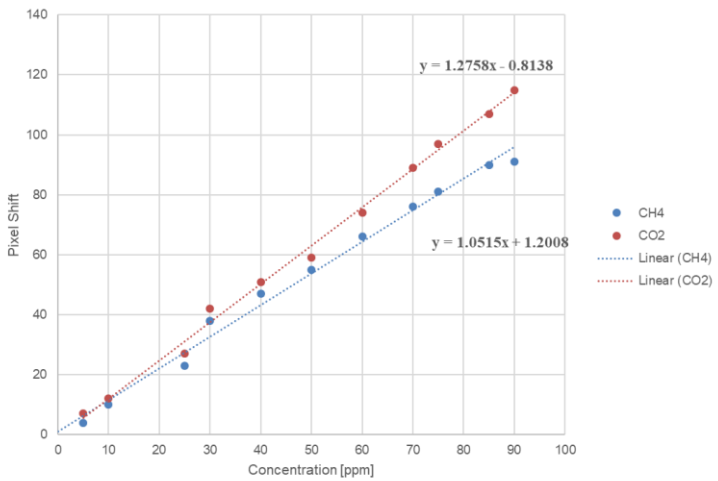


SPR SENSOR: FLUIDS DELIVERY

cryptophane-A+PDMS

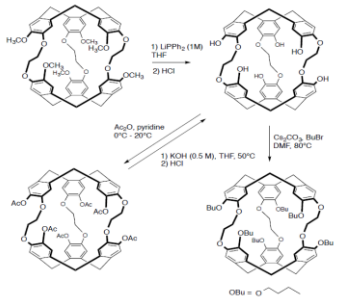


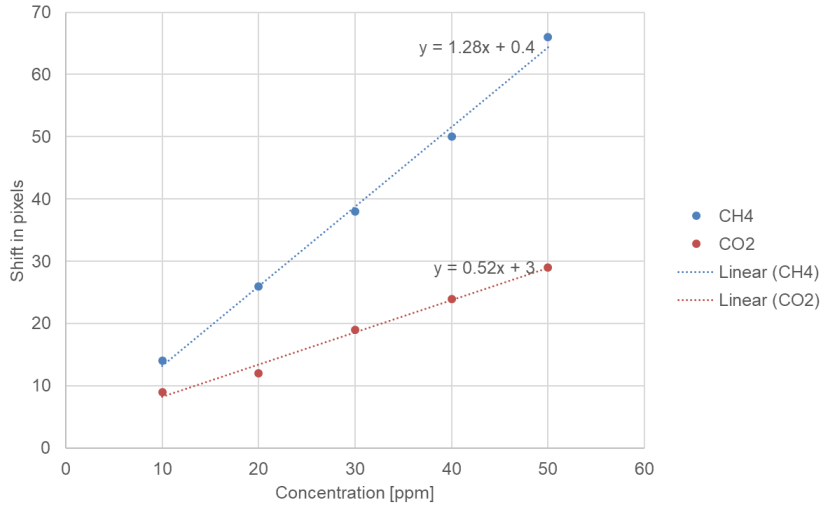
Cryptophane-A



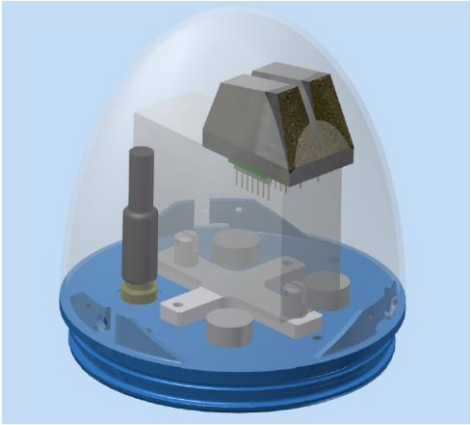
Interference effects Enhanced ~%30

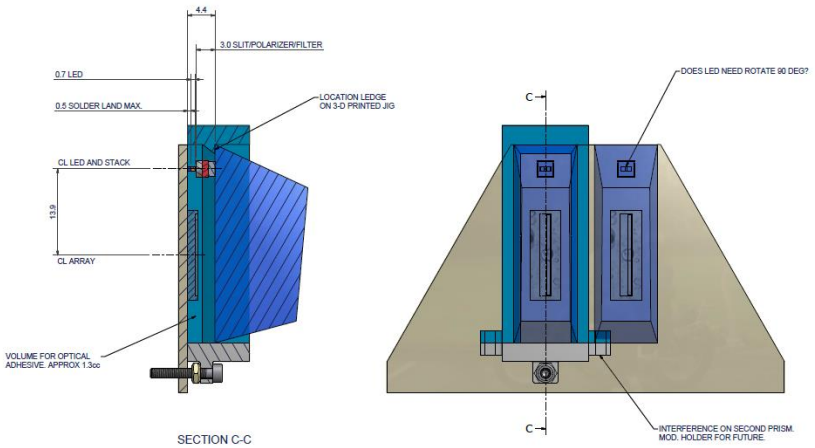
cryptophane(OBu)6 +TEFLON AF





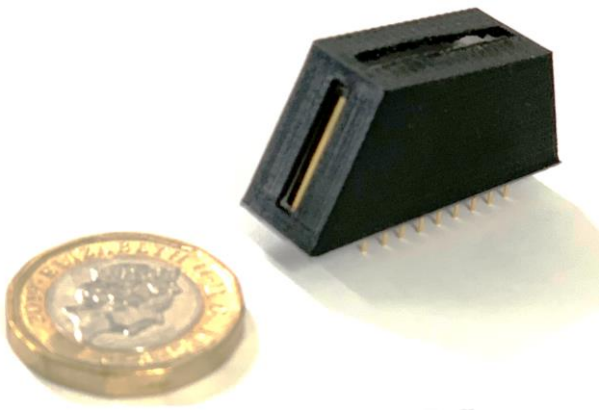
SPR METHANE SENSOR

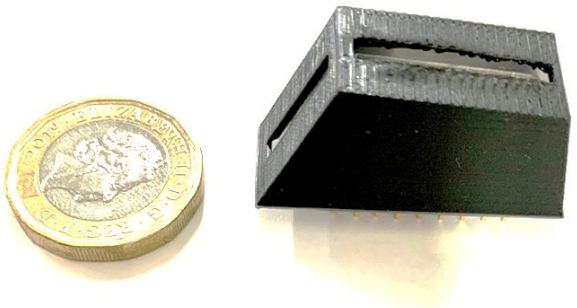




- Integration to the nose Kone of the Ecosub.
- Determining the precise sensor parameters to enable integrating the electronics of the sensor (PCB)
- The prism material was changes to SF10 to avoid gluing issues of the sensitive layer.
- Prototyping the potting and the sealing of the sensor to the nose of the Ecosub.

SPR METHANE SENSOR

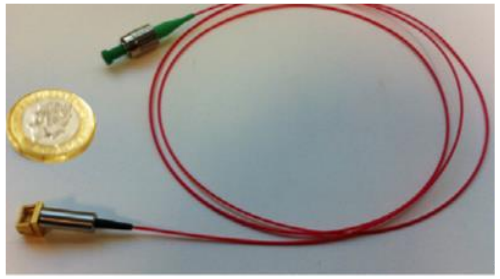




High resolution (0.1nM) ,dynamic range from 0.1nM to 200nM
Response time of 1s.

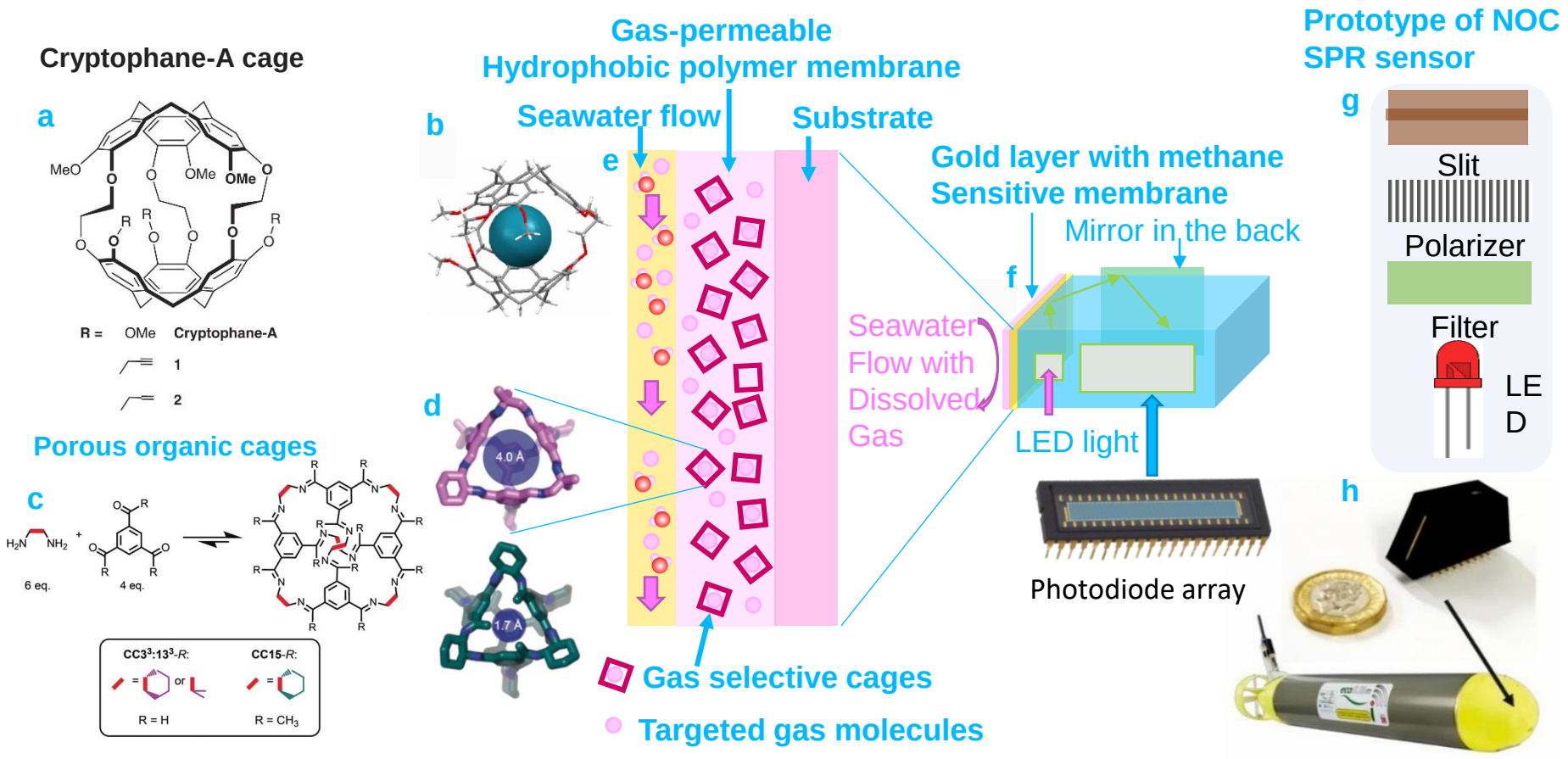
2nM resolution and dynamic range from 2nM to 830nM.
Response time of 1s

SPR SENSOR: SPECS



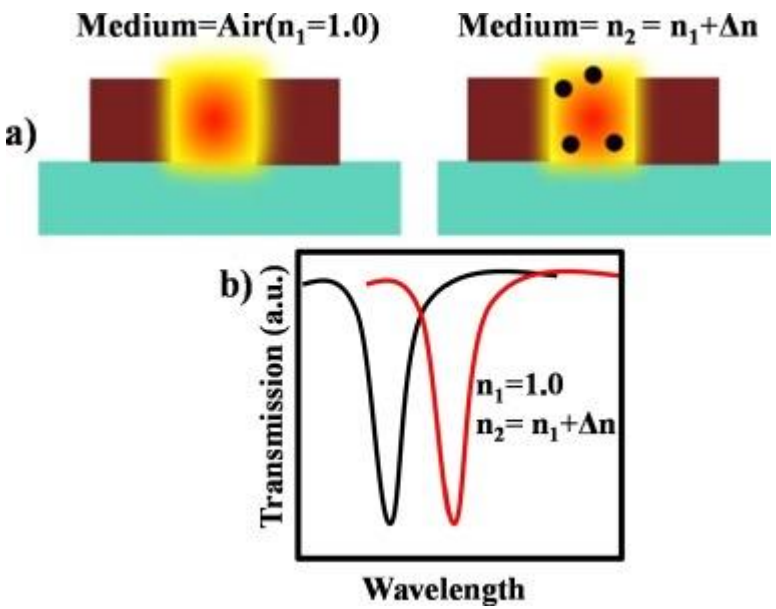
- Supply voltage, 5.0V
- LED current 270mA
- Sensitive surface size 15x1mm
- Operating temperature range 0-70C
- Refractive Index Measurement 1.320-1.468
- Resolution (refractive index) 5x10 ^(-6)

