



GRYF
Manufacturer of Electronic
Measuring Instruments

Physical Principles of Measurement in Aquaculture

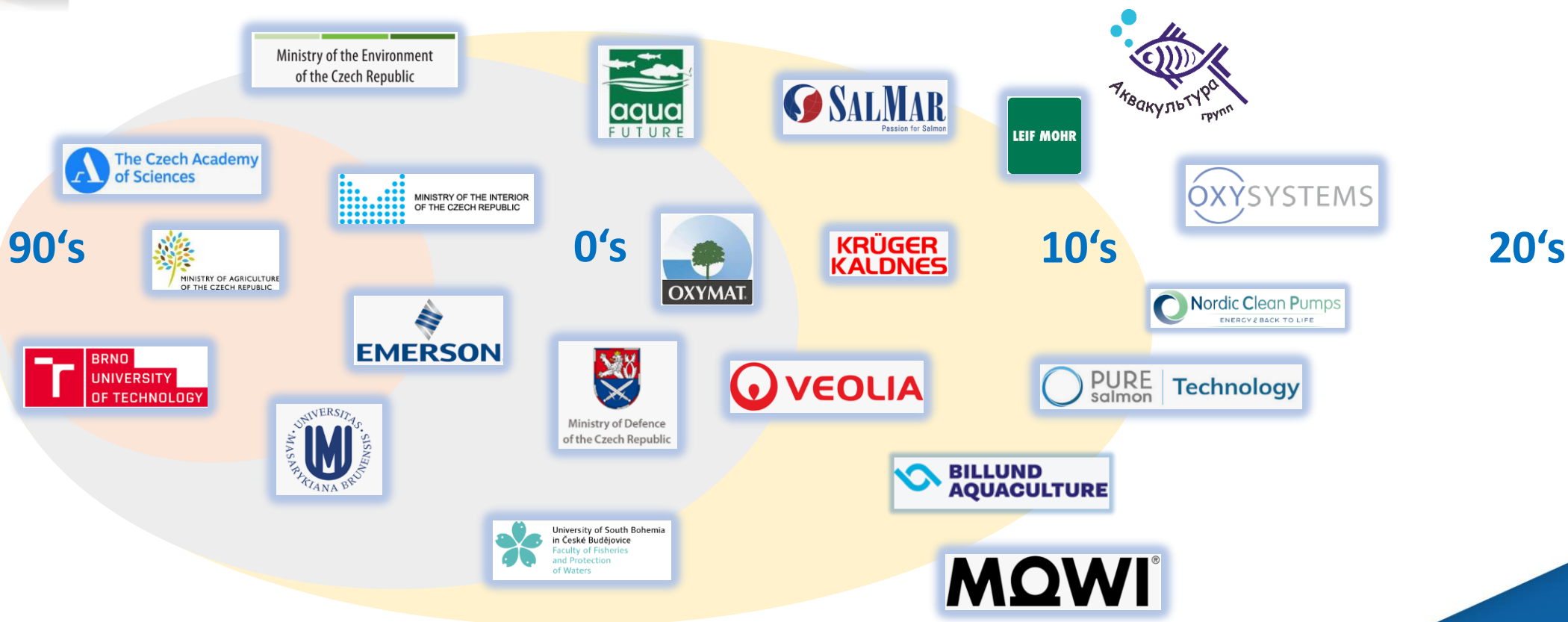
From Research to Practical Application

Introduction to GRYF R&D Department

