SEA BEAR
Diving Technology

O2 Sensor Technology for Rebreathers

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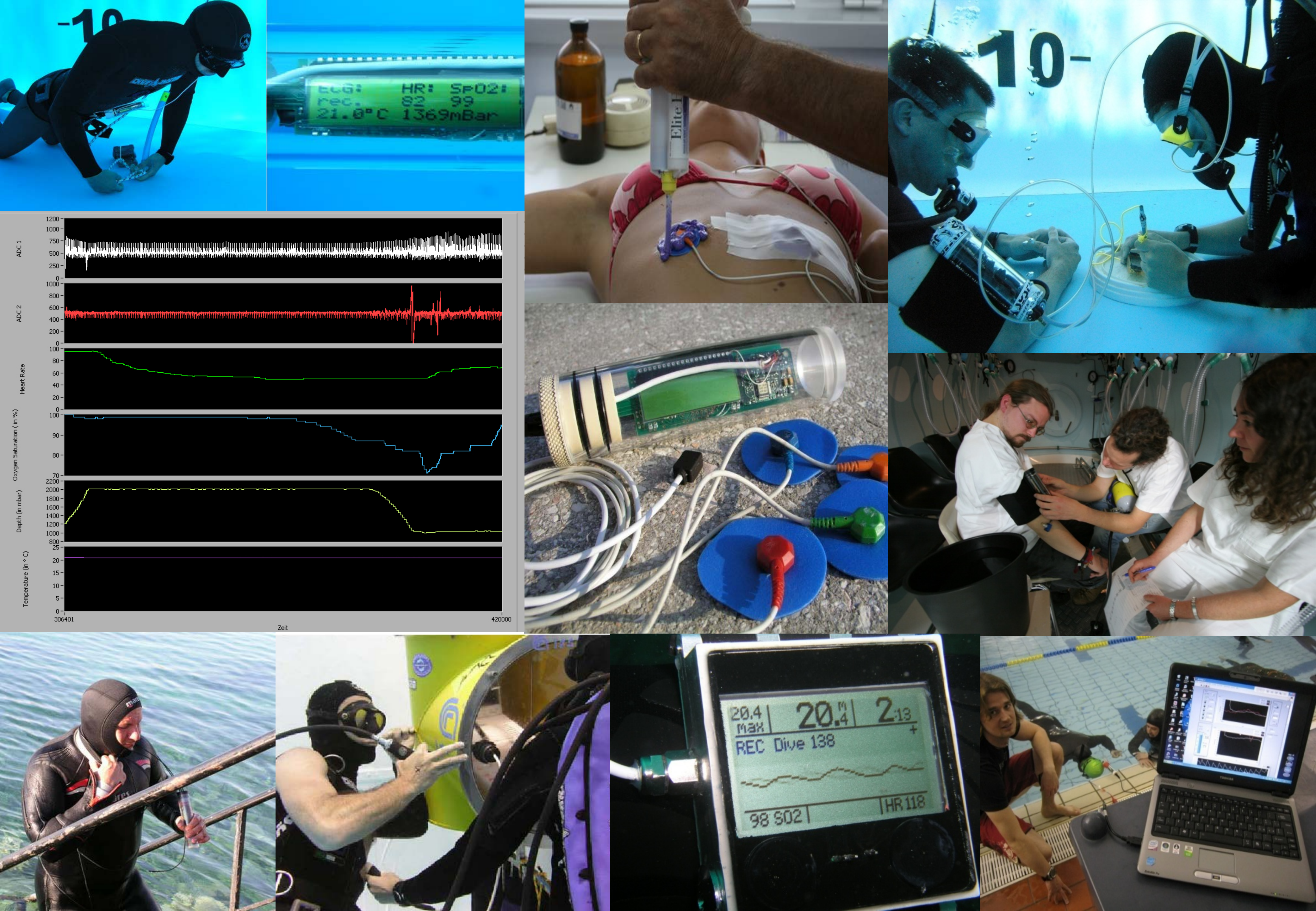
IMEGO
Solutions beyond sensors


Quechua



-10
ECG: HR: SpO2:
rec. 82 99
21.0°C 1369mBar
Elite
10-
ADC 1
ADC 2
Heart Rate
Oxygen Saturation (in %)
Depth (in mbar)
Temperature (in ° C)
306401
420000
Zeit
20.4 max
20.4 M
2:13
REC Dive 138
98 SO2
HR 118

Outline

- **Sensors in rebreathers**
  - Understanding O2 sensors
  - Failure modes
  - Validation versus voting
- **Electronics used in rebreathers**
  - CE Certification
  - Liability
- **The future: Research in sensor technology**
  - Smart galvanic O2 sensor
  - Galvanic O2 sensor alternatives
  - Optical sensors
  - Solid state sensors

Rebreathers

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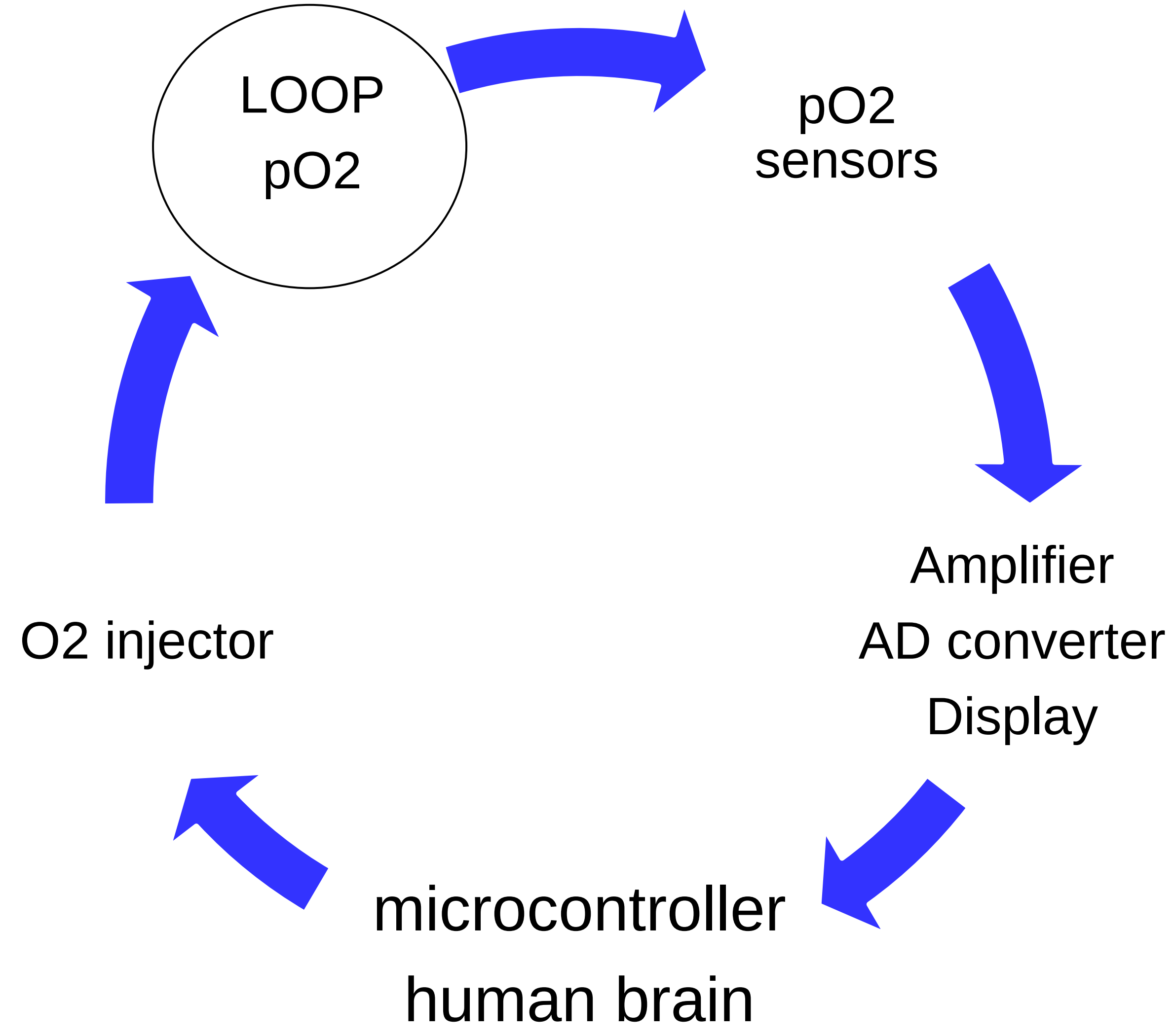
- **Closed Circuit (long autonomy, stealth, warm breathing gas,..)**
- **Small lightweight systems can be designed**
- **O2 is added either manually (MCCR) or automatically with a microcontroller and a solenoid**
- **<u>One main problem: gas sensing</u>**