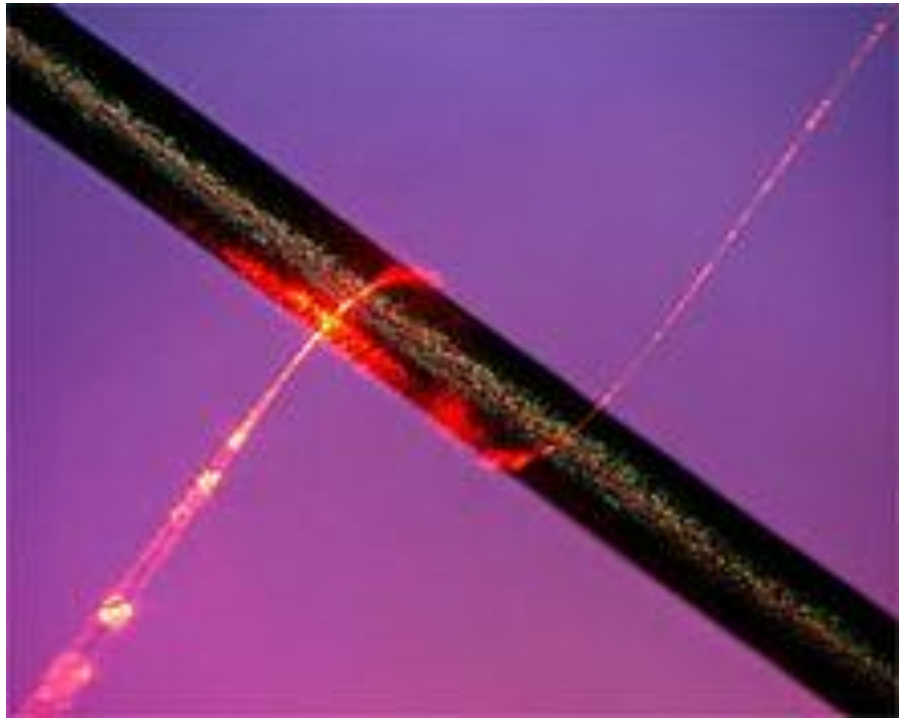
SPR Methane sensor

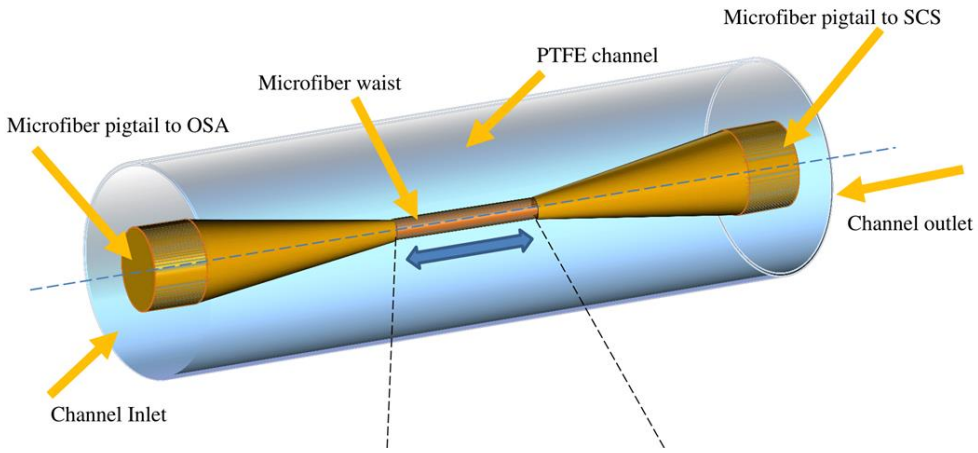


RI Sensors

- Microfibre sensors, wrapped around human hair
- Stronger than steel
- Packaged and protected by selective membrane.
- The membrane increases the field interacting with the dissolved hydrocarbons.



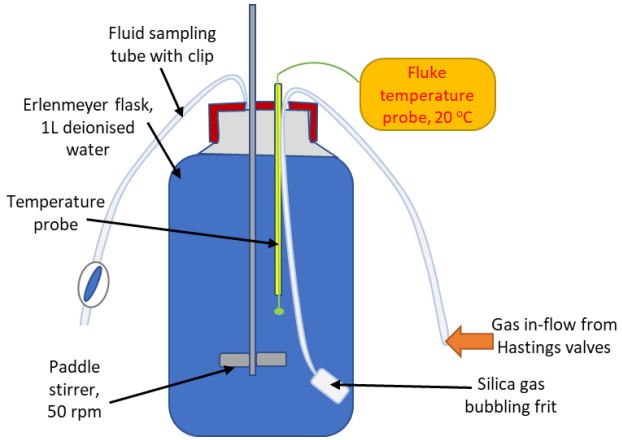


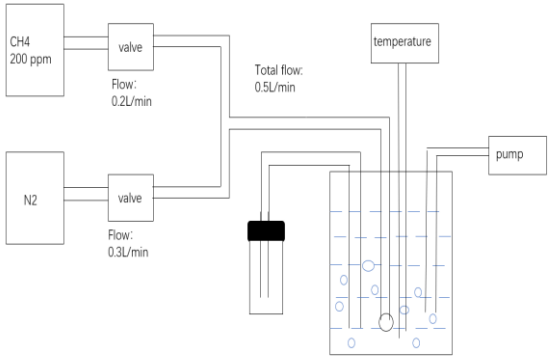


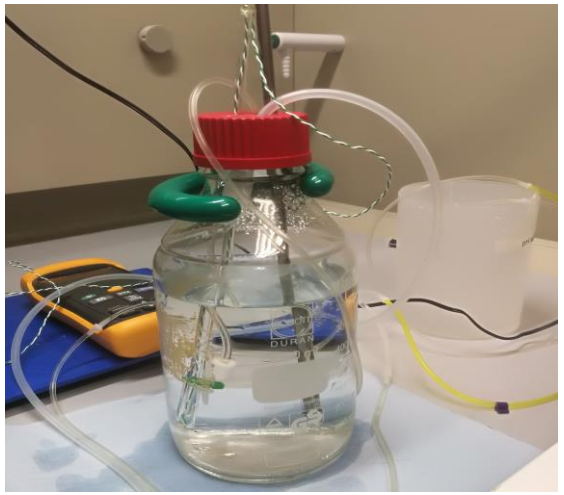
PDMS+Cryptophane

RI Sensors

9µm microfiber embedded with a grating cavity was used for measuring Dissolved methane.