Research in water and gas measurement since 1990



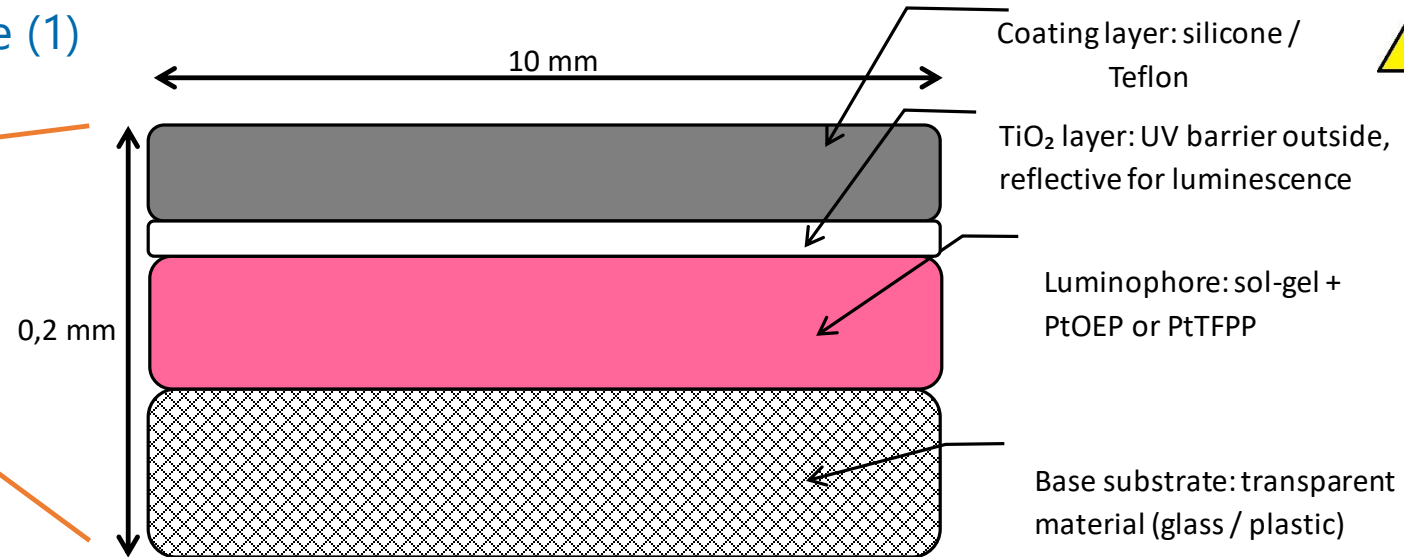
We are proud partners of all those who are not afraid to bring innovation.



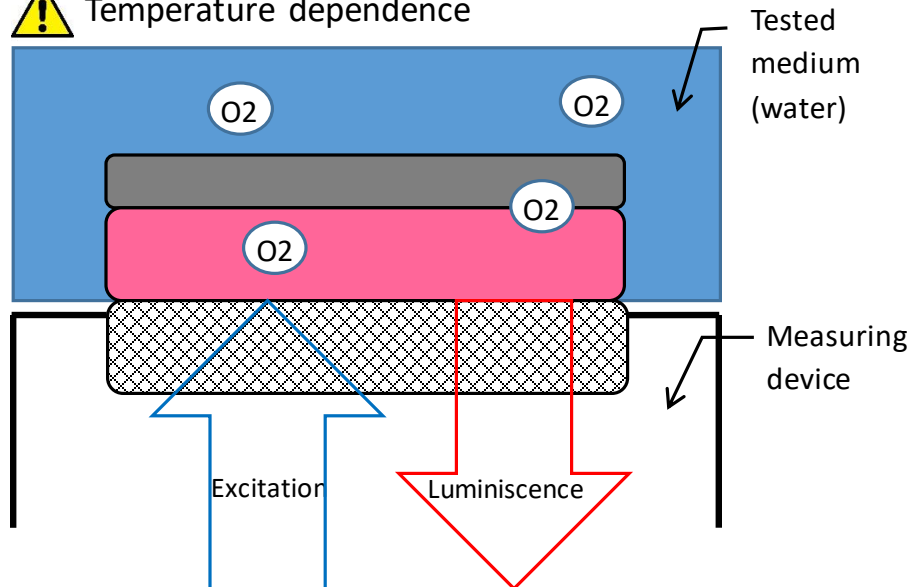
Optical Oxygen Measurement

Physical Principle (1)