Rebreather pO2 control



Sensor R&D for Medical Devices

- **Do not abuse the sensor**
- **Calibrate the sensor under similar conditions as during measurement**
- **Calibrate in the measurement range**
- **Multiple point calibration**
- **Same temperature**

pO2 sensors in diving

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- **We use pO2 sensors in harsh conditions**
- **We abuse the sensors (shocks, high temperature, high pressure, ….. all outside of the sensor specifications)**
- **We calibrate the sensor at 0.2 – 1 bar at ambient temperature**
- **BUT we use the sensor up to 1.6 bar AND temperatures up to 50°C**

Take Home Message 1

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Rebreather divers use sensors outside the manufacturers specifications

Do not blame the sensor manufacturers for sensor cell failures

Rebreather market is small in comparison to medical market – burden of liability forces sensor manufacturers not to sell to rebreather industry

Understanding pO2 Sensors

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Galvanic pO2 Sensor

- **standard in diving**
- **the anode material (typical Pb is oxidized) -> limited lifetime**

Cathode reaction:

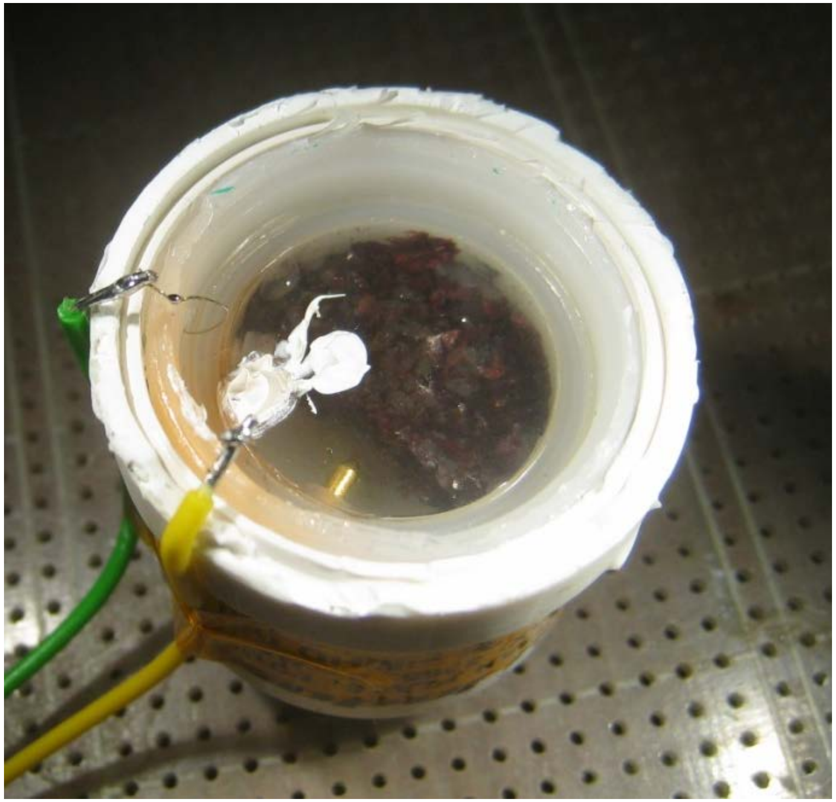
$$O_2 + 2H_2O + 4e^- \Leftrightarrow 4OH^-$$

Anode reaction:

$$2Pb + 4OH^- \Leftrightarrow 2PbO + 2H_2O + 4e^-$$

Overall cell reaction:

$$2Pb + O_2 \Rightarrow 2PbO_2$$



Take Home Message 2

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Rebreather design:

Avoid any differential pressure between sensor membrane and backside

Diffusion limited sensor

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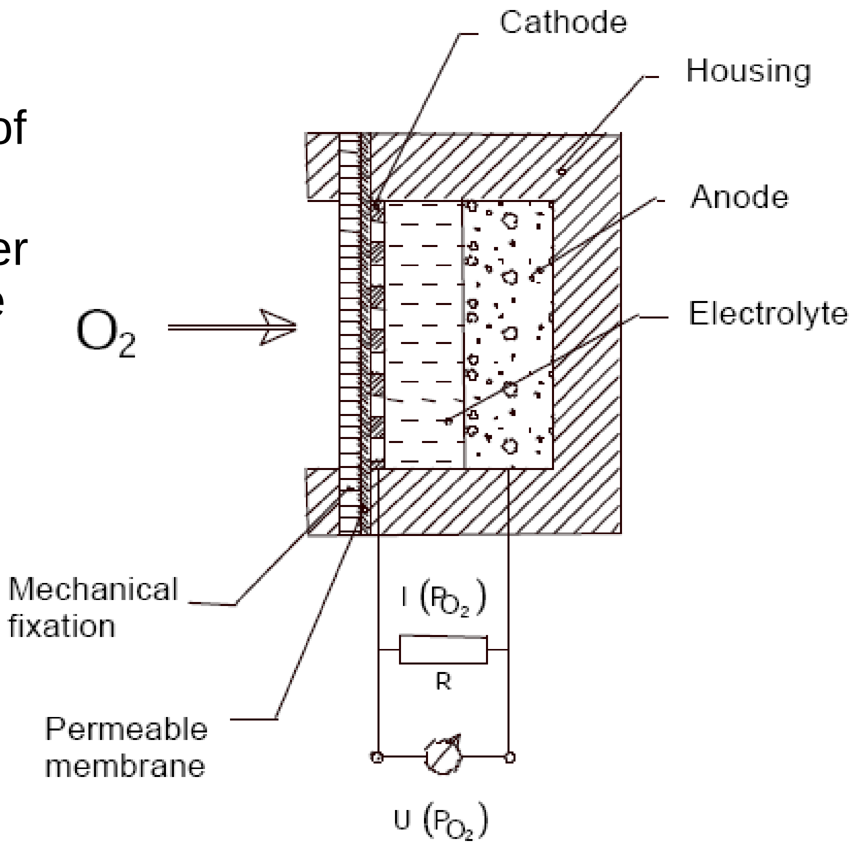
- **Electrochemical reaction is non linear**
- **Trick:**
  - Diffusion barrier/layer / membrane layer in front of the cathode
  - O_2 is diffusing through the diffusion limiting barrier and gets dissociated and reduced at the cathode to hydroxyl ions
  - All O2 molecules get dissociated – thus pO2 at the cathode is close to 0
  - The sensor current becomes proportional to the diffusion of O2 molecules through the diffusion layer
  - Diffusion of O2 molecules is linear to the pO2 in front of the membrane – thus there is a linear relation between pO2 and sensor current