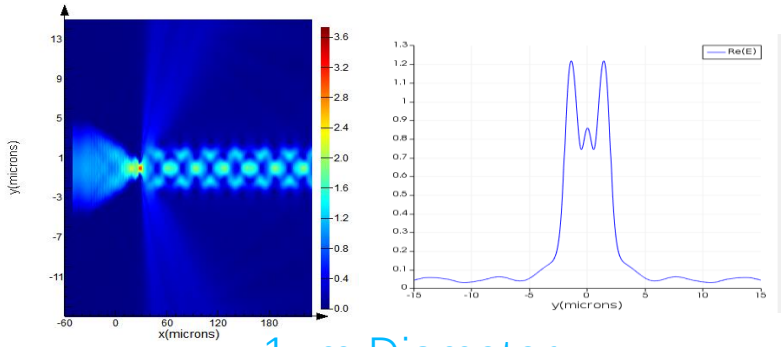




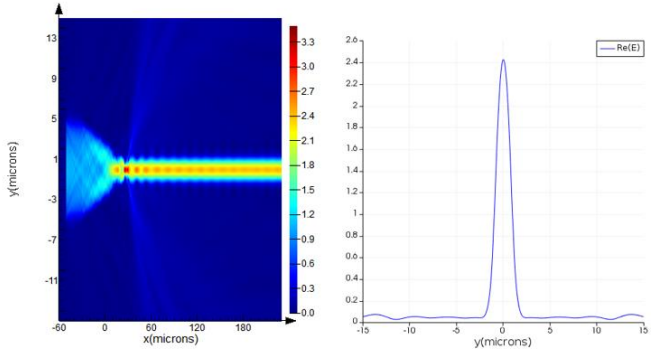


RI Sensors

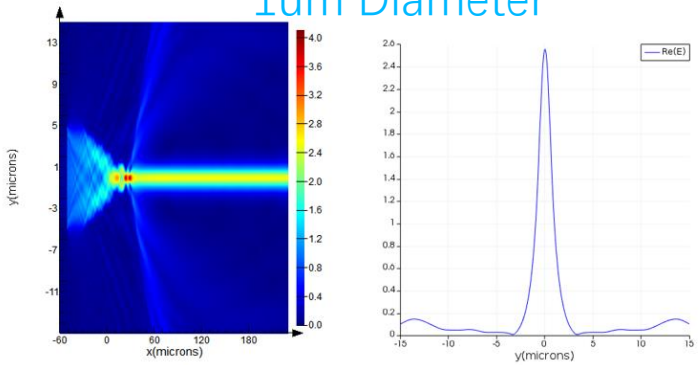
4um Diameter



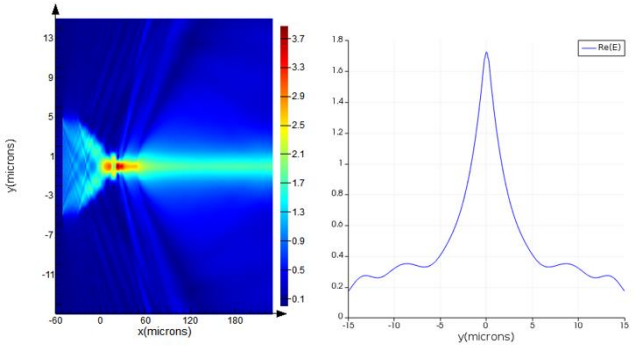
2um Diameter



1um Diameter

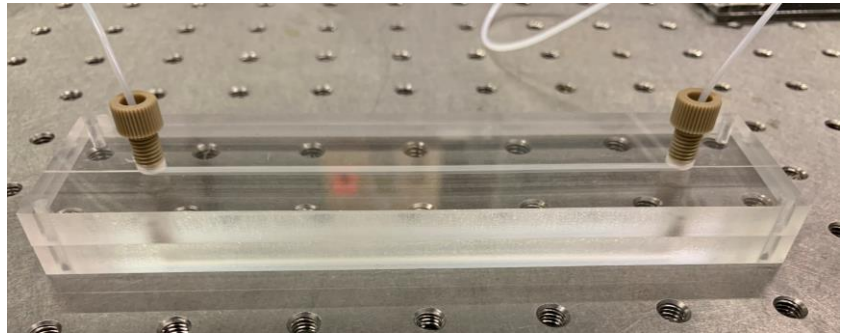


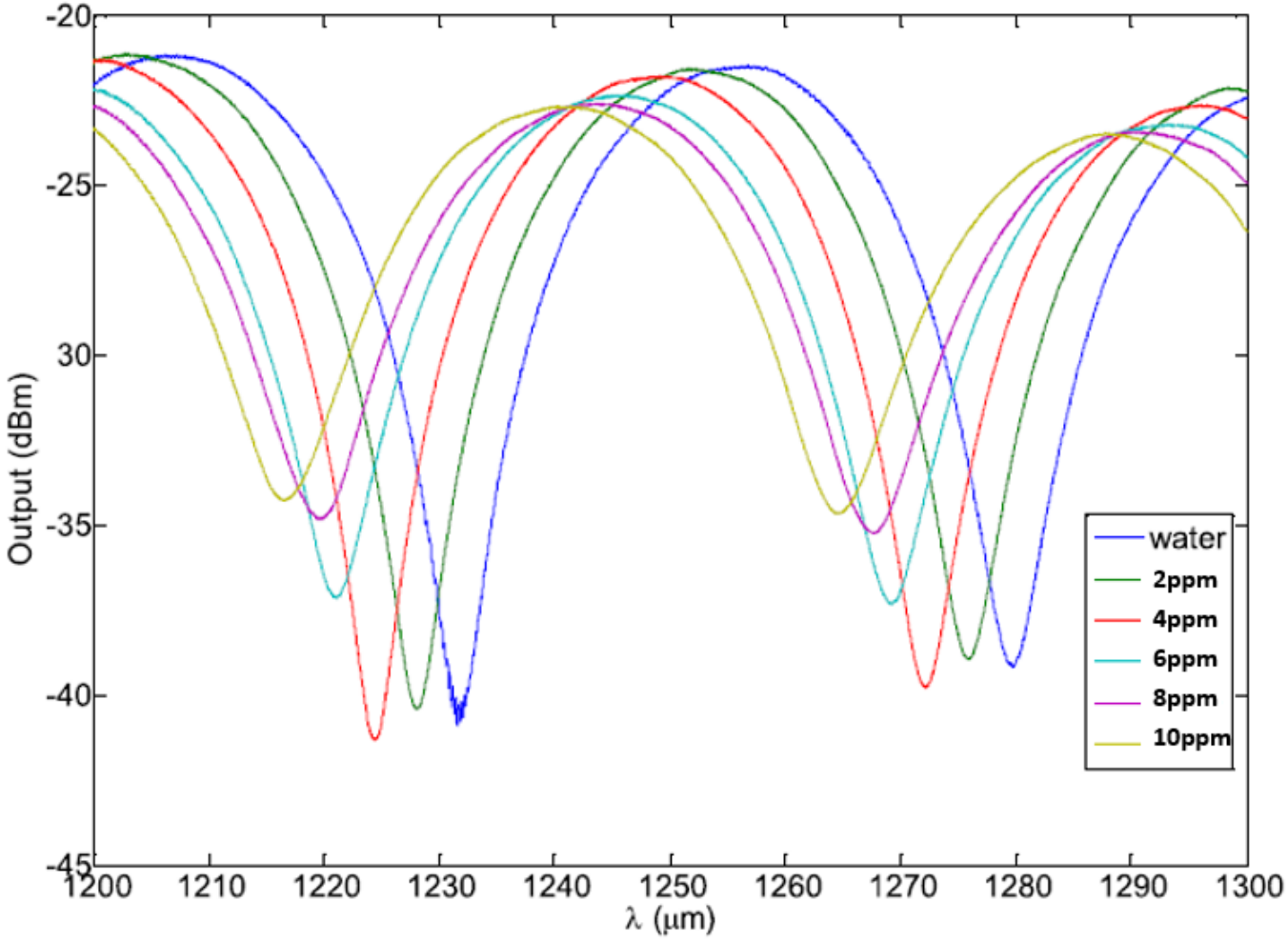
0.4um Diameter



RI Sensors

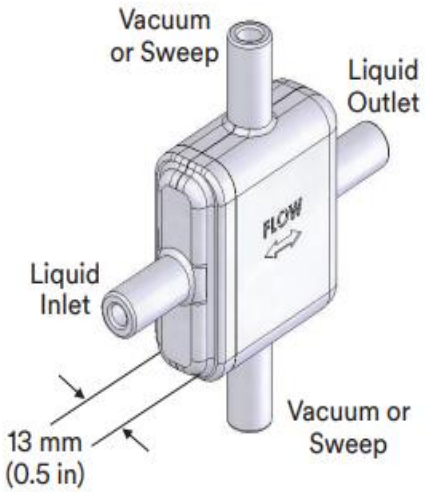
- Sensitivity without membrane of 0.1nm/ppm.
- Sensitivity with membrane of 1.5nm/ppm.
- Response time 65S

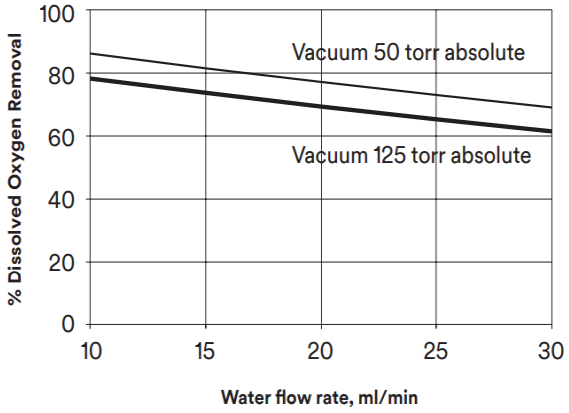


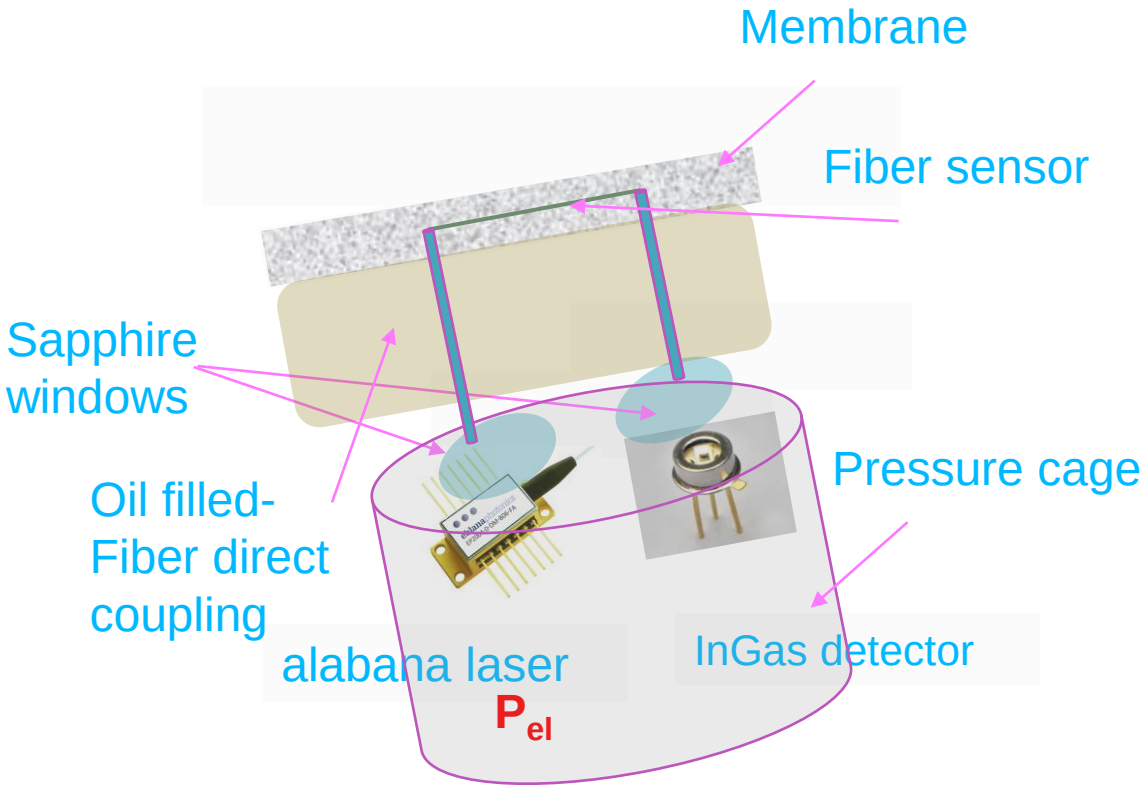


DEEP SEA DISSOLVED GAS SENSOR

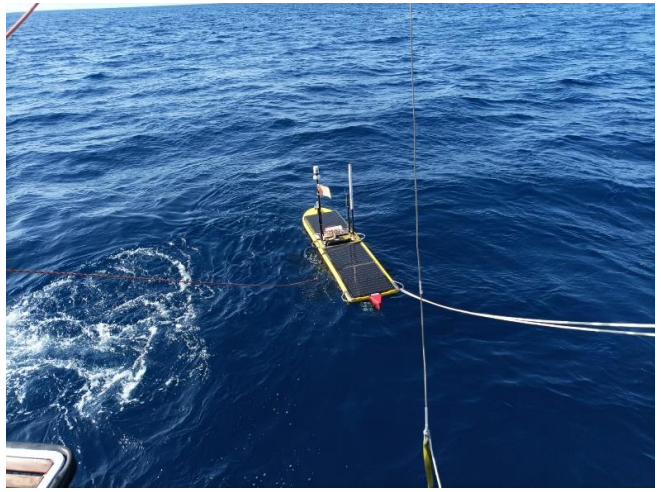
- Use standard pre-concentration membrane on fiber without the water repelant condition (PDMS+Crypt).
- Pressure cage that encapsulate the laser and detector.