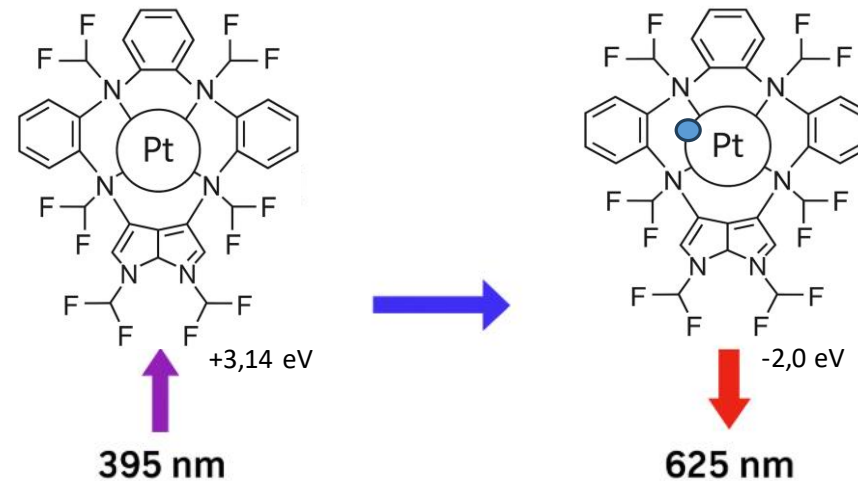
⚠ Permeability



⚠ Temperature dependence

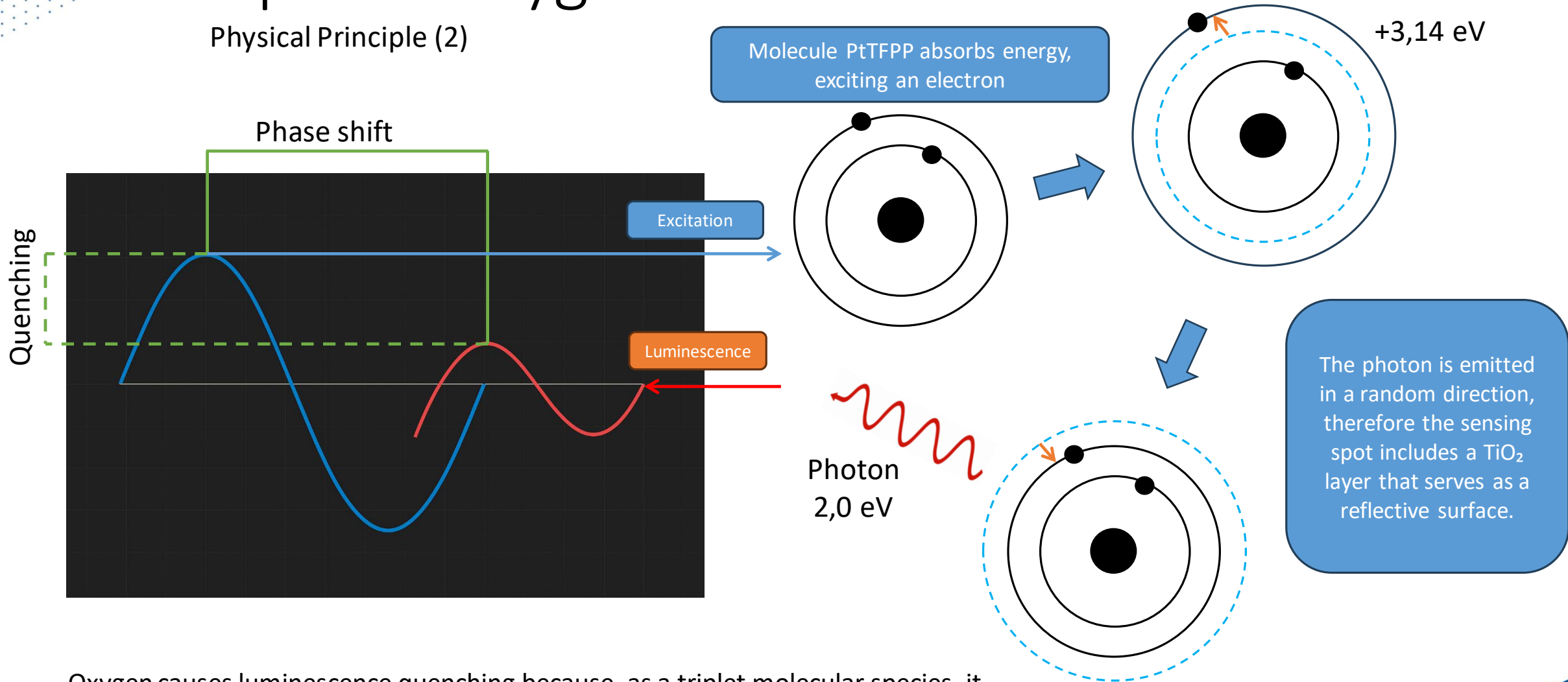


If oxygen is present, no luminescence occurs



Optical Oxygen Measurement

Physical Principle (2)