Temperature & pO2 sensors

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- In a rebreather the pO2 sensors can be exposed to temperatures from possibly 0-50°C
- Diffusion through the membrane to the cathode is temperature dependent: typical + 2-3% per °C
- Remember: The sensor current is in theory proportional to the diffusion of O2 molecules through the sensor layer
- O2 Diffusion/sensor current rises 2 - 3% per °C

Sensor electronics

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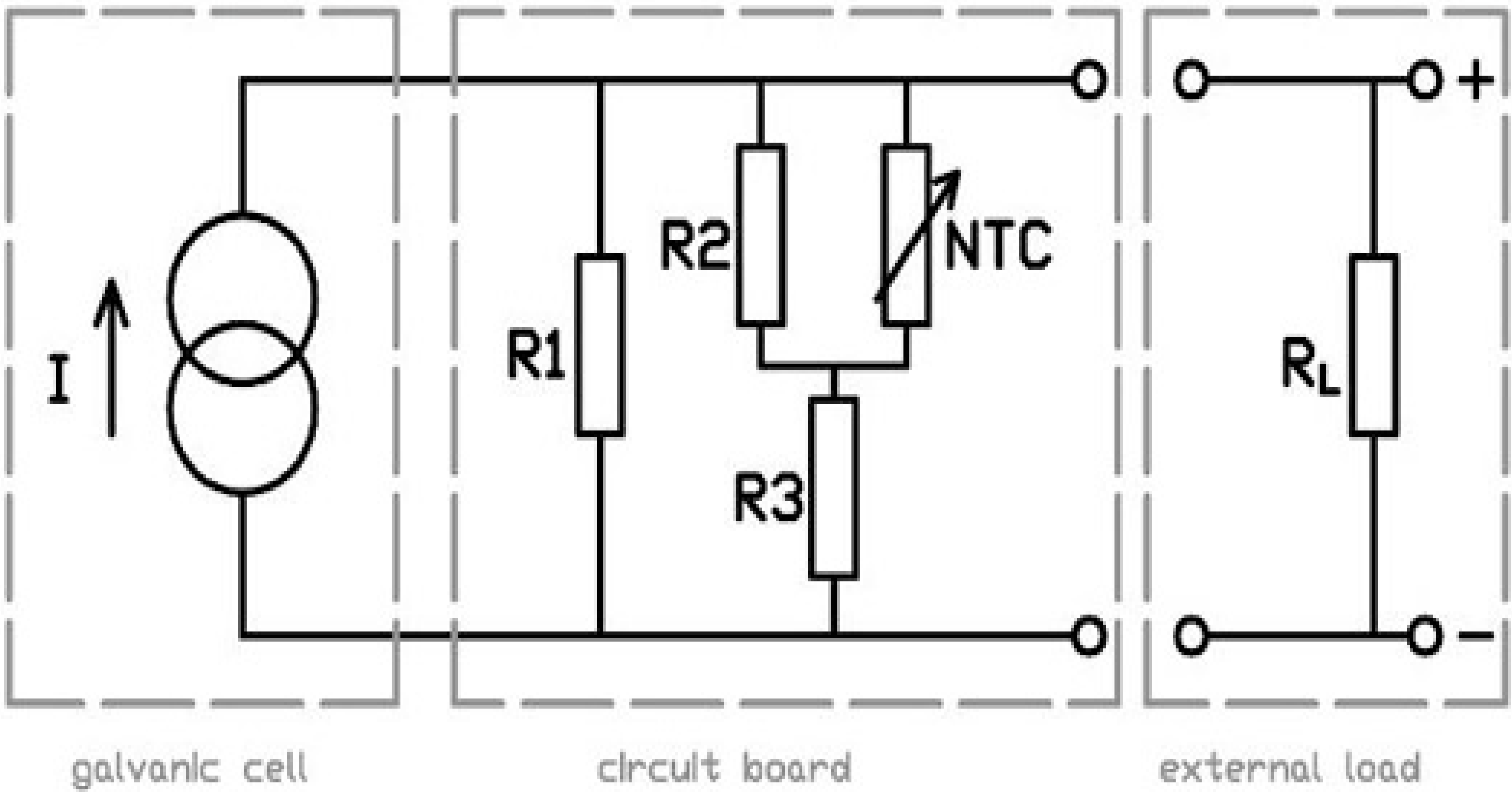

From Paul Raymaekers, How Oxygen Sensors Work
http://www.revo-rebreathers.com/uploads/downloadsitems/Understanding_oxygen_sensors.pdf

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Sensing problem: does the galvanic pO2 sensor cell have the same temperature as the sensing element?

- Typically the sensing element is mounted on the PCB behind the sensor cell
- To guarantee correct temperature of the sensing element, thermal conductive paste is applied between the sensor cell and the PCB
- However, not all sensors have paste in between, in particular some sensors used for NITROX analysis do not – thus they are not suitable for diving!
- Some sensor have the sensing element in the electrolyte (ideal, but additional manufacturing effort).

Take Home Message 3

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- **The temperature compensating circuit needs to have the same temperature as the electrolyte and the sensor membrane**
- **Do not use medical pO2 sensors or pO2 sensors from NITROX analyzers for rebreather diving**
- **Rebreather design: AVOID temperature gradients in the sensors**

