# **DIVING-PAM-II/02**

## Underwater Oxygen Sensor

# **Manual**

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## 1 Safety Instructions

#### 1.1 General Safety Instructions

- The Underwater Oxygen Sensor DIVING-PAM-II/O2 (denoted hereinafter as "device") should be used only by qualified personal.
- Read safety and operating instructions in the manual prior to operation of the device.
- Follow safety and operating instructions of the manual, as well as the appropriate laws and guidelines for safety in the laboratory.
- Keep devices and sensors outside the reach of children.
- Ensure that no liquids, foreign objects, dust, sand, or dirt get inside the unit or into the connector.
- Do not put the devices and sensors near sources of heat.
- Connect the device only to the port indicated in the operating instructions.
- The devices should only be repaired by qualified personnel.
   There are no serviceable parts inside the device. Opening the housing will invalidate the warranty!
- The devices and sensors are not intended for medical or military purposes or any other safety-critical applications.
- The devices and sensors must not be used for applications in humans; not for in vivo examination on humans, not for human-diagnostic or any therapeutic purposes.

#### 1.2 Special Safety Instructions

- The OXCAL capsules for O<sub>2</sub> calibration contain sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>). Before use, read instructions in the safety data sheet delivered with the OXCAL capsules.



OXCAL first aid measures

<u>General notes:</u> Take off contaminated clothing.

<u>Following inhalation:</u> Provide fresh air. In all cases of doubt, or when symptoms persist, seek medical advice.

<u>Following skin contact:</u> Rinse skin with water/shower <u>Following eye contact:</u> Rinse cautiously with water for several minutes. In all cases of doubt, or when symptoms persist, seek medical advice.

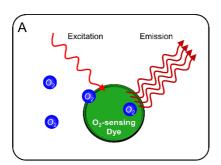
<u>Following ingestion:</u> Rinse mouth. Call a doctor if you feel unwell.

### 2 Introduction

#### 2.1 Measuring Principle

This manual introduces the "Underwater Oxygen Sensor DIVING-PAM-II/O2" which is an accessory for the DIVING-PAM-II. Typical applications for the DIVING-PAM-II/O2 are measurements of bathymetric oxygen profiles and monitoring of long-term declines in oceanic oxygen concentrations associated with climate change.

The DIVING-PAM-II/O2 is an optode-type sensor. The oxygen-responsive element of the optode is a sensor spot which carries a luminescent dye. The yield for luminescence of the dye is quenched by oxygen. In practice, not the luminescence intensity is measured but the phase shift of luminescence relative to the sine-modulated excitation light.



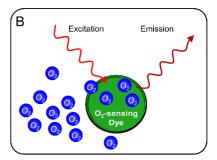


Fig. 1: Principle of O<sub>2</sub> Detection

A, high luminescence intensity at low oxygen concentrations. B, low lumimescence intensity at high oxygen concentrations. According to <a href="https://www.pyroscience.com">www.pyroscience.com</a>, modified.

The optode technology excels by its long-term stability of calibration, relatively small dimensions, and long storage time of optode sensors.

#### 2.2 Extent of Delivery

- Underwater Oxygen Sensor DIVING-PAM-II/O2, with PT100 resistance thermometer.
- 2 m underwater cable 000130204945
- Two spare oxygen sensor spots OXSP5
- Holder for DIVING-PAM-II/O2 consisting of the mounting brackets 000246001714 and 000246003914 and 1 ring holder 000244905514.
- OXCAL O2 Calibration Capsules (10 pieces)

## 3 Setup

#### 3.1 Mounting

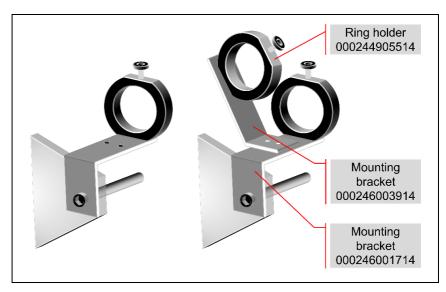


Fig. 2: DIVING-PAM-II/O2 holder

Left, standard holder. Right, dual holder for DIVING-PAM-II/O2 and MINI-SPEC.