Oxygen causes luminescence quenching because, as a triplet molecular species, it absorbs energy from the triplet excited state of the luminophore through **collisional transfer**, resulting in de-excitation of the luminophore **without photon emission**.

What does the oxygen probe actually measure?

...none of what it interprets

The probe measures the level of luminescence

Through calibration, we tell it which level represents 0% and which represents 100% oxygen saturation.



The function is not linear

Everything else is a matter of software and compensation of additional influences.

Compensation and Interpretation

How do we get from luminescence measurement to the level of oxygen saturation?

- Temperature compensation:
 - The temperature sensor must be fast, accurate, and **free from the heat influence** of the probe electronics
- Salinity compensation:
 - **Dynamic compensation** must be applied primarily in **brackish waters**.
- Barometric pressure compensation:
 - Cannot be performed inside the probe – compensation must be done by the PLC with a pressure sensor.

Example: Trondheim, NO

Atmospheric pressure oscillation during the year: 970 hPa – 1045 hPa

At water temperature 10°C and salinity 35 ppt:

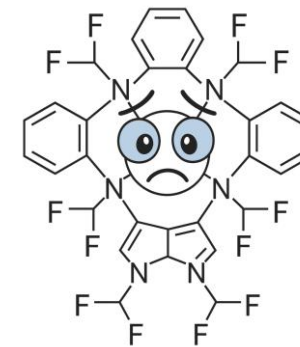
- 100% saturation at **970 hPa: 7.7 mg/L**
- 100% saturation at **1045 hPa: 8.3 mg/L**

=> **Measurement error up to 9.3%**

The probe itself is NEVER capable of providing accurate information about saturation.

Biofouling and Maintenance

What nature can do – and how to (properly) prevent it



**On the surface of the sensing spot,
the following deposits accumulate:**

- Fat from feed residues
- Bacteria and algae

these can:

- Consume oxygen
- Immobilize oxygen
- Produce oxygen

FAQ

Q: How often should the probe be cleaned?

A: It depends on the feed composition, fluid dynamics, and biological activity of the environment.

Q: How often should the probe be calibrated?

A: The more frequently the probe is cleaned, the more frequently calibration is required (because the sensing surface is gradually abraded).

If the probe surface shows signs of biofilm or oil (fat), it must be cleaned. After every 5th cleaning, calibrate 100%; after every 20th cleaning, calibrate 0% as well.

There is no probe that does not require regular cleaning and calibration

TDGP Measurement

Why is measuring TDGP in RAS just as important as measuring oxygen?



Display of GRYF IFF Nitro system

Relative abundance		
D.O2	34.1	
D.CO2	3.4	
D.N2	62.5	

Oxygen measurement can tell us that there is little oxygen. However, it does not tell us whether it makes sense to add more.

Real-time TDGP measurement (T90 < 15 min) allows us to:

- Avoid overall dangerous supersaturation
- Avoid inefficient oxygenation
- Together with O₂ and CO₂ measurement, calculate the N₂ concentration and effectively control degassing