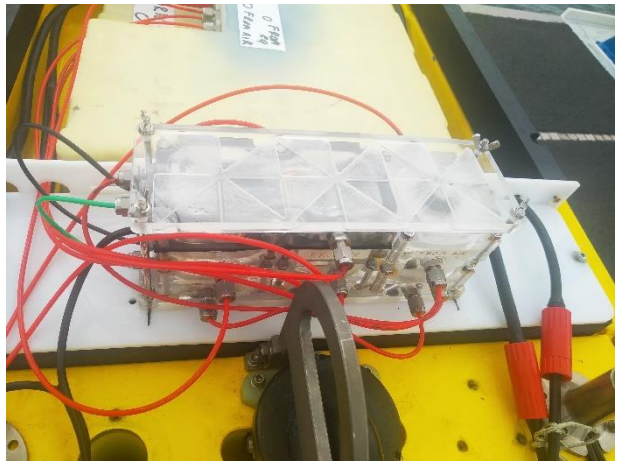


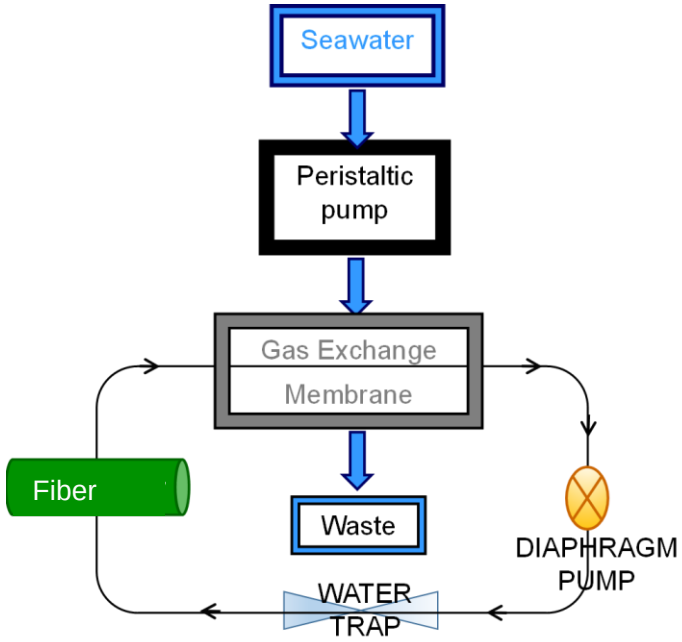


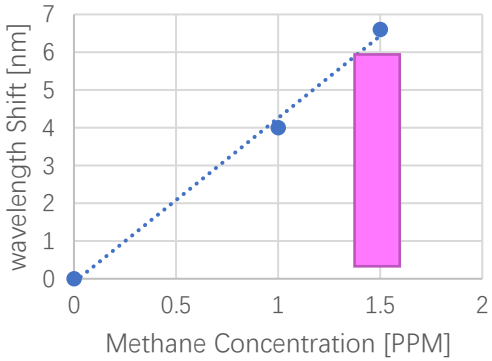


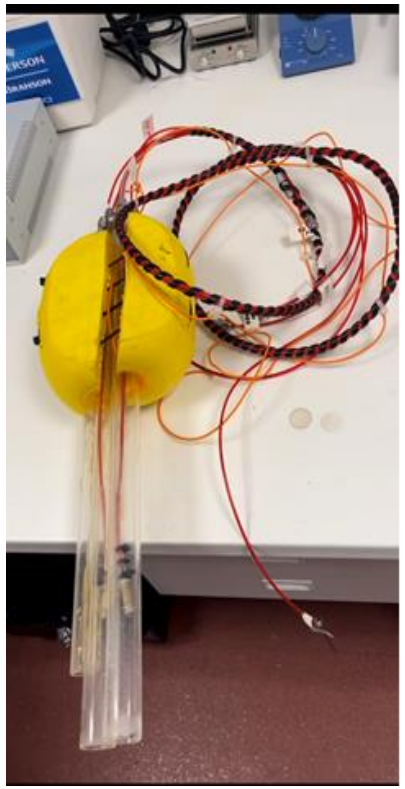
RI Sensors: surface flux trial

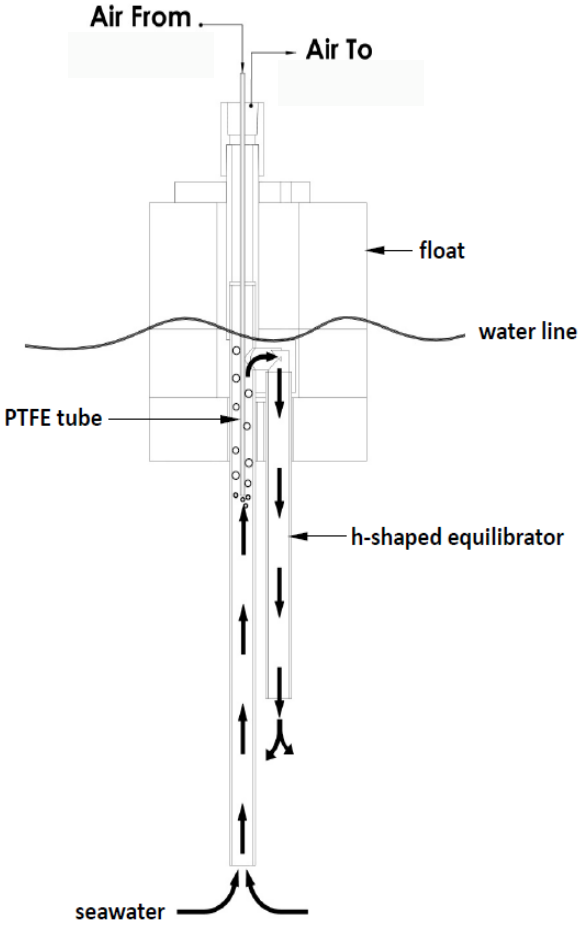




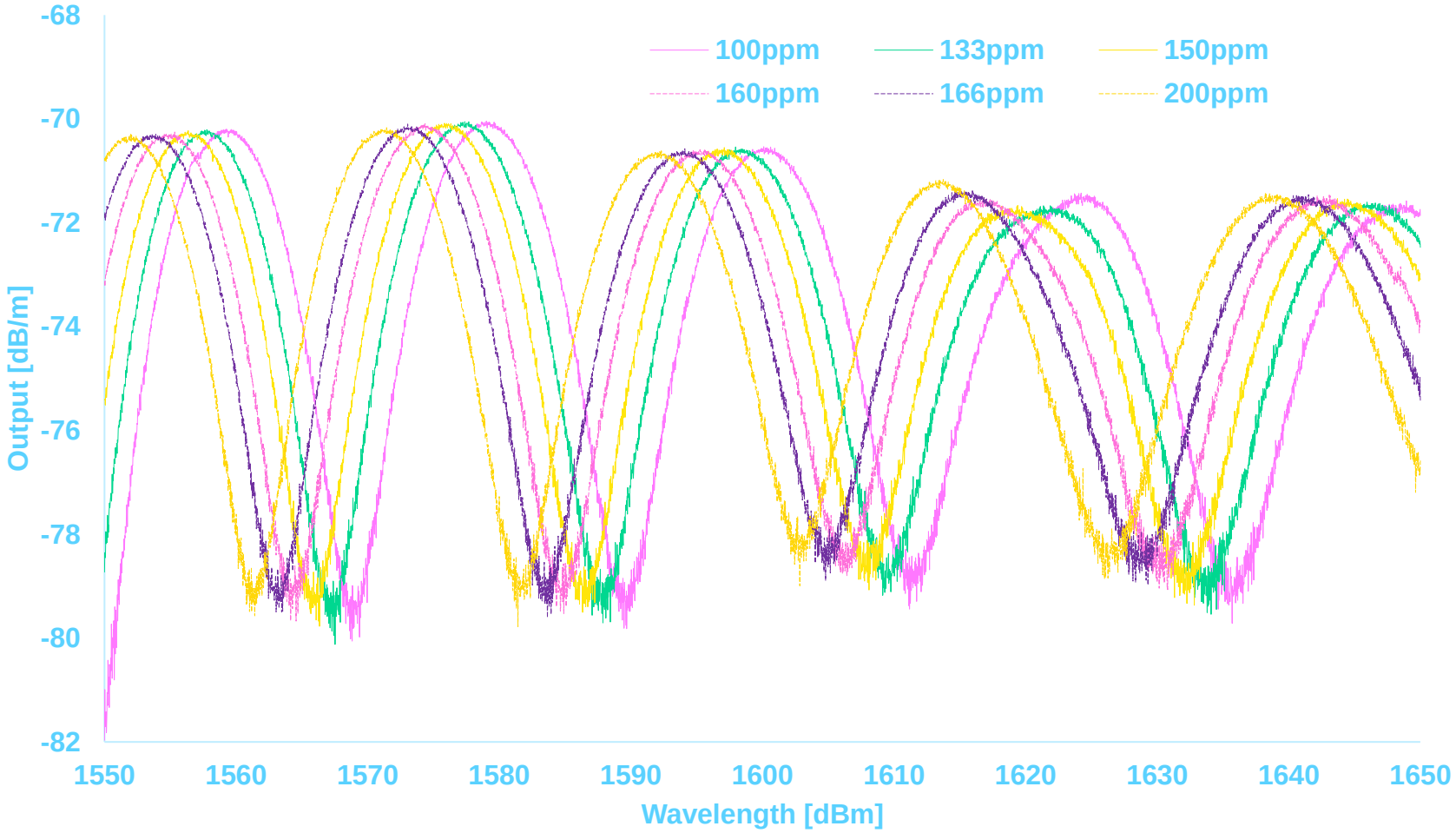




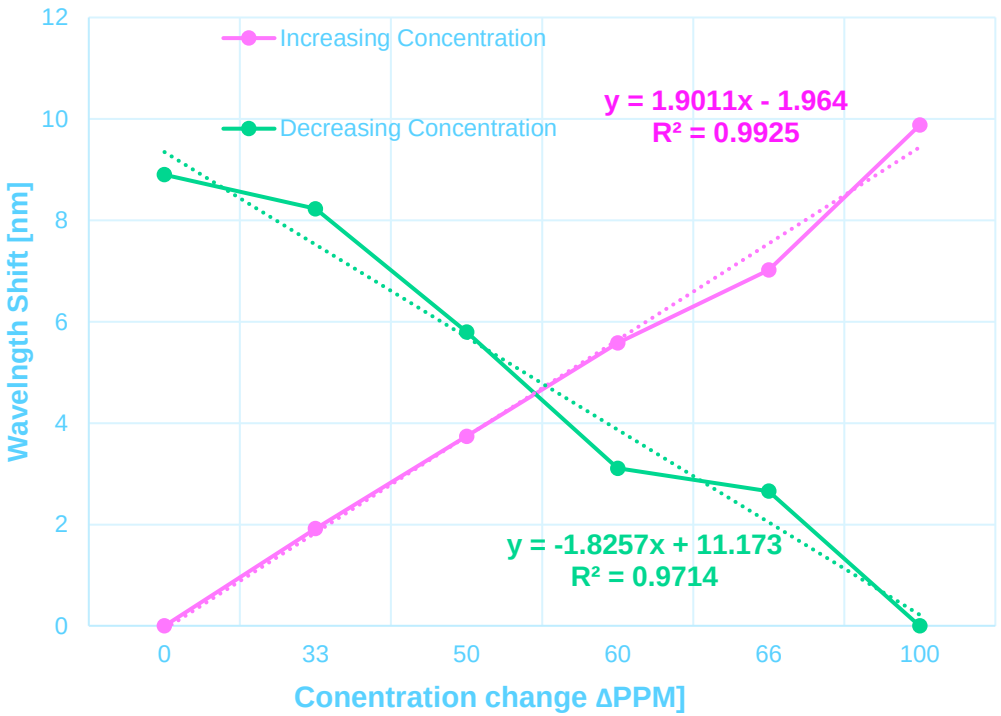


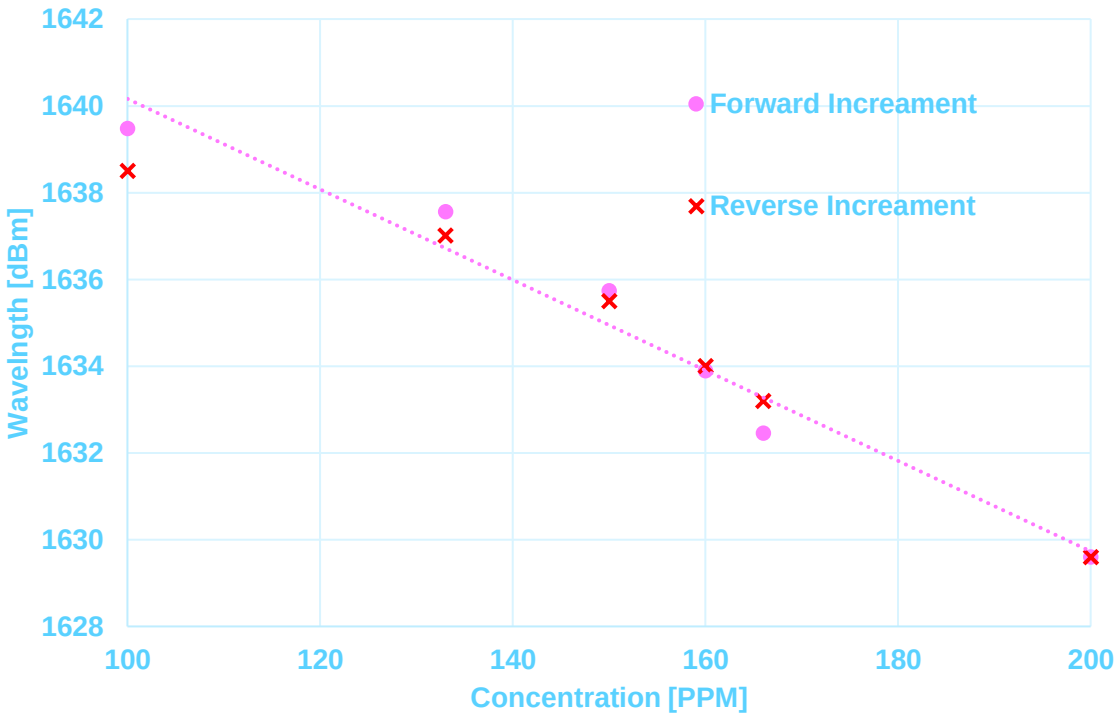


Methane sensor response

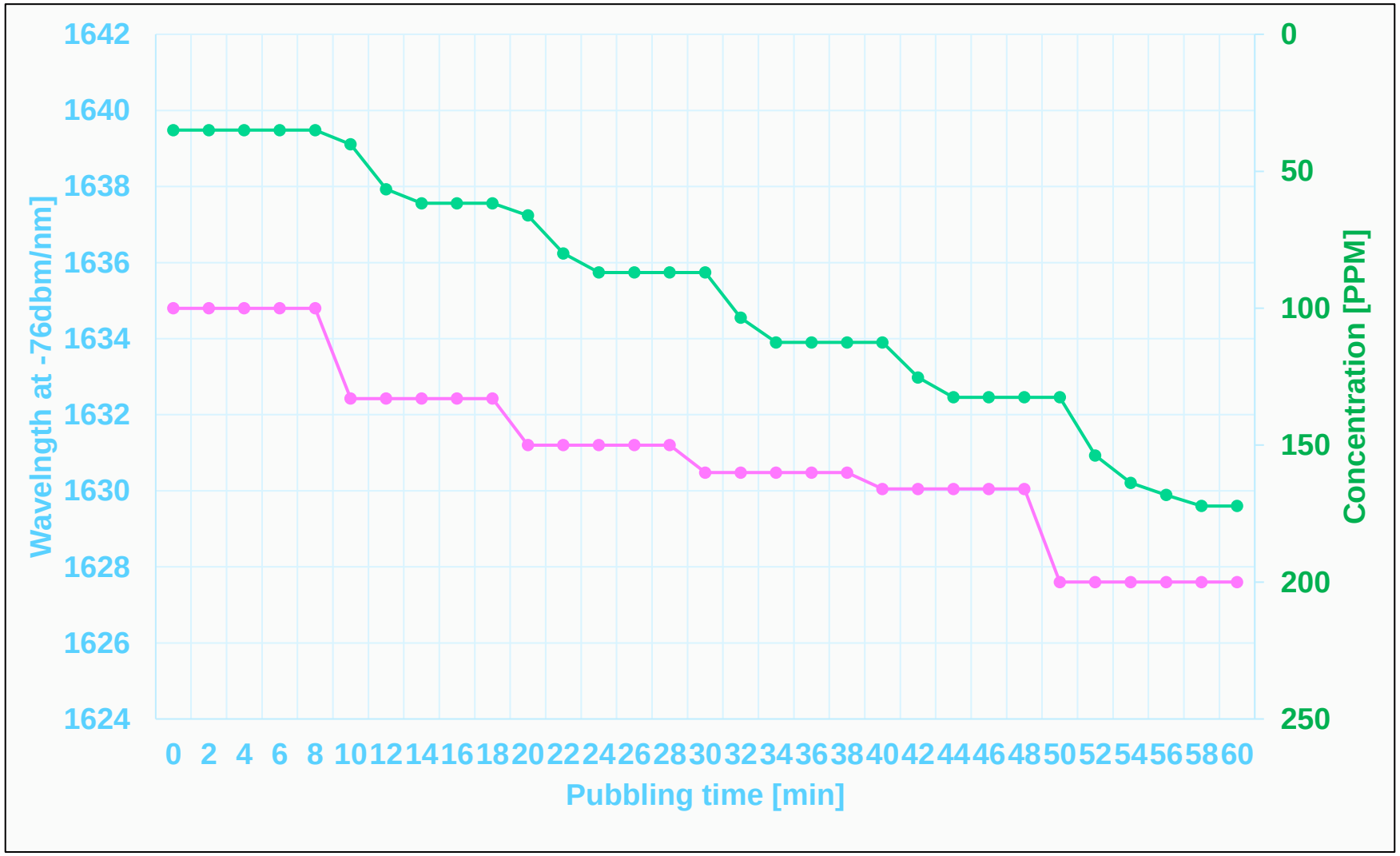


Methane sensor response





Methane sensor response



National Oceanography Centre

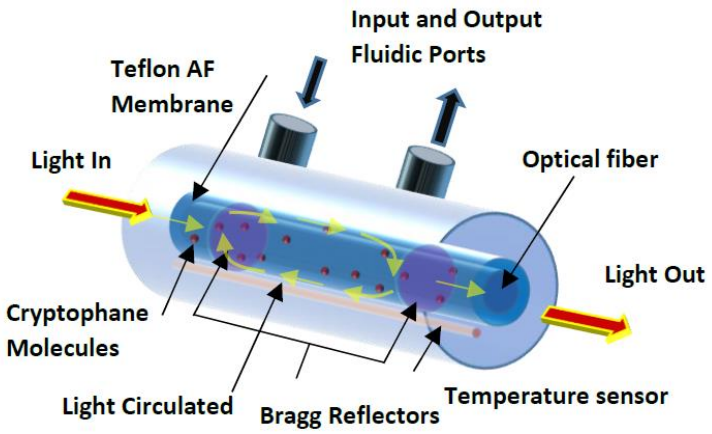