The DIVING-PAM-II/O2 sensor is delivered together with a ring holder (order number 000244905514) and a mounting bracket (order number 000246003914). Both parts form a holder for the DIVING-PAM-II/O2. To mount the holder, fasten mounting bracket (#000246003914) to mounting bracket #000246001714 (see Fig. 2). Then fasten second ring holder as shown in Fig. 2.

An additional mounting bracket #000246001714 is part of delivery. This second mounting bracket is provided for owners of the first models in the series. These models have a mounting bracket with only two holes drilled in.

The DIVING-PAM-II/O2 sensor is connected via a 4-pole underwater cable to one of the two AUX ports of the DIVING-PAM-II. For a proper and watertight connection, consider the instructions given in Fig. 3.

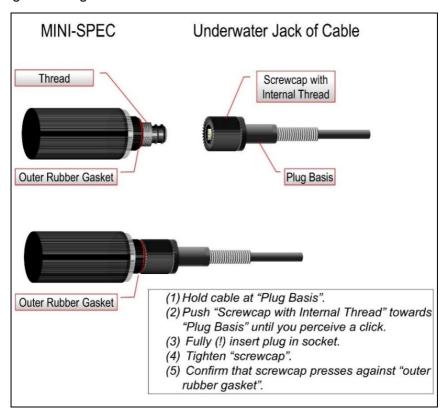


Fig. 3: Connection of MINI-SPEC/MP

#### 3.2 Sensor Spot Properties

The DIVING-PAM-II/O2 sensor measured oxygen optically. A sensor spot, carrying a luminescent dye, changes its yield for lumi-

nescence dependent on oxygen concentration (Fig. 1). The fluorescent dye is excited via fiberoptics. Dye luminescence is guided by the same fiberoptics to the high-precision oxygen meter.

Each sensor spot is provided with a code that contains important information for the oxygen meter (Table 1): (a) the intensity setting of the LED exciting the luminescent dye, and (b) the signal amplification factor. At Walz, information (a) and (b) is transferred to the oxygen meter. The information on pre-calibration (see Table 1) is not needed, as the sensor must be calibrated by the user (Chapter 4, page 9).

The effect of temperature on dye luminescence is automatically compensated using the temperature measured by a PT 100 resistance thermometer (Fig. 4, page 8).

| CODE    | S           | Α             | 6             | - | 540             | - | 216    |
|---------|-------------|---------------|---------------|---|-----------------|---|--------|
| MEANING | Sensor Type | LED Intensity | Amplification |   | Pre-Calibration |   | ration |
|         |             |               | Factor        |   | 0%              |   | 21%    |

Table 1: Sensor Code

## 3.3 Sensor Spot Replacement

Long-term use decreases signal strength of the sensor spot. Below a certain level, oxygen cannot be measured, and the corresponding data fields display a dash and an error message pops up (compare Table 2, page 13). In this case, the sensor spot must be renewed.

The minimum number of measurements by a single oxygen sensor is estimated to be 1,000,000 corresponding to almost 300 hours of measuring time for 1 Hz measuring frequency. Switching

off the oxygen sensor (by turning off the DIVING-PAM-II) between experiments extents the sensor lifetime.

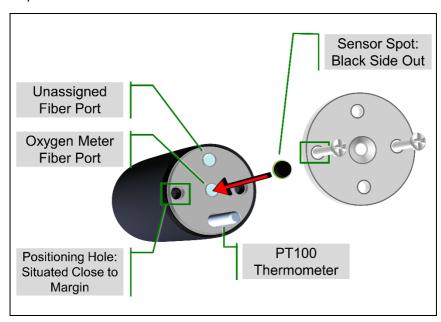


Fig. 4: Underwater Oxygen Sensor DIVING-PAM-II/O2

To change the sensor spot, remove the two plastic screws at the end of the DIVING-PAM-II/O2 sensor and remove acrylic glass disk (see top right side of Fig. 4, page 8). The sensor spot covers the oximeter fiber port. Place the new sensor spot exactly on the oximeter fiber port. Make sure that the black (optically isolating) side is outward directed. Incorrect orientation will render the sensor spot inoperable.

Note that one hole in the acrylic glass disk is moved more to the edge than the other holes (Denoted "Positioning Hole in Fig. 4, page 8, marked by green rectangle). When replacing the acrylic disc, ensure that this hole is positioned over the corresponding hole in the oxygen meter.