Response time (t90) of pO2 sensors

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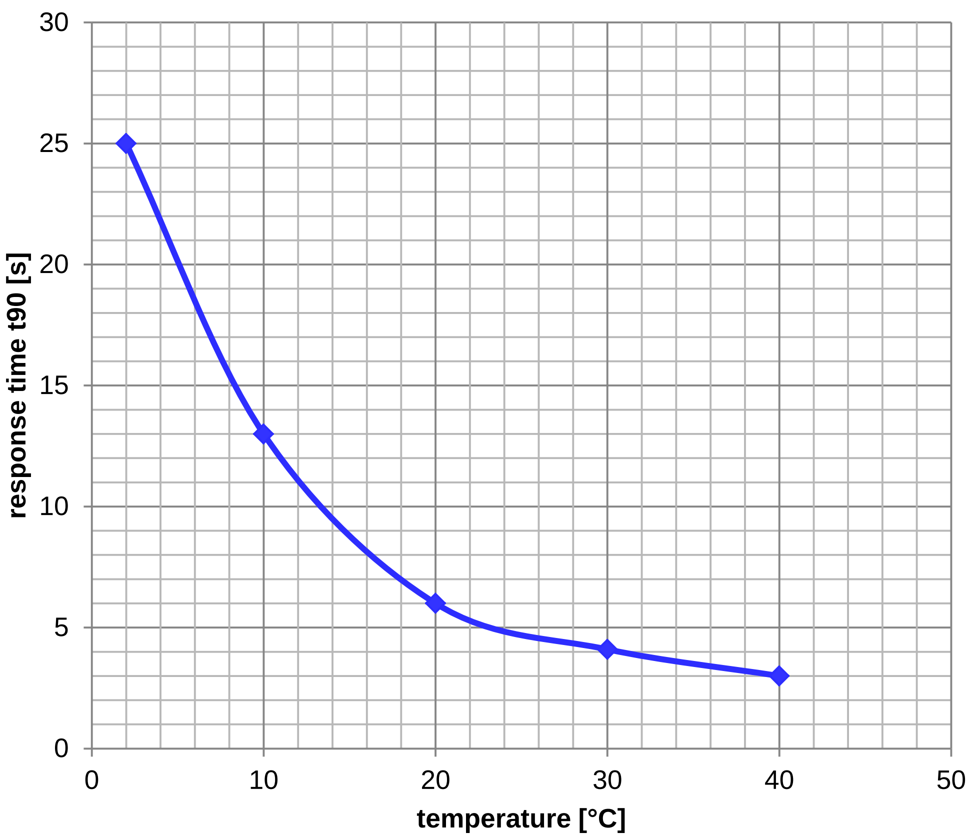
- **Response time depends on the gas diffusion through the membrane/diffusion layer**

- **Typical response time (t90) is 6-10s at room temperature**



Take Home Message 4

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At low temperatures galvanic pO2 sensors are slow

Aging/Failure of pO2 sensors

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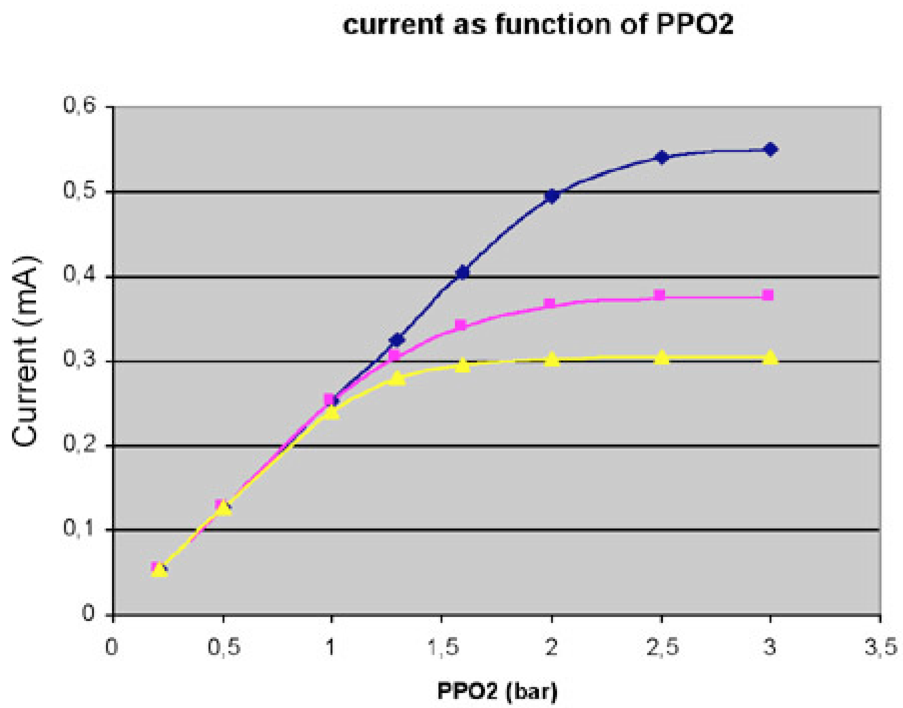
- **anode exhaustion -> current limitation**
  - pO2
  - Temperature
- **cathode poisoning (cathode get‘s passivated)**
- **Mechanical problems**
  - Leaking of electrolyte
  - Damage of the sensor
  - Small hole in the membrane leads to higher currents
- **Electrical problems**
  - Corrosion
  - Component failure
  - Incorrect read out / problems with the pO2 meters
  - Electrical interferences

Current limitation:

- **The anode is the fuel of the galvanic sensor cell (similar to a battery)**
- **Once the anode is exhausted, there is no sensor current anymore**
- **Current limitation describes the effect where not all available O2 molecules reaching the cathode are reduced**



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Testing cells for current limitation:

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- **Pressure pot method (Cell Checker):**
  - pressurizing sensors with O2 of air
  - Checking readings for linearity in the hyperbaric range (pO2 > 1 bar)
- **Problem:**
  - Correct interpretation of the results !!!
  - A sensor that is not current limited to f.i. 1.6 bar in the test pot is no warrantee that the sensor is also not current limited during diving !!!
  - Reason: cells in the cell checker are at room temperature, in the rebreather at the exit of the scrubber possibly 40-45°C – thus diffusion of O2 to cathode is much higher, however, current limitation is caused by exhausted anode, and current limitation may start at a much lower pO2 than in the pressure pot test
  - <u>Our acceptance threshold: 2.5 bar pO2 (at room temperature)</u>
- **Better approach: testing cells at 6m with O2**

Message to take home - 4

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Pressure pot testing of pO2 sensors:

Do not use sensors in rebreathers that cannot read at least 2.5 bar pO2

Or: test pO2 sensors for current limitation at the end of the dive (as they will then be at operational temperature)

Lifetime of pO2 sensors

How to specify the lifetime of the sensors?

- Lifetime in months at storage in air at room temperature (24-60)
- Lifetime in Vol%O2 h (500 000 – 1 000 000)

Example: storage of a sensor in air at 20°C / 30 °C

- 21% * 365 * 24h = 183960 Vol%O2 h
- 21% * 365 * 24h * $1.03^{(30°C-20°C)}$ = 21%*365*24h * 1.34 = 246506

Lifetime of pO2 sensors (2)

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Diving:

- **One dive, pO2 1,3, 20°C**

  130% * 1h = 130 Vo%O2 h

- **One dive, pO2 1,3, 45°C**

  130% * 1h* 1.03 $^{(45°C-20°C)}$ = 272 Vol% O2 h

Lifetime of pO2 sensors (3)

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2 years, 100 diving hours each, rest storage at room temperature:

- **54438 Vol%O2 h from diving**
- **357920 Vol%O2 h from storage**

In reality: sensors last typically between 12 and 18 months – thus far less than specified by industry

Accelerated aging of pO2 sensors

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pO2 sensors are designed for application in:

- Standard atmospheric pressure
- Room temperature
- no CO2

However in diving pO2 sensors are subject to:

- High pO2
- High temperatures
- High pressures (bubble formation is also possible in the electrolyte)
- High humidity
- Increased pCO2
- Mechanical shocks (transportation on a RIB …)
- Corrosion (salt content of gas), salt water drops.