Spectroscopy sensors

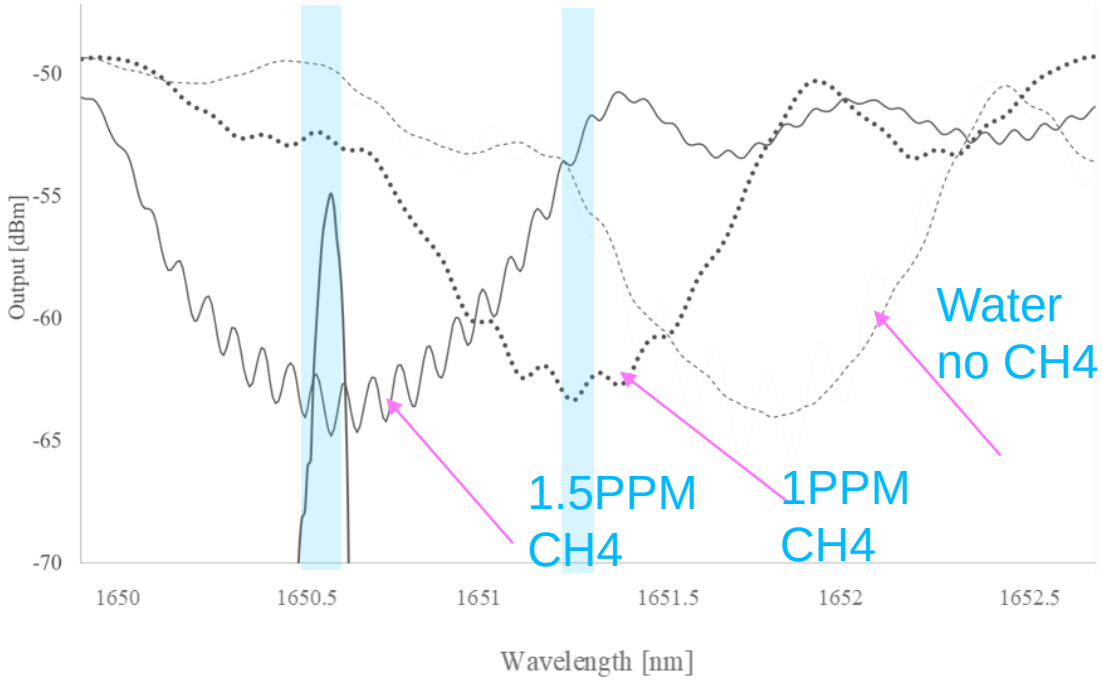
Spectroscopy Sensors:

Methods: Beer-Lamber law

- light of intensity I_0 , propagates through a solution with concentration c and length l, output light will reduce to I because of some light get absorbed by the solute molecules.
- $I = I_0^{-\alpha l} = I_0^{-c\varepsilon l} = I_0^{-c\sigma l}$
- The concentration of the target molecules can be obtained by detecting the intensity change between the input and output .

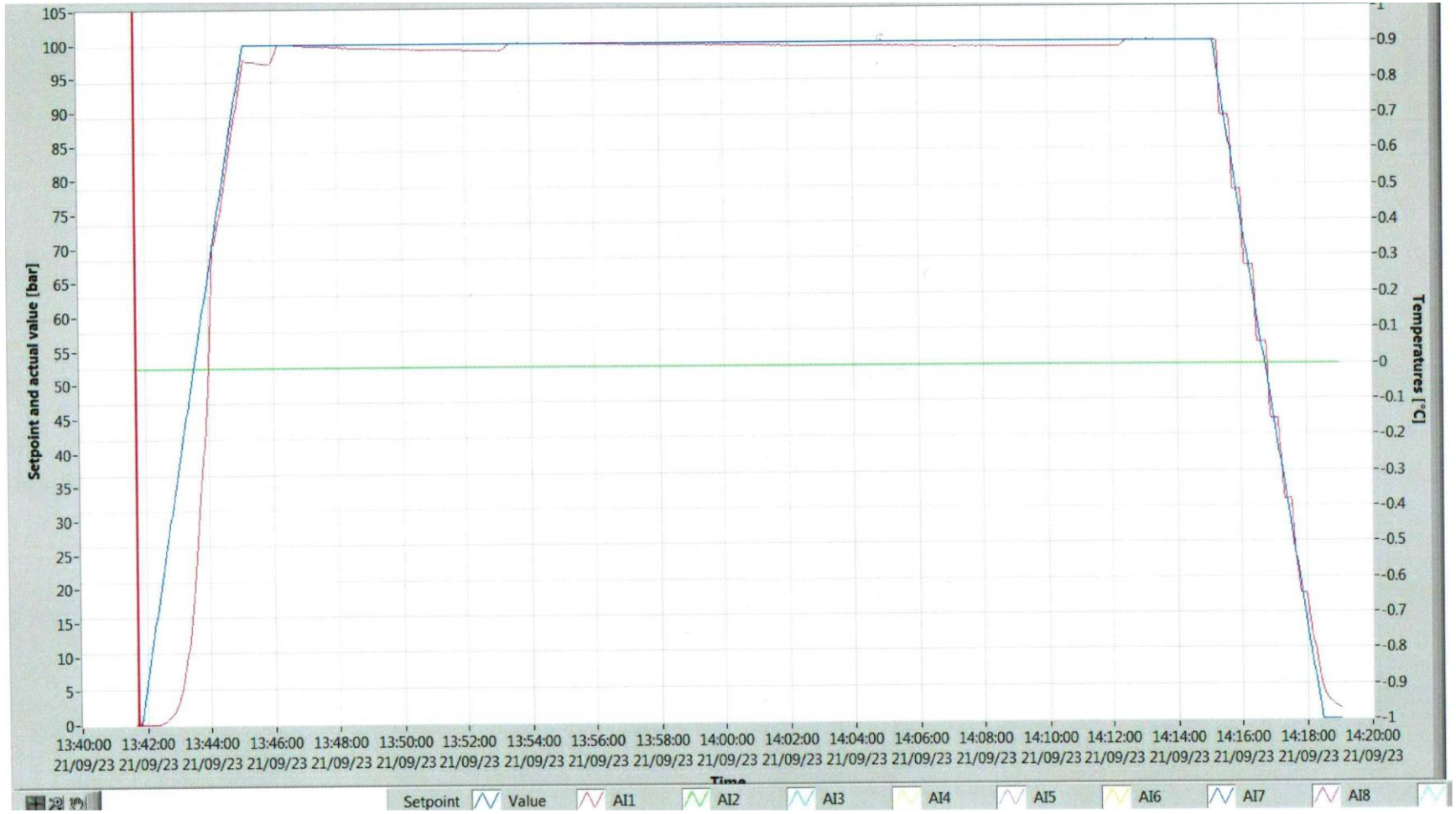
Spectroscopy Sensors:





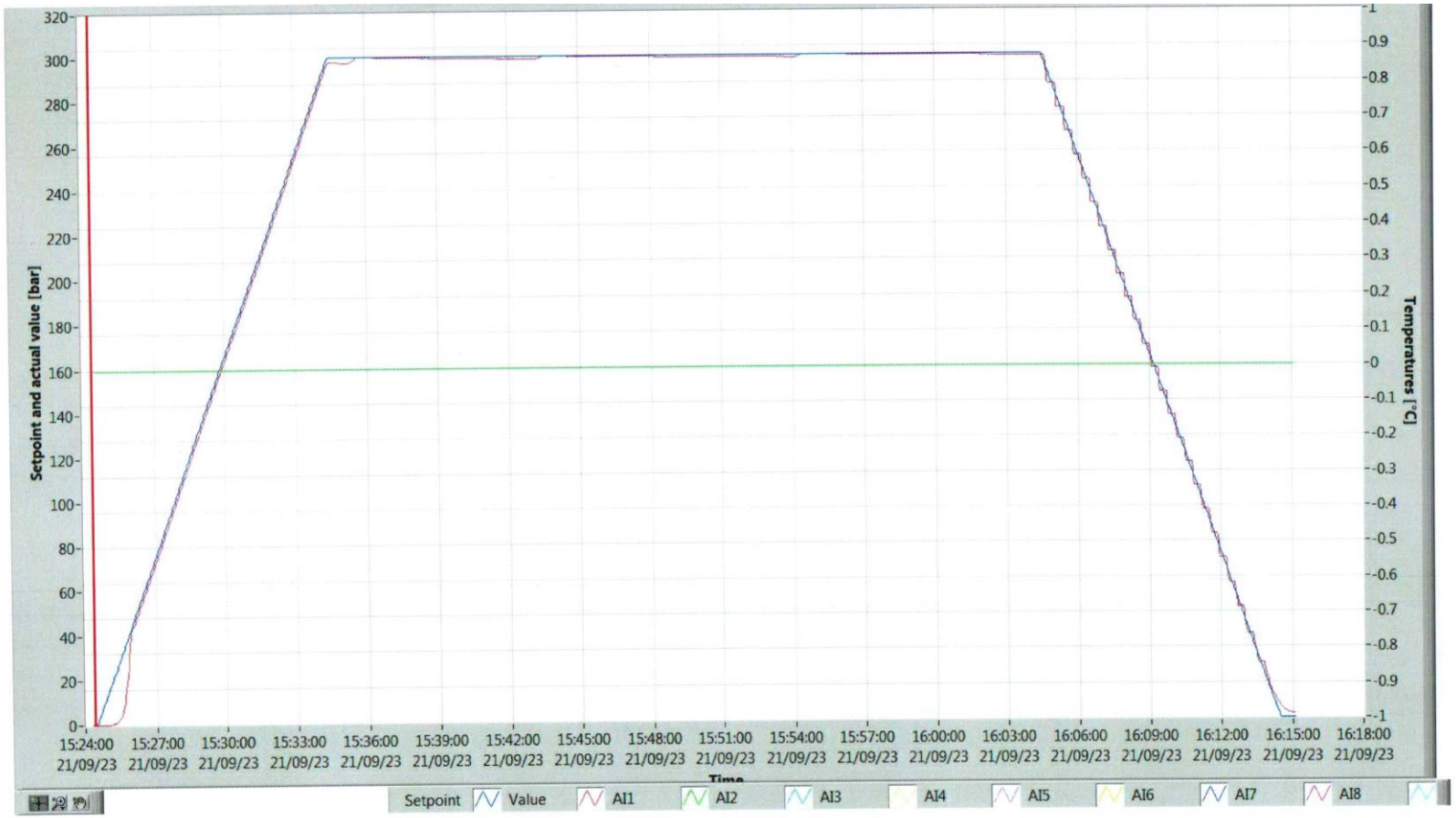
DEEP SEA DISSOLVED GAS SENSOR

3000 m
300
Bar



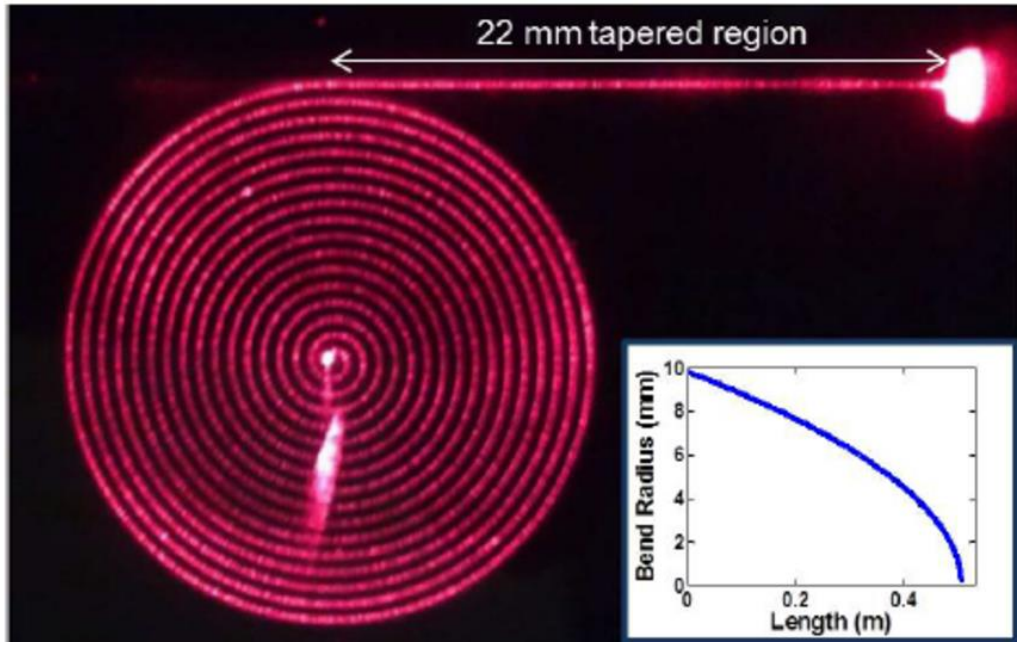
DEEP SEA DISSOLVED GAS SENSOR

6500 m
650
Bar

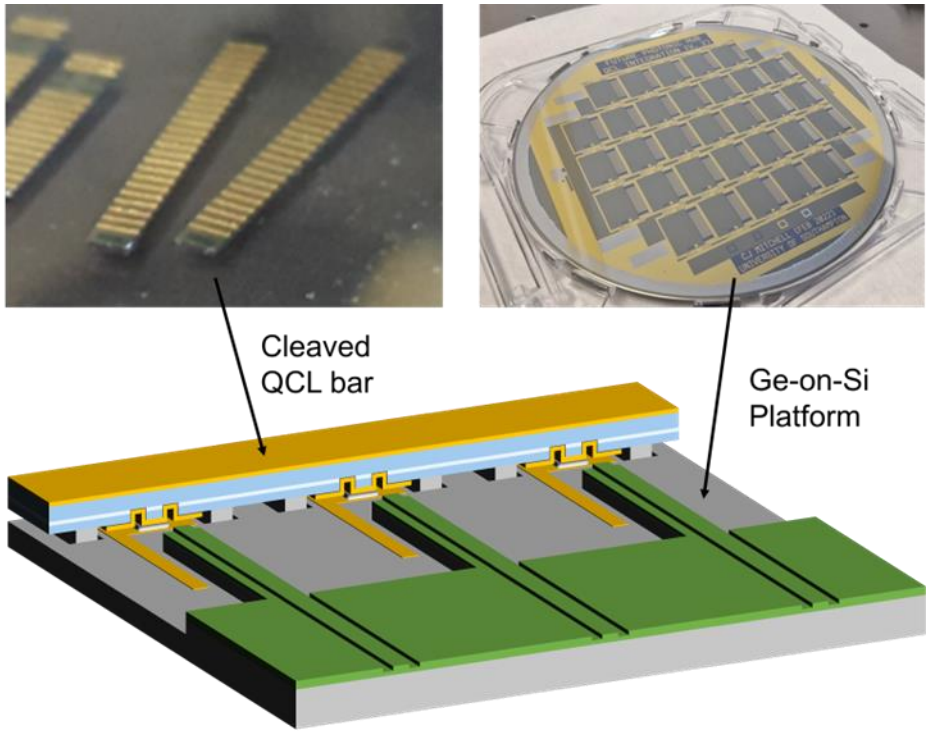


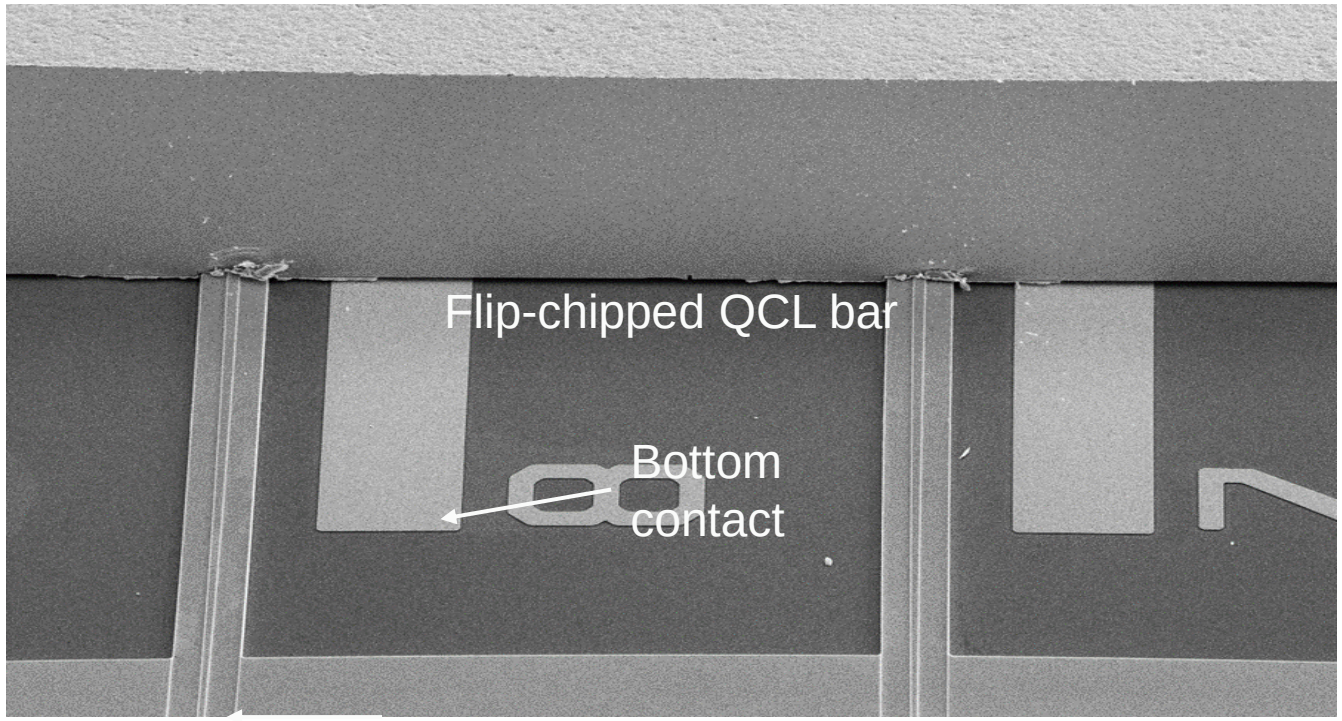
EPSRC Programme Grant investigates using Silicon photonics for ocean monitoring

- Highly repeatable and optimized manufacturing.
- Surface uniform in atomic level scale.

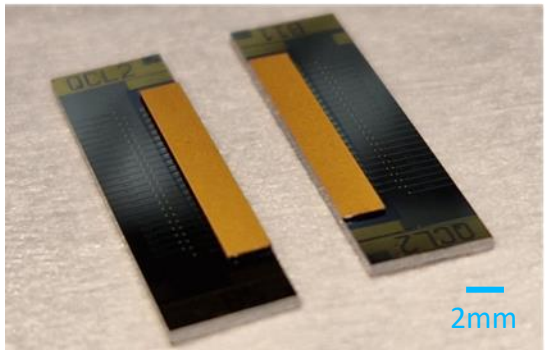


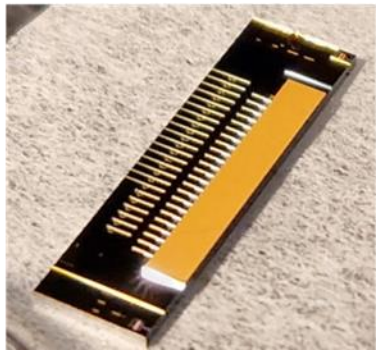
Integration Overview





Ge Waveguide



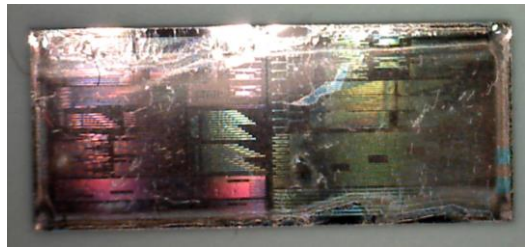


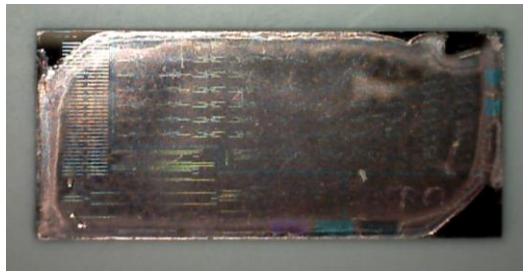
- A laser bar consisting of 24x QCLs is flip-chip bonded on silicon
- Integrated QCLs are coupled with Ge-on-Si waveguides
- Two types of waveguide are processed on the Ge-on-Si platform, i.e., edge-emitting waveguide and grating out coupler waveguide

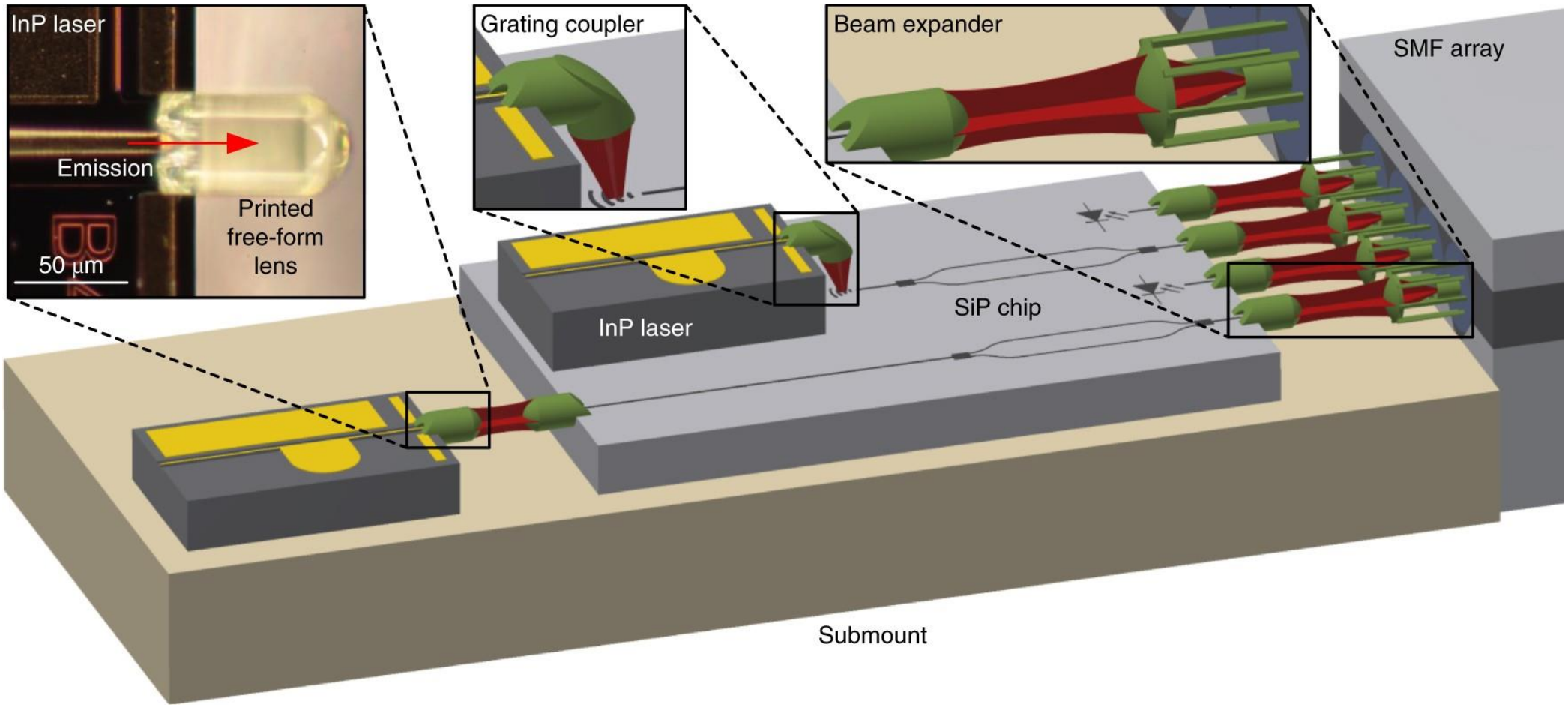
DEEP SEA DISSOLVED GAS SENSOR

Pressure testing:

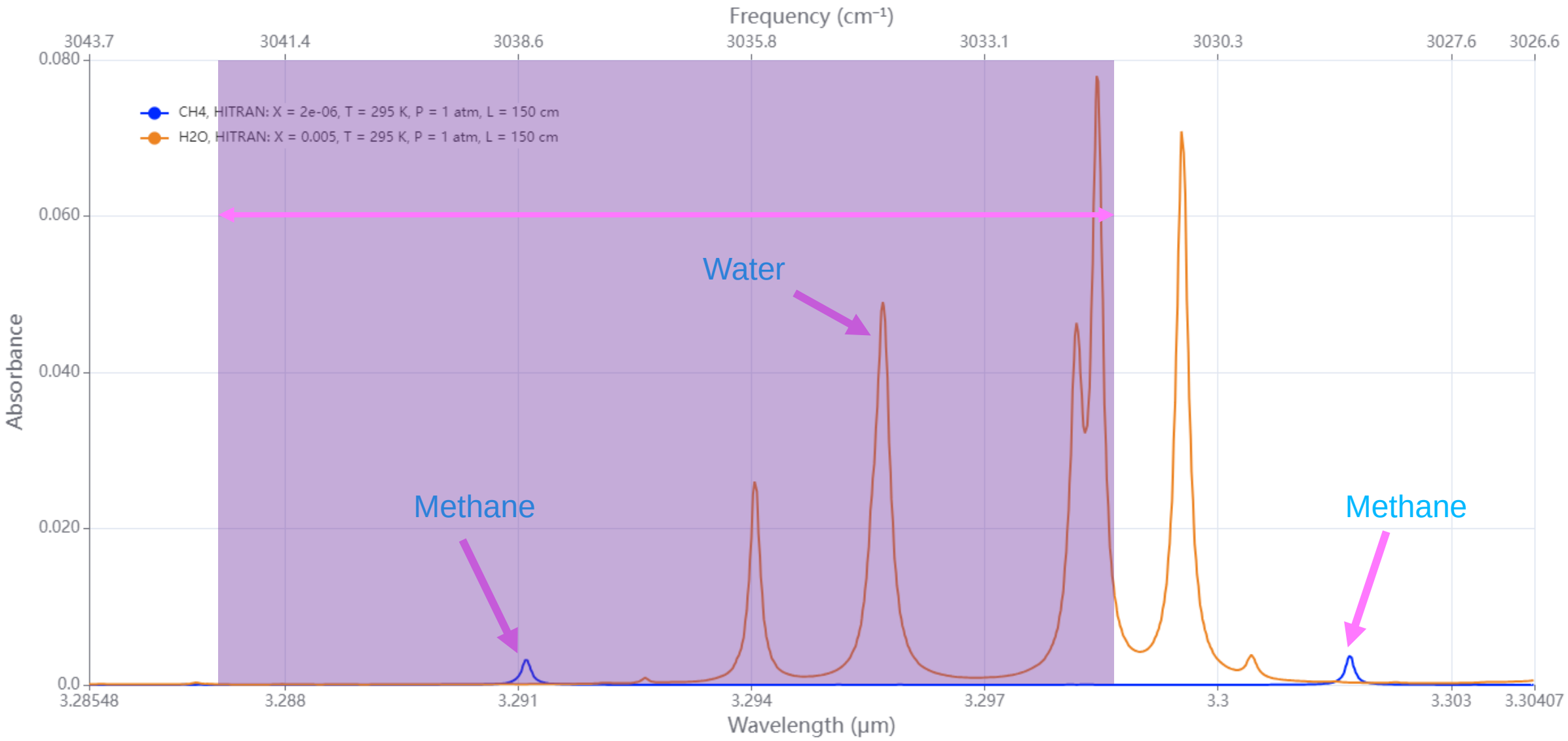
- successful trial with pressure testing (GE, SOI, suspended silicon, SiN)
- Used soft potting with permeable membrane (sensing surface) at the top and the optical glue from the bottom.



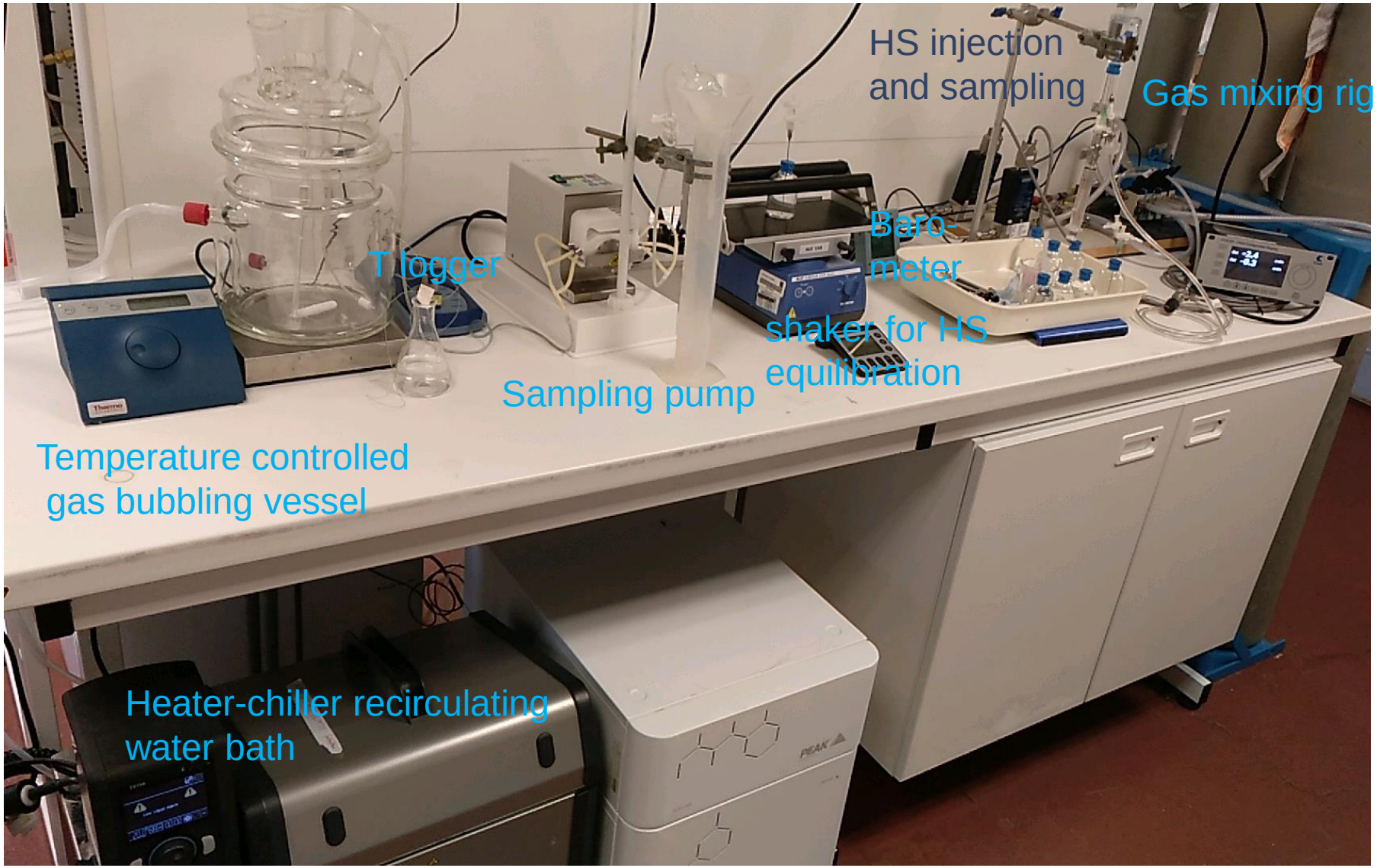



InP laser
Emission
Printed
free-form
lens
50 µm
Grating coupler
Beam expander
SMF array
InP laser
SiP chip
Submount

CALIBRATION


Frequency (cm⁻¹)
3043.7
3041.4
3038.6
3035.8
3033.1
3030.3
3027.6
3026.6
0.080
0.060
0.040
0.020
0.0
Absorbance
CH4, HITRAN: X = 2e-06, T = 295 K, P = 1 atm, L = 150 cm
H2O, HITRAN: X = 0.005, T = 295 K, P = 1 atm, L = 150 cm
Water
Methane
Methane
3.28548
3.288
3.291
3.294
3.297
3.3
3.303
3.30407
Wavelength (μm)

DISSOLVED GREENHOUSE GAS MEASUREMENTS VIA HEADSPACE (HS) GENERATION AND SAMPLING



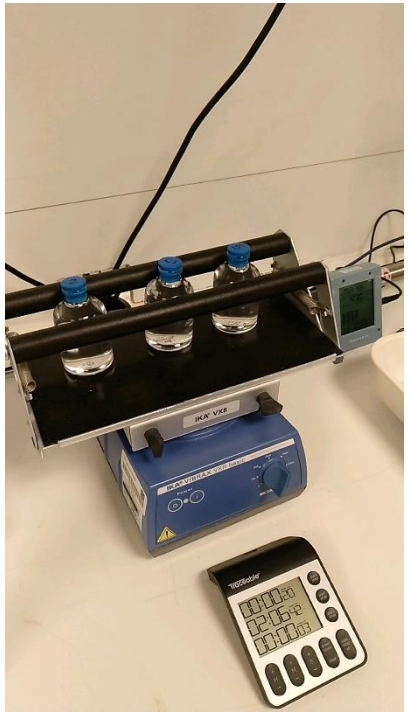
DISSOLVED GREENHOUSE GAS MEASUREMENTS VIA HEADSPACE (HS) GENERATION AND SAMPLING

Standard preparation by bubbling a set gas mix through water

Known sample volume sealed in crimped glass vials with rubber bung

HS injection of defined volume (N_2)

HS equilibration with a water sample

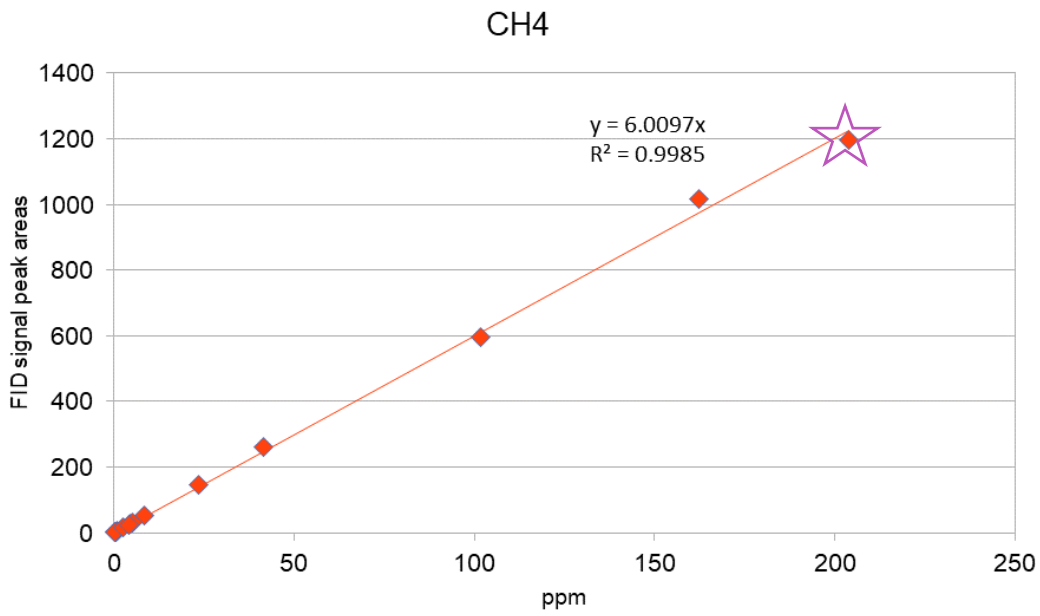


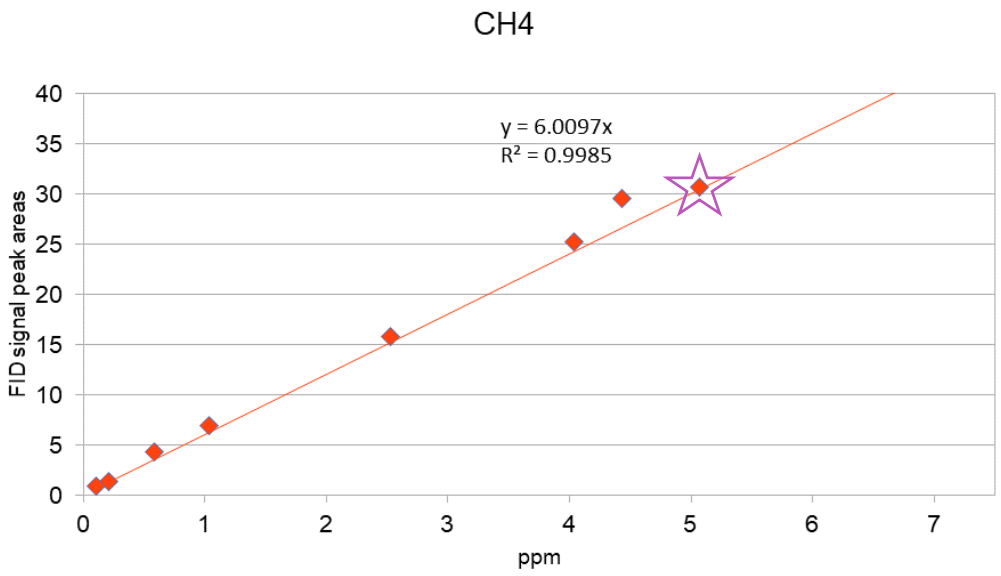
Sampling of HS with gas-tight syringe for injection into GC