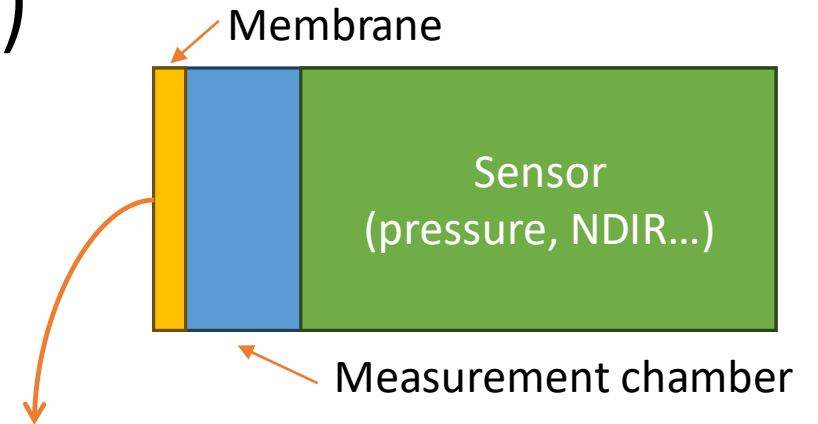
Gas	Behavior type	Risk during supersaturation	Dominant harmful mechanism
O ₂	metabolically active	>180 % → oxidative stress	toxic excess, radicals
N ₂ (and Ar)	Inert	> 105 % → GBD	physical embolism
CO ₂	Reactive, buffering	already >20–30 mg/L harmgul	acidosis, blocked CO ₂ release

Real-time TDGP measurement cannot be performed with submersible probes

The Key to TDGP (and CO₂)

Why are submersible probes unreliable?

- Rapid gas permeation means the membrane cannot be gas-selective – it also allows water vapor to pass through.
- If water vapor penetrates the membrane, it condenses in the measuring chamber. Heating slows down this process but does not stop it.
- Without drying (regeneration) of the chamber, its lifetime is limited.
- Regeneration cannot be performed in a submersible probe.



Gas	Silicone (Barrer)	Teflon (Barrer)	Microporous Polypropylene (Barrer)
O ₂	600 – 800	0.02 – 0.04	1 – 3
CO ₂	3000 – 4000	0.1 – 0.2	5 – 10
N ₂	200 – 400	0.01 – 0.02	0.5 – 1
Water vapor (H ₂ O)	15,000 – 30,000	1 – 10	1 – 3

“Achilles’ heel” of
measuring chambers.

1 Barrer means that through a material with an area of 1 cm² and thickness 1 cm, 10⁻¹⁰ cm³ of gas passes per second (under standard conditions and with a pressure difference of 1.3 hPa between both sides).

The key is not a selectively permeable membrane, but the regeneration of the measuring chamber

Gas Permeation Through Membranes

Theory and Reality

Molecule	Kinetic diameter (pm)	% H ₂ O	Note
H ₂	289 pm	107%	very small, extremely fast diffusion
H ₂ O	270 pm	100%	polar, strongly interacts with material
O ₂	346 pm	128%	reference for most gas membranes
N ₂	364 pm	135%	slightly larger than O ₂
CO ₂	330 pm	122%	linear, but effective diameter smaller than N ₂
Ar	340 pm	126%	inert, similar to O ₂

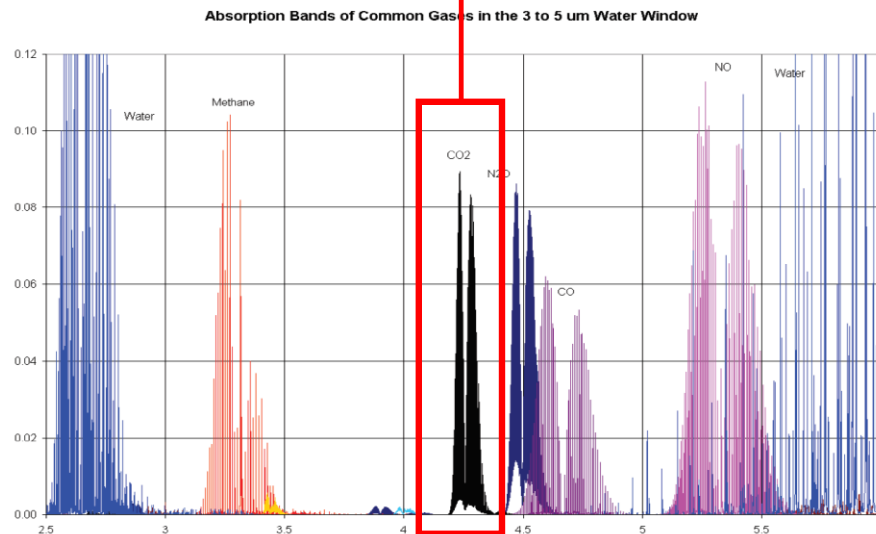
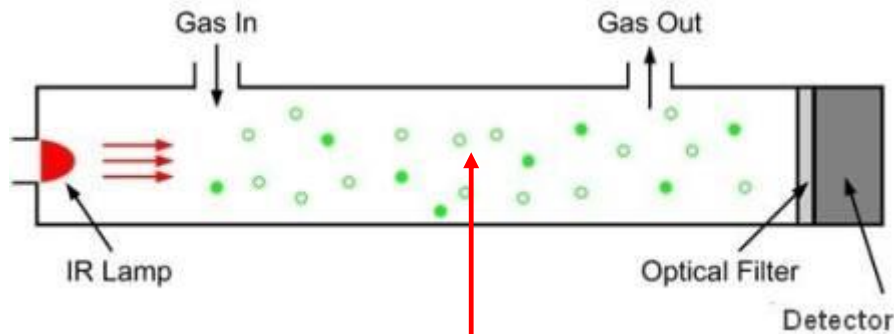
he kinetic diameter does not determine **how large** the molecule is, but **how large the “space around it” effectively becomes during movement** due to its intermolecular interactions.