Failure statistics

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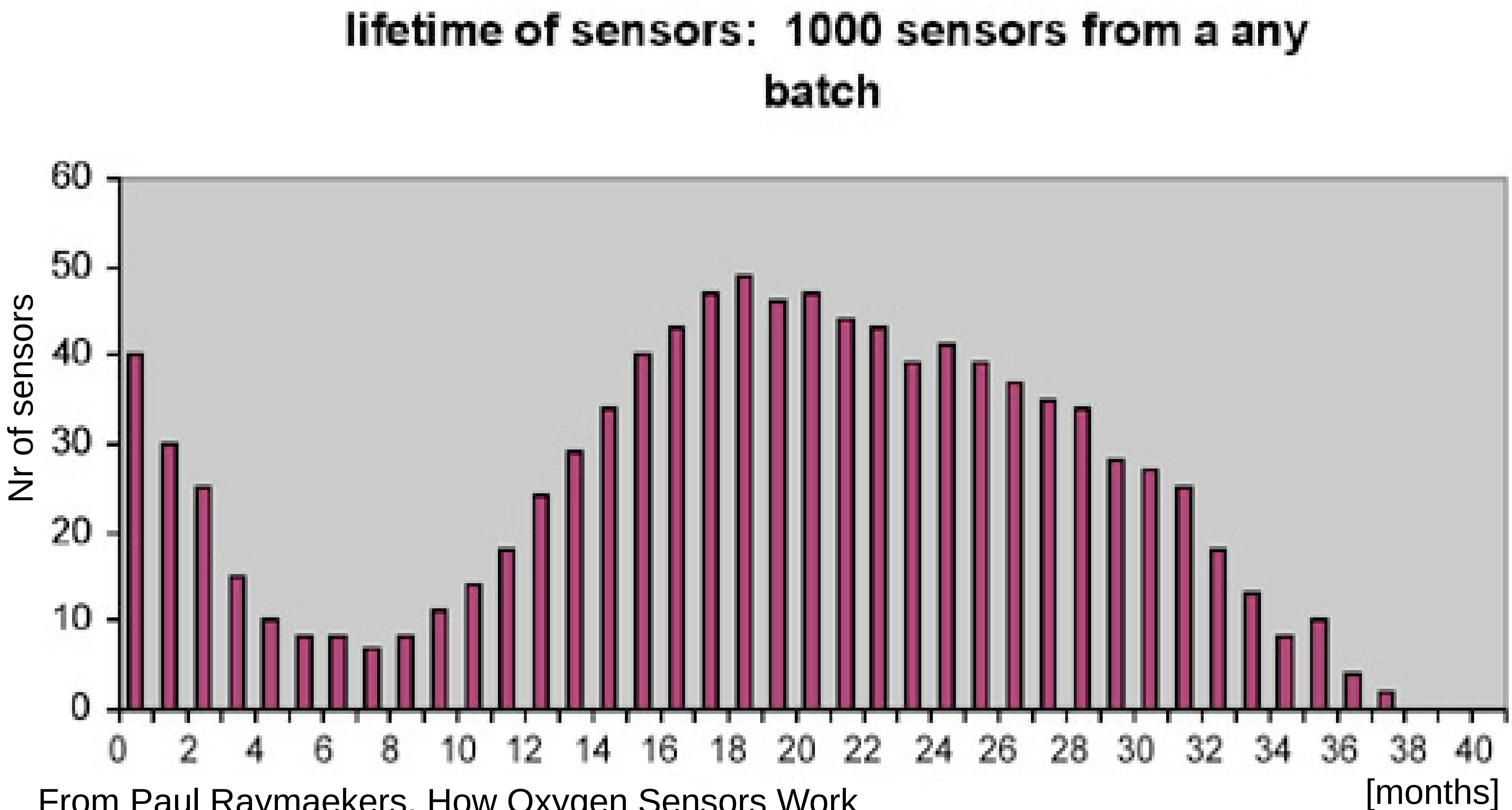

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Voting algorithm

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- **Advocate 3 or more sensors in a rebreather**
- **Comparison of the sensor signals**
- **Statistics were presented showing that the risk of a multiple sensor failure is relatively low**
- **These statistics are based on the assumption, that sensor <u>fail independently</u>**
- **In general true, but only for laboratory conditions where sensors are used within their specifications**
- **Thus: incorrect approach – sensor failures in a rebreather are caused by a "common" history**

Take Home Message 5

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Sensor failures in rebreathers are caused by abuse of the sensors

Sensors in a rebreather have a common history

Assumption that Sensors fail independently in a rebreather is wrong

Checking pO2 sensors during diving

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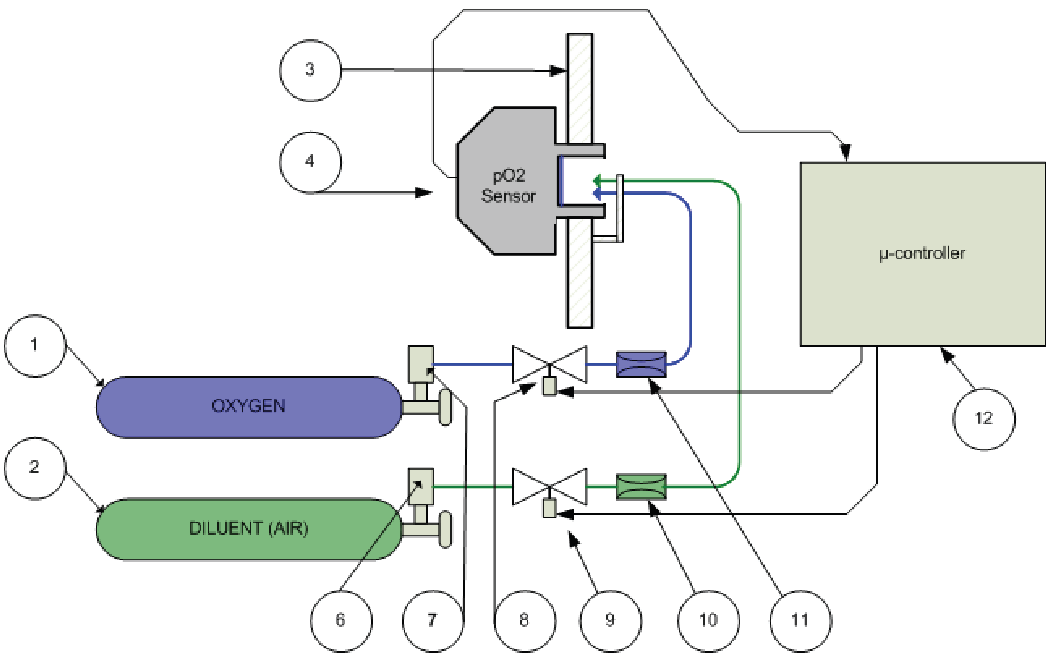
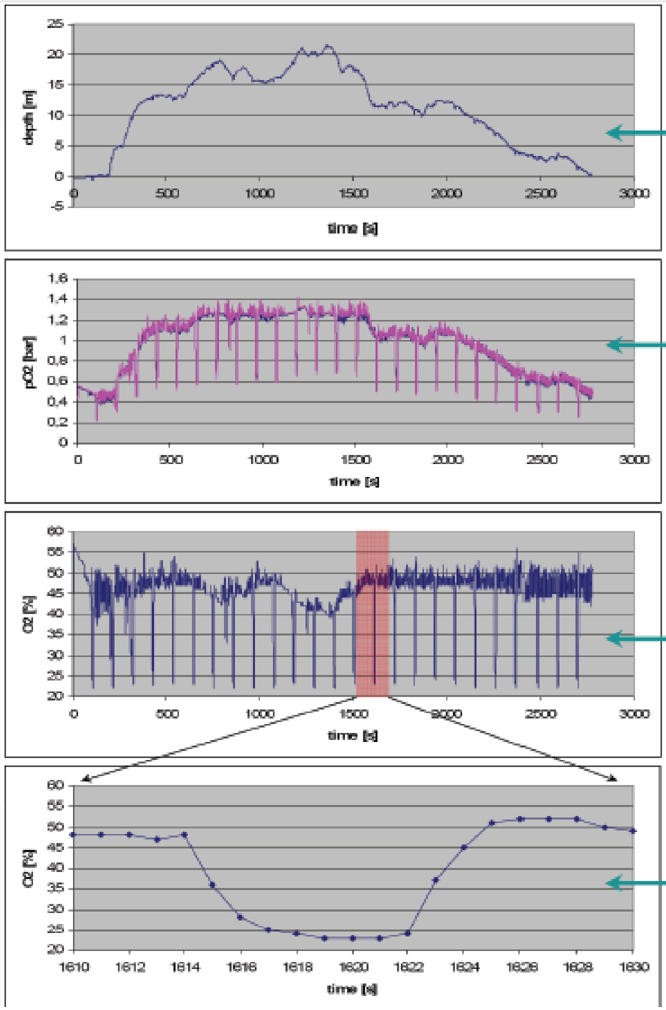
- **Manual or automatic voting algorithm (minimum 3 sensors)**
- **Dil/O2 flush to check pO2 sensors for function and linearity in hyperbaric O2**
- **Dil / O2 flush requires training and know how – probably not suitable for recreational divers on a daily basis**
- **Automatic „true“ validation of pO2 sensors**