HS equilibration with water sample

This procedure needs many (tricky) handling steps for each sample and many parameters monitored (time, T, p, V,)

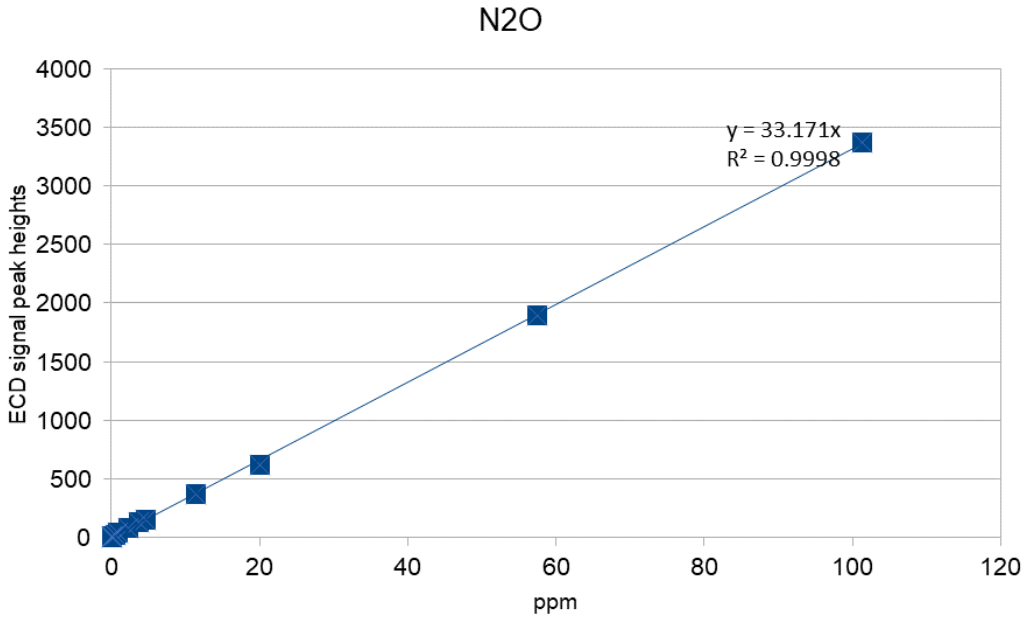
CALIBRATION OF GC FOR METHANE (ATMOSPHERIC ~2 PPM)

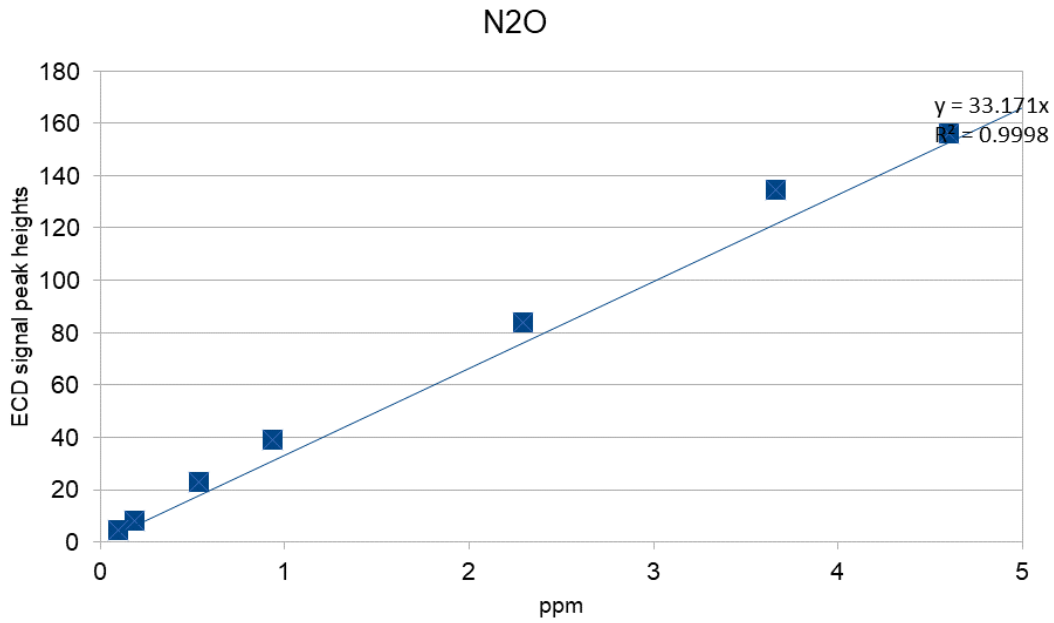




Complete range of methane concentrations using 5ppm and 200ppm methane cylinder and the gas mixing rig.
All nice and linear down to 0.1ppm

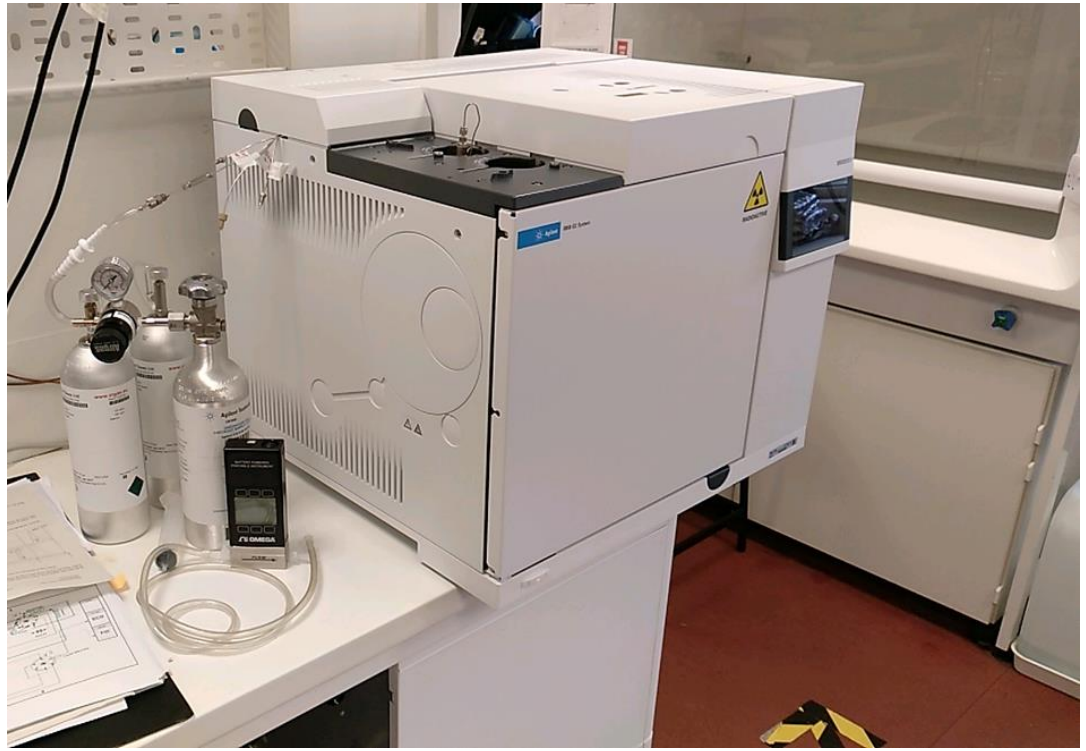
CALIBRATION OF GC FOR N_2O (ATMOSPHERIC ~0.3 PPM)



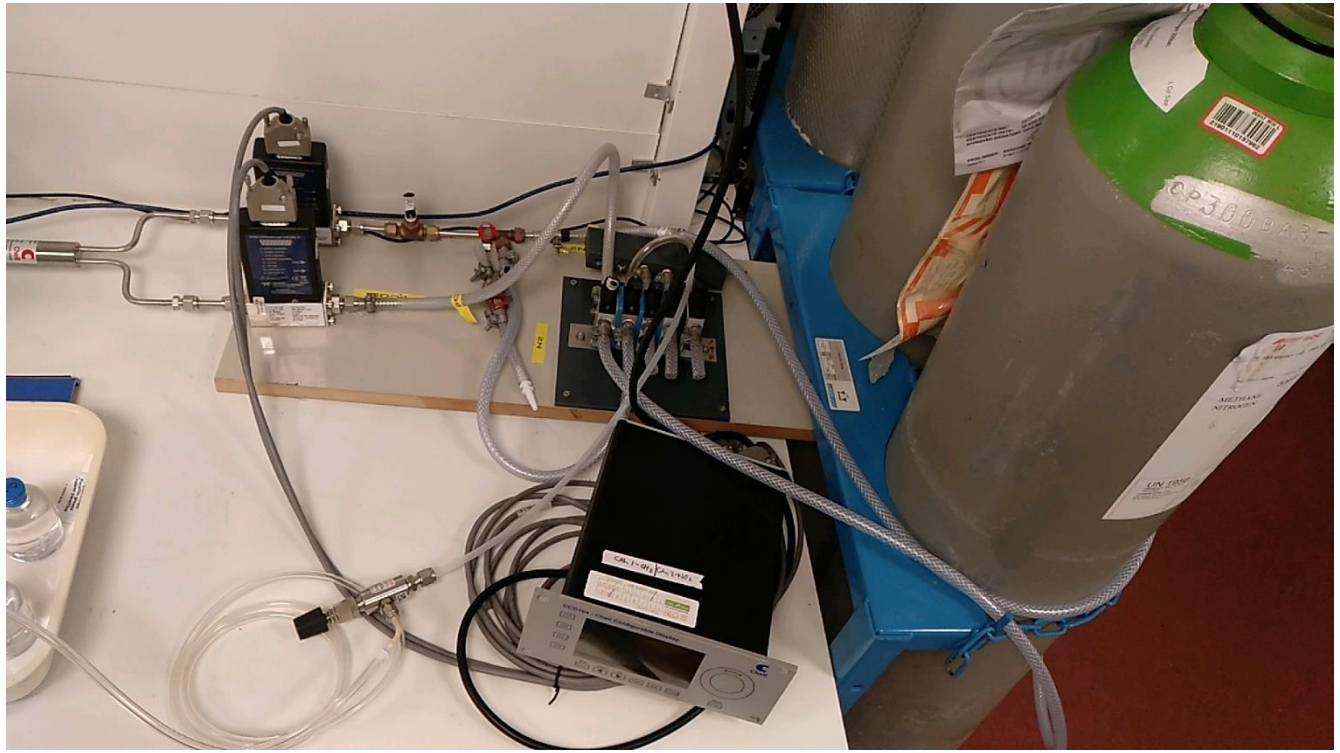


complete range of N_2O concentrations using 5ppm and 500ppm N_2O cylinder and the gas mixing rig.
LOD <0.1ppm
After months of instrument problems we will be able to **calibrate for CO_2**.

MEASURING METHANE, NITROUS OXIDE, AND CO_2 IN THE GAS PHASE



Greenhouse gas analyser (Agilent 8860 GC)



Gas mixing rig: mixer, mass flow controllers and control unit for direct injection into GC or
preparation of dissolved samples via bubbling

National Oceanography Centre

CONCLUSIONS

Photonics WILL play a vital role in ocean sensing soon.

Proof of concept demo for photonics rigidity.

Focus the fabrication on the application

What can we do to accelerate this revolution?

NERC funded technologies?

FROM TWO WORLDS

OTE NOC

Fibres and sensors ORC