Because of its polarity, H₂O can penetrate narrower pores, whereas H₂—although smaller—encounters a stronger repulsive barrier and thus *behaves as if it were larger*.

Reality: H₂O passes through the membrane more easily due to its polarity than any other gas, including hydrogen.

CO₂ Measurement

NDIR (Non-Dispersive Infrared) Sensors



Physical Principle

Light with a wavelength of $4.26 \mu\text{m}$ (± 0.05 – $0.10 \mu\text{m}$) cannot bypass a CO₂ molecule – it is absorbed by it.

Because this wavelength is specific to CO₂ (unlike many other gases), it is used for (very precise) measurements, not only in aquaculture.

As with TDGP, the principle is simple. In practice, however, the issue is “flooding” of the sensor/chamber with water, and therefore submersible probes are unsuitable for continuous measurement.

Nitrogen and Argon (hereinafter referred to as Nitrogen)

Inert and Deadly

- Both gases are very difficult to measure.
- From the perspective of their relevance to aquaculture, it makes little sense to separate them; therefore, when we speak of nitrogen, we generally mean both gases.
- Nitrogen is important because it is a product of ammonia conversion in biofilters and significantly contributes to TDG.
- Its concentration is described by the following equation:

$$p_{N_2+Ar} = \text{TDG}_{\text{wet}} - p_{O_2} - p_{CO_2} - p_{H_2O}(T)$$

The outlet water from the biofilter is *poor in oxygen* but contains a large amount of free nitrogen (N₂), which is often in supersaturation.

Before effective oxygenation can begin, nitrogen must be removed.