pO2 sensor signal validation





Depth profile of a 47 min test dive to a maximum depth of 22m.

Signals of the 2 pO2 sensors. Every 120s a sensor signal validation is carried out (spikes)

%O2 calculated from the pO2 value and the actual depth. All "validation spikes" drop below 25%.

Detailed view of one sensor signal validation cycle

Sensor head Poseidon MK6

RoHS directive

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- Restriction of Hazardeous Substances
- Linked with the waste Electrical and Electronic Device Directive
- RoHS restricts the use of Lead (Pb)
- The anode of O2 sensor cells is made from Pb
- Recast of the RoHS directive End of 2010
- Medical consumables are now also included in this directive – thus RoHS has also to be applied to O2 sensor cells

RoHS directive & diving

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- **There are alternative lead free O2 sensor cells that have the potential to substitute the Pb based sensors in medical applications**
- **The sensor cells are currently under investigation in our laboratory**
- **First results show that these type of new Pb free sensors cannot be directly used in a rebreather – further development is required**
- **There might be a major shortage in Pb sensors starting from 2013, when the recast will be in force**

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Electronics in Rebreathers

Design of rebreather electronics

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- **Well designed electronics**
- **A failure must be immediately recognizable**
  - **for example HUD – red LED flashes in the case of a failure … what if you have a sudden battery failure?**
- **2 Approaches:**
  - **Redundant electronics**
  - **Networks, where network nodes perform data plausibility checks and each node can trigger warnings**
  - **-> only possible if sensor nodes are independent from each other (including electronics)**

CE certification of rebreather electronics

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- **The rebreather electronics (set point controller, etc..) has to be tested as part of the testing of the rebreather**
- **Case:**
  - Take a CE certified MCCR rebreather
  - Take a CE certified diving computer
  - Use the diving computer as setpoint controller
  - Diving computer has CE ceritfication + rebreather has a CE certification -> the combination alone without testing the whole package under EN14143 is NOT CE compliant !!!

CE certification of a Diving computer?

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EN13193:2000 (depth and time measurement, robustness)

- **EN13319:2000 was prepared by the CEN/TC136 group for “Sports, playground and other recreational equipment”**
- **EN13319:2000 is not listed under Directive 89/686/EEC for Personal protective equipment**
- **Decompression calculations are excluded from the standard**
- **pO2 control is not even mentioned**

Other standards for Diving computer?

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- **EMC 89/336/EEC: electromagnetic compatibility**
- **EN250: tank pressure reading**
- **ISO 1413: Horology – Shock resistant watches**

Certification of Rebreather electroncis?

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- **The rebreather together with the electronics have to fulfill EN14143**

- **What about EN61508 ?**
  - EN61508 is references in EN14143:2003
  - It is an application independent standard
  - Enhances safety by risk reduction
  - The standard describes a general development life cycle required for building a safe system
  - EN61508 is not included in the updated preliminary version of EN14143
  - Widely discussed

Liability ?

- **CE and Liability are two different things**
- **State of the art product live cycles have to be applied (otherwise it is gross negligence)**
- **EN61508 is state of the art (as it is included in EN14143:2003)**
- **To be legally on the safe side, manufacturers should apply EN61508, a tailored standard or an equivalent standard.**

The future pO2 sensors

Smart galvanic pO2 sensor

- Microcontroller based
- Integrated oxygen hour meter
- Calibration history stored on the sensor
- Unique digital sensor id
- Can electronically check for current limitation
- Can electronically check cathode

Optical sensors - OPTODES

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- Measurement of O_2 with an optical sensor
- Illumination of a fluorescenting oxygen indicator
- Fluorescence is maximum in the absence of O_2
- O_2 molecules quench fluorescence
- No linear sensor response - sensors are most sensitive at low pO_2s (traces of pO_2)
- For long, sensors were not able to measure with an acceptable precision above 0.5-1 bar pO_2
- Stern-Volmer relationship

OPTODE breakthough

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OPTODES – recent advances / breakthrough

- Research Group at the Technical University of Graz, Austria under Prof. Klimant has developed a new sensor material (REDFLASH technology)
- Sensor material can be used for measuring pO2 > 1 bar with sufficient accuracy
- Response time in air 1-3 s (dependent on thickness of sensor spot)
- Technology is now expolited by german company
- All research background data about optical indicators and their synthesis are published in open scientific literature

OPTODES - VISION

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Optical sensor consists of 2 components:

- **sensor spot**
- **sensor optics/electronics (contactless sensor, no corrosion problems, etc..)**

- **sensor spot is cheap (can be sprayed, painted,…)**
- **sensor spot can be a single use sensor (one sensor for each dive) -> aging problem is overcome**

- **sensor spot can be combined for example with a single use scrubber cartridge**

O2 Solid State Sensors Technology

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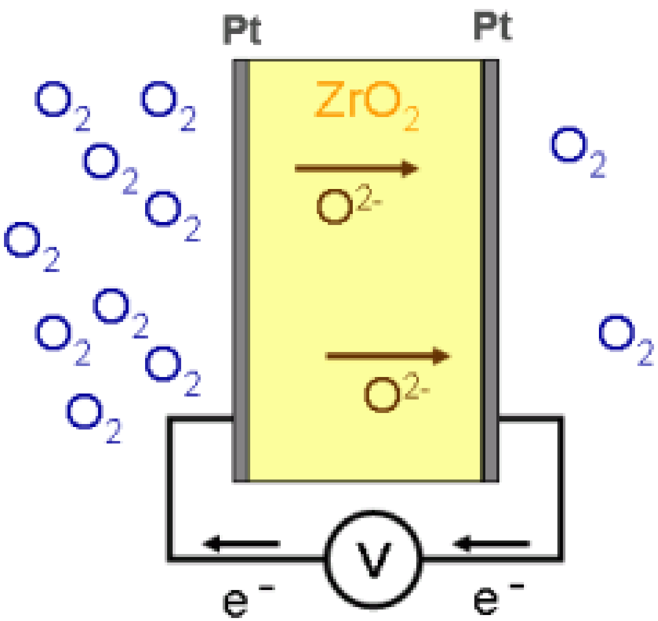
- **Based on the ionic conductivity of solid ceramics**
- **Well established application: Combustion control: O2 measurment in cars**
- **Zirconia/Ceria**
- **Require heating**
- **Due to their size require large heating power**
- **Potentiometric sensor principle requires reference gas**