### 4 Calibration

### 4.1 Preparation

All devices and sensors must be placed for at least 30 minutes under constant environmental conditions, before the calibration is performed. The two-point calibration requires calibration liquids representing the upper and lower limit of the measuring range. When the sensor is placed into a new calibration standard, wait until the sensor reading is stable, then calibrate.

#### 4.1.1 Zero % Calibration Liquids

#### **OXCAL**

Part of delivery are 0% calibration capsules called OXCAL (Pyro-Science, Aachen, Germany). One capsule gives 50 mL 0% calibration standard.

Use a 50 mL sealable wide-neck container. Add magnetic stir bar and capsule. Fill up to the rim with demineralized water. DO NOT use saline water (e.g., seawater). Close container. Avoid head-space and air bubbles in container.

Place on a magnetic stirrer and stir until the salt is completely dissolved. Stop stirring and leave to stand for about 15 minutes. Immerse sensor into 0% calibration solution. Let equilibrate and perform calibration. Do not store the sensors in this solution and rinse carefully after the calibration with demineralized water.

#### **OTHERS**

- Water thoroughly bubbled with nitrogen gas (pass gas through an air stone).
- Procedure according to: Delieu T, Walker DA (1972) An improved cathode for the measurement of photosynthetic oxygen evolution by isolated chloroplasts. New Phytologist 71: 201-225

"A few small crystals of sodium dithionite are added to stirred water in the cells which are then closed with the plungers. This reacts with dissolved oxygen according to the equation

$$Na_2S_2O_4 + O_2 + H_2O \rightarrow NaHSO_4 + NaHSO_3$$

and since the reaction goes rapidly to virtual completion this procedure is equivalent, but more convenient, than prolonged flushing with 0,-free nitrogen."

#### 4.1.2 Hundred % Calibration Liquids

- Water bubbled with air (pass air through an air stone connected to an air pump, e. g., an aquarium pump).
- If an air pump is not available, fill water into a flask leaving about 50% air in the head space and shake it strongly for about 3 minutes.

#### 4.2 User Interface

Control the calibration process either by the touchscreen interface of the fluorometer, or by WinControl-3. To use the touchscreen, go to window "Oxygen Sensor Settings" (Fig. 5) via the sequence Main Menu → Sensors → Oxygen Sensor. The window "Oxygen

Sensor Settings" also contains settings of the DIVING-PAM-II/O2 sensor.

| Oxygen Sensor Settings |               |      |
|------------------------|---------------|------|
| Meas. Interval (s)     | 2             |      |
| Blank Out LED          | off           | •    |
| Settings               | $\rightarrow$ |      |
| Output Format          | $\rightarrow$ | ▼    |
| Calibrate 0%           | $\rightarrow$ |      |
| Calibrate 100%         | $\rightarrow$ | SET  |
|                        |               |      |
| dPhi (deg)             |               | EXIT |
|                        |               |      |

Fig. 5: Oxygen Sensor Settings

The currently measured oxygen concentration is displayed on window "Primary Data" (Fig. 6).

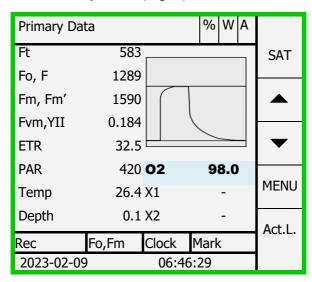


Fig. 6: Primary Data

When using the software WinControl-3, go to window "Sensors", to get access to settings and calibration of the  $O_2$  sensor (Fig. 7). All messages and settings related to the oxygen sensor are explained in Table 2. The button Start Calibration opens the calibration window (Fig. 8).