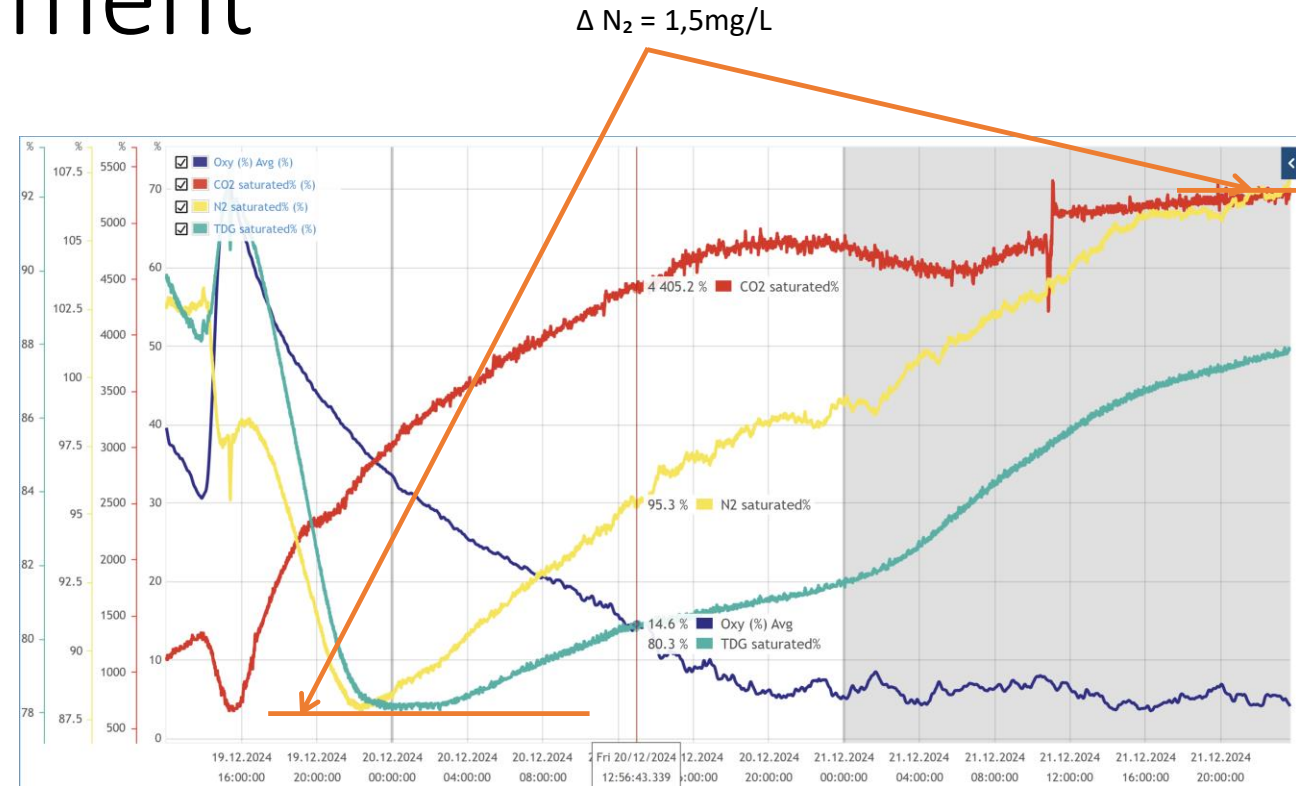
The energy consumption of degassing systems represents approximately **10% of the total operating costs** of an intensive RAS system.

Are the costs of degassing empirically confirmed—and the equation as well?

„Christmas Experiment“

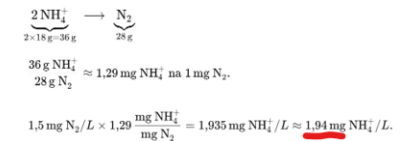
Biology Has the Final Word

- **19 December 2024:** As part of the IFF Nitro pilot operation at the MOWI Hellur farm, we locked the system with biologically active water to test the accuracy of the N₂ concentration calculation.
- After **60 hours**, the O₂ concentration dropped to nearly zero, while the calculated difference in N₂ reached **1.5 mg/L**, where it stabilized.
- For verification, we used **stoichiometric equations** to back-calculate the probable initial ammonia content.
- The calculated ammonia value was **1.94 mg/L NH₄⁺**.
- The difference between the calculated and measured values was 6%.



Customer confirmation

The monitored system was operating at peak performance, just before fish transfer. The biofilter was running at its limit; independent measurement determined **1.83 mg/L NH₄⁺**.



Conclusion of the Experiment

With results verified under laboratory conditions

- The ammonia experiment was repeated under laboratory conditions. It was found that the 6% deviation was caused by the fact that the **presence of ammonia was not considered** in the calculation of N₂ from TDGP, O₂, and CO₂.
- If ammonia had been correctly included in the calculation, the calculated nitrogen value would have been lower — and the subsequent ammonia concentration would have differed from the measured value **by less than 1%**.
- **It can therefore be concluded that:**
 - Nitrogen measurement (by calculation) can be introduced into the routine practice of fish farms.
 - TDGP and CO₂ measurements are valid and capable of continuous operation with the modified equation:

$$p_{\text{N}_2+\text{Ar}} = \text{TDG}_{\text{wet}} - p_{\text{O}_2} - p_{\text{CO}_2} \boxed{- p_{\text{NH}_3}} - p_{\text{H}_2\text{O}}(T)$$

The experiment helped correct a long-standing equation, but most importantly proved the accuracy of both measurement and calculation.



End of Presentation

Thank you for your attention