Micro Solid State Sensors for O2 and CO2

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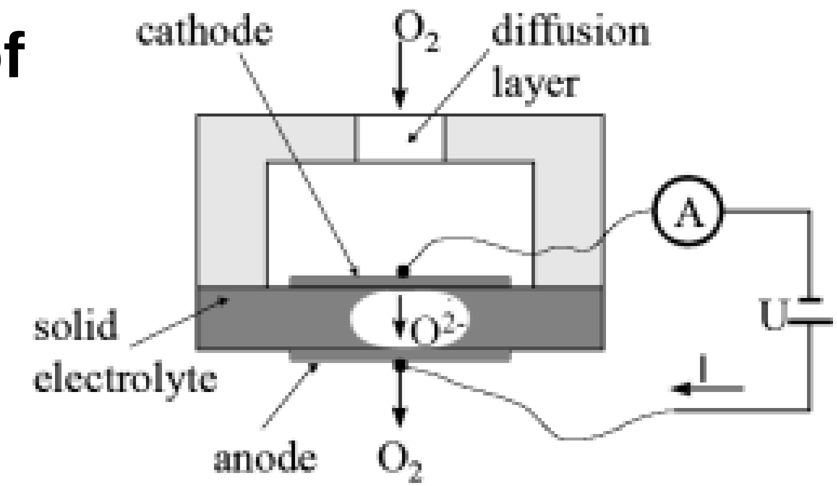
- Based on the ionic conductivity of Zirconia/Ceria (for O2) and NASICON (for CO2)
- Sensorelement require heating to 650°C/550°C
- Microfabricated - small size
- Sensor element: 2.5 x 2.5 x 1 mm³
- Non consuming / quasi indefinite lifetime
- Amperometric sensor principle (O2)
- Potentiometric sensor (CO2)



Prototype sensor system integration

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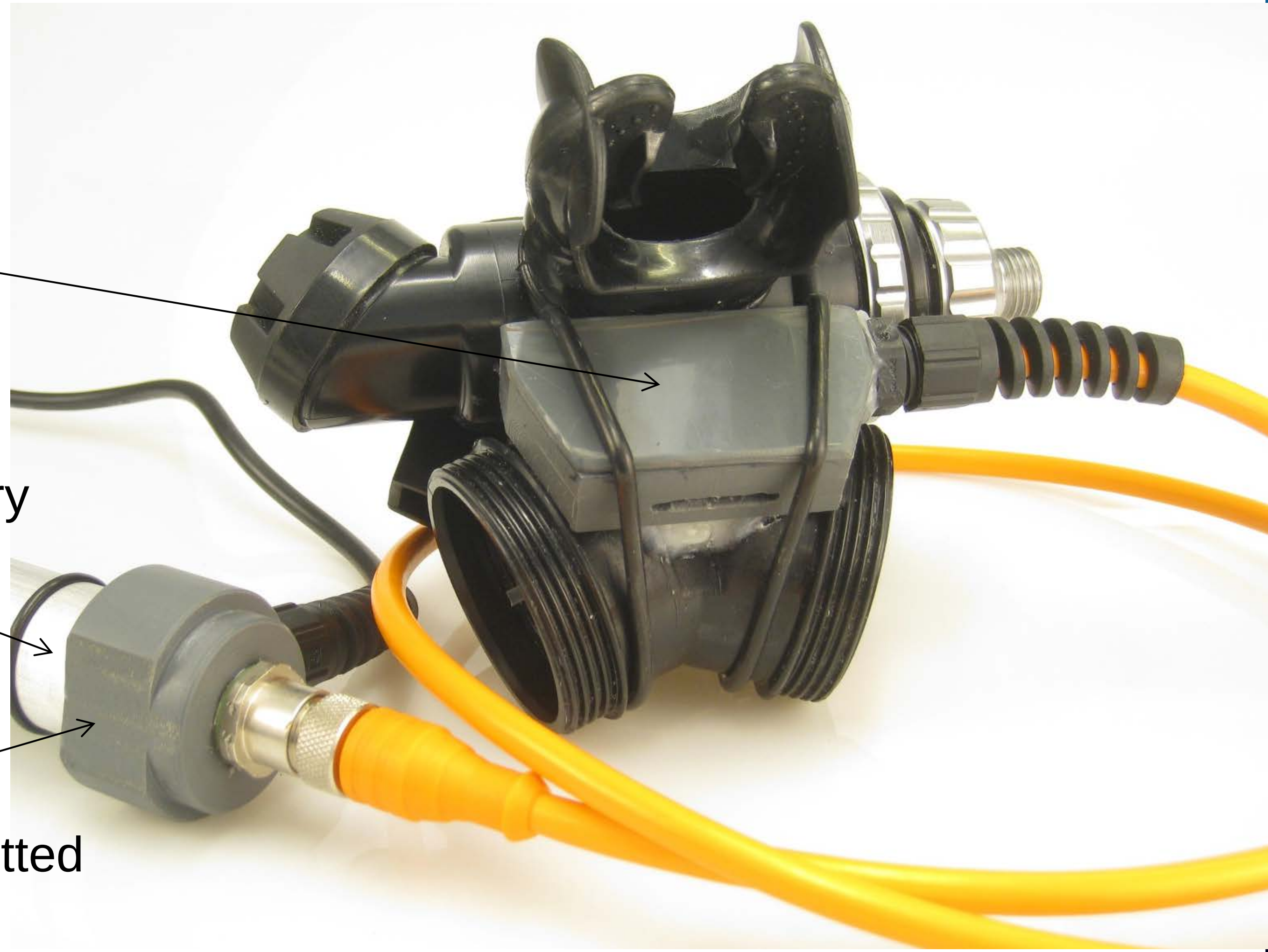
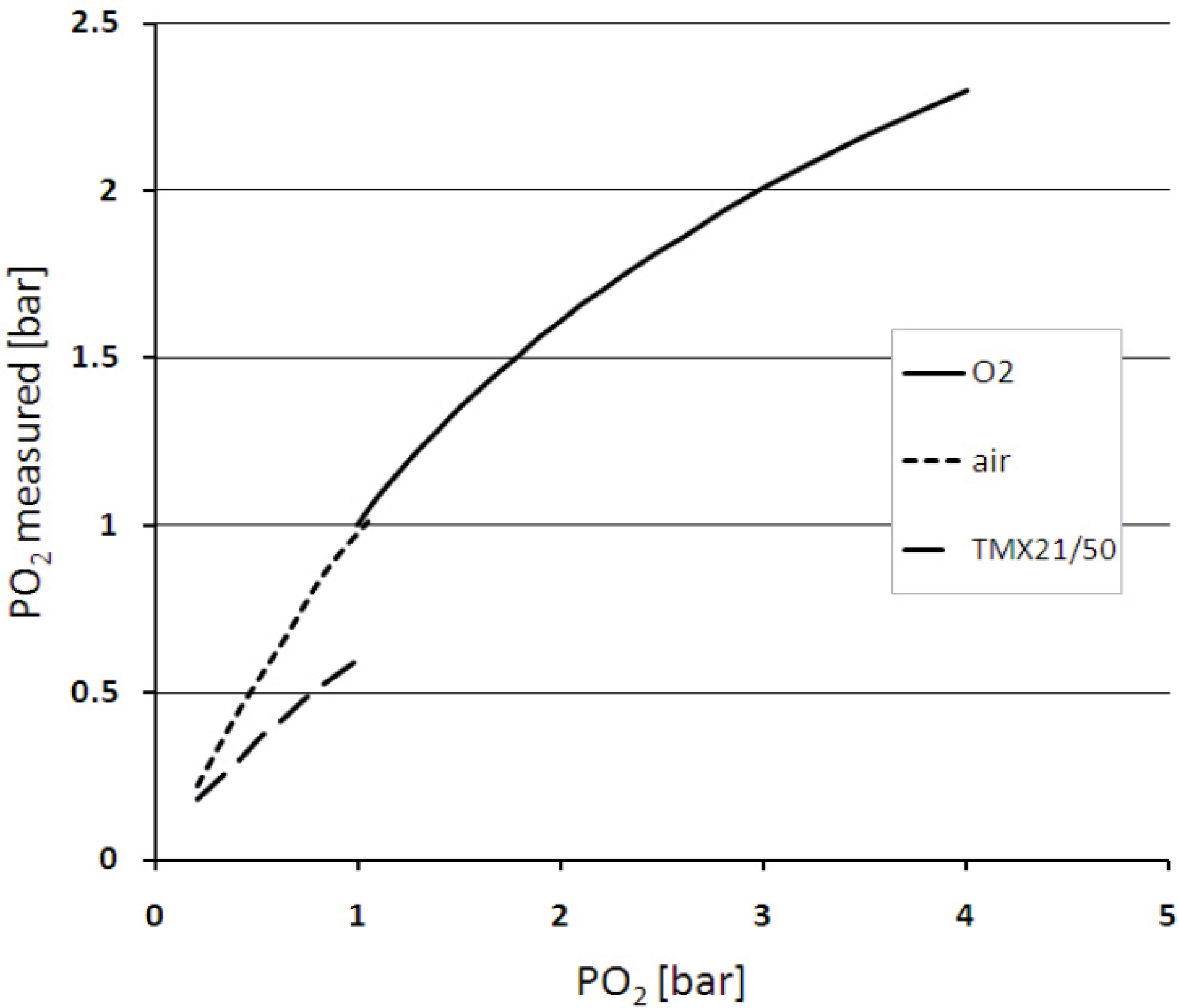
Sensors & Electronics