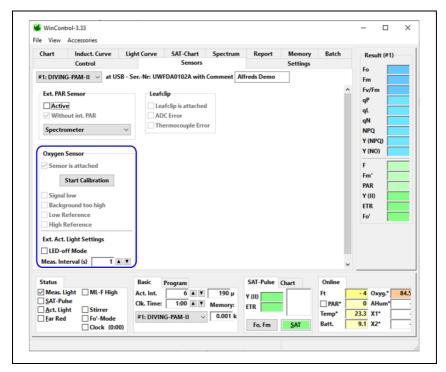


Fig. 7: Sensor Window of WinControl-3

The blue box highlights the area concerning the oxygen sensor-

| ☑ Sensor is attached     | The marked checkbox indicates the detection of the oxygen sensor by the fluorometer.   |
|--------------------------|--|
| ☐ Signal low             | The marked checkbox indicates that the signal intensity is below the threshold for required for reliable oxygen determination.  Check correct position of sensor spot (see Fig. 4, page 8). If no errors are found, the sensor spot may be exhausted and needs to be replaced. |
| ☐ Background too high    | The marked checkbox indicates that external light interferes with oxygen measurements. Possible reasons are light-reflecting air bubbles reflecting external light into the sensor, or light sources shining sideward on the oxygen sensor.                                    |
| ☐ Low reference          | Indicates severe error when checked. Send to manufacturer.   |
| ☐ High reference         | Indicates severe error when checked. Send to manufacturer.   |
| Ext. Act. Light Settings |  |
| ☐ LED-off mode           | Activate checkbox when an external light source (e.g., External LED Light Source 2054-L) causes high signal noise. Thereafter, the external light source will be switched off when oxygen is measured.   |
| Meas. Interval (s)       | The number specifies the interval between oxygen measurements. Default value is 1 second. Adjustable values range from 1 – 60 seconds.   |

Table 2: Sensor Messages and Settings

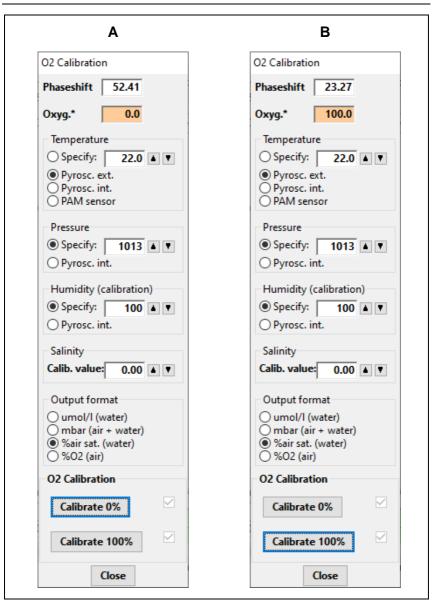


Fig. 8: O2 Calibration Window.

A, 0 % calibration. B, 100 % calibration

### 4.2.1 Settings

The following settings are recommended for measurements with suspensions.

Temperature: Select "Pyrosc. ext".

<u>Pressure:</u> Select "Specify:" and enter current atmospheric pressure. When a barometer is not available, take the information from the internet (e.g., https://barometricpressure.app/).

<u>Humidity (calibration):</u> For calibration in aqueous solutions, choose "Specify" and enter 100 (%).)

<u>Salinity:</u> Salinity plays a role only when the output format is µmol/L (see Oxygen Sensors, Fiber-optic and Contactless, USER MAN-UAL, OPERATING INSTRUCTIONS, <a href="https://www.pyroscience.com/en/">https://www.pyroscience.com/en/</a>).

Enter the dissolved salt content of the medium used for oxygen measurements (in g/L). To measure oxygen in media containing high sugar contents, do not choose  $\mu$ mol/L as format as the Software does not deal with the "salting-out effect" of sugars. A paper dealing with sugar-dependent solubility of  $O_2$  is:

Rischbieter E, Schumpe A, Wunder V (1996) Gas solubilities in aqueous solutions of organic substances: Journal of Chemical & Engineering Data 41: 809-812.

<u>Units of calibration:</u> Choose one of the three options available for the water phase:

- Dissolved O<sub>2</sub> concentration, μmol/L (applicable for water phase).
- Partial pressure pO<sub>2</sub>, mbar = hPa (applicable for gas and water phase).
- Percent air saturation, % (applicable for water phase).

 The option "Volume percent O2, %" is solely applicable for the air phase.

#### 4.2.2 Calibration

Zero calibration: Immerse sensor in Zero % calibration liquid, wait for constant oxygen signal and press Calibrate 0%.

<u>100 % calibration:</u> After careful rinsing, immerse in 100 % calibration liquid, wait for constant signal, press Calibrate 100 %.