Li Ion rechargable battery
4h autonomy



Micro solenoid can be fitted

O2 sensor, hyperbaric test in 100% O2



Signals of solid state sensors in a rebreather

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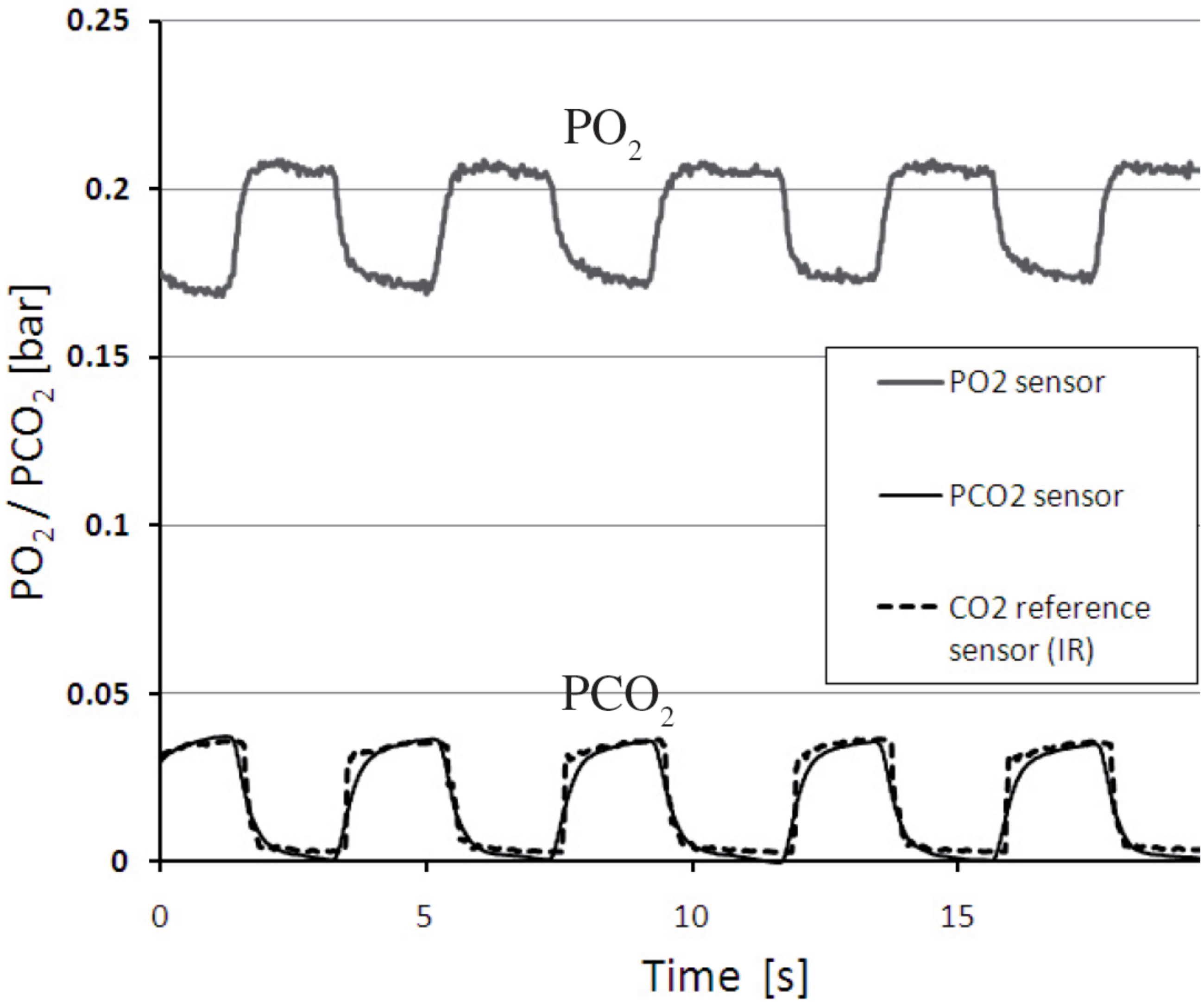

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- **my research group in Austria**

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Based in Graz, Austria

Diving Instrumentation
Underwater research
Diving Physiology
Decompression theory
Diving Computers
Head up Displays
Rebreathers
Sensor technologies