After calibration, rinse thoroughly with distilled water

<u>Stability:</u> The calibration of the sensor is rather stable. Still, it is a good practice to check the calibration at regular intervals.

Expected phase shift: Dphi is the phase shift of light emission by the sensor spot relative to excitation light. dphi is not linearly related to oxygen abundance. Increasing oxygen levels correspond to decreasing dphi values. Anoxic conditions will give about dphi=53, ambient air will give about dphi=20. (Fig. 8, page 14).

## 5 Specifications

#### Underwater Oxygen Sensor DIVING-PAM-II/O2

**Design:** POM tube, at one end face, optical sensor spot fixed by a Perspex disk with central hole and PT100 resistance thermometer, at the other end face, 4-pole underwater socket. Temperature-compensated oxygen measurement by a high precision optical oxygen meter connected to the sensor spot by fiberoptics. Including a 2 m underwater cable 000130204945, two spare oxygen sensor spots OXSP5, and a holder (weight 75 g, maximum dimensions 6.5 cm x 6 cm x 12 cm, L x W x H) to attach both the DIVING-PAM-II/O2 and the spectrometer MINI-SPEC to the DIVING-PAM-Il optoelectronic unit, consisting of the mounting brackets 000246003914 000246001714 and and ring holder 000244905514.

Maximum diving depth: 50 m

**Dimensions:** 3.25 cm diameter, 17.5 cm length

Weight: 135 g

### 6 Guarantee

#### 6.1 Manufacturer's Guarantee

Under this Manufacturer's Guarantee ("Guarantee"), subject to the Conditions and Instructions below, Heinz Walz GmbH, Germany ("Manufacturer"), guarantees (§443 BGB) to the end customer and user ("Customer") that all products supplied by it shall substantially conform in material respects to the Specifications for 24 months from the delivery date (date on invoice). In this Guarantee, "Specifications" means the product's features (as may be amended by Manufacturer from time to time), which are set out under the headings "specifications" and/or "technical specifications" within the product's respective brochure, data sheet, or respective tab on the Manufacturer's website for such product, and which may be included with the documents for the product when delivered. In case of an eligible guarantee claim, this Guarantee entitles the Customer to repair or replacement, at the Manufacturer's option, and this Guarantee does not include any other rights or remedies.

#### 6.2 Conditions

This Guarantee shall not apply to:

- Any defects or damage directly or indirectly caused by or resulting from the use of unauthorized replacement parts and/or service performed by unauthorized personnel.
- Any product supplied by the Heinz Walz GmbH, Germany which has been subjected to misuse, abuse, abnormal use, negligence, alteration or accident.

- Damage caused from improper packaging during shipment or any acts of God.
- Batteries, cables, calibrations, fiberoptics, fuses, gas filters, lamps, thermocouples, and underwater cables.
- Defects that could reasonably have been detected upon inspection of the product when received by the Customer and not promptly noticed within ten (10) days to Heinz Walz GmbH.
- Submersible parts of the DIVING-PAM or the underwater version of the MONITORING-PAM have been tested to be watertight down to the maximum operating depth indicated in the respective manual. Guarantee shall not apply for diving depths exceeding the maximum operating depth. Further, guarantee shall not apply for damage resulting from improper operation of devices, in particular, the failure to properly seal ports or sockets.

#### 6.3 Instructions

- To obtain guarantee service, please follow the instructions below:
- The Walz Service Information Form available at <a href="https://www.walz.com/support/repair\_service.html">https://www.walz.com/support/repair\_service.html</a> must be completed and returned to Heinz Walz GmbH, Germany.
- The product must be returned to Heinz Walz GmbH, Germany, within 30 days after Heinz Walz GmbH, Germany has received written notice of the defect. Postage, insurance, and/or shipping costs incurred in returning equipment for guarantee service are at customer expense. Duty and taxes are covered by Walz.

- All products being returned for guarantee service must be carefully packed and sent freight prepaid.
- Heinz Walz GmbH, Germany is not responsible or liable for missing components or damage to the unit caused by handling during shipping. All claims or damage should be directed to the shipping carrier.

#### 6.4 Applicable law

This Guarantee is governed by German law. Place of jurisdiction is Bamberg, Germany.

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