

# Amperometric H<sub>2</sub>O<sub>2</sub> Micro-sensor

## H2O2-L Manual



## **Amperometric $H_2O_2$ -micro-sensor, OEM version**

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## 1 Preface

The amperometric H<sub>2</sub>O<sub>2</sub> micro-sensor has been developed for the *in-situ* determination of H<sub>2</sub>O<sub>2</sub>-containing aqueous solutions. Compared to all the other commercially available H<sub>2</sub>O<sub>2</sub> measuring systems and to permanganate and iodometric methods the new micro-sensor has some advantages, such as high economy, low detection limits, low analyte consumption and fast response times. Streaming, as it is well-known from all membrane-covered sensors, is not necessary.

The laboratory sensor with integrated electronic device contains an exchange sensor tip to allow also an exchange between H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>S and O<sub>2</sub> sensor tips, if the customer is interested in.

**The perfect functioning of the amperometric micro-sensor can only be ensured, if the user observes the safety precautions as well as the specific safety guidelines stated in the present operating instruction.**

## 2 Technical Data\*)

### H<sub>2</sub>O<sub>2</sub> laboratory sensor with integrated electronic device:

- ☞ measuring principle: - membrane covered, amperometric sensor  
- 3 electrodes
- ☞ separation of the sensor's electrolyte from the sample by means of very thin permeation membranes which are only pervious for gases
- ☞ integrated electronic device for the provision of the polarisation voltage
- ☞ sensor housing made of titanium
- ☞ protection cage
- ☞ exchangeable sensor tips (for H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>S and for O<sub>2</sub>)
- ☞ sensor tips: H<sub>2</sub>O<sub>2</sub>: type I: 0,02...10% H<sub>2</sub>O<sub>2</sub>  
H<sub>2</sub>S: type I: 50 µg/l ... 10 mg/l H<sub>2</sub>S  
type II: 500 µg/l ... 50 mg/l H<sub>2</sub>S  
type III: 10 µg/l ... 3 mg/l H<sub>2</sub>S  
O<sub>2</sub>: 0...150% saturation  
other measuring ranges on request
- ☞ streaming of the membrane or stirring of the analyte is not necessary
- ☞ the sample is in contact with the materials glass and titanium
- ☞ accuracy of the sensor: 2% f.s.
- ☞ temperature range for measuring and storage: 0°C ... 30°C
- ☞ short response times
- ☞ life time (depending on H<sub>2</sub>O<sub>2</sub> stress and on sample matrix): 5...9 months
- ☞ signal is not influenced by salt concentrations of up to 40 g/l

Regarding the electrical interfacing please check carefully the separate information sheet.

\*) Changes for technical improvement are reserved.

## 3 Preparation and measurement

### 3.1 Putting into operation

Before putting into operation please realise the **electrical connection** of your sensor as described in the separate instruction sheet.

Please check up also the link between the sensor tip and the housing always before every putting into operation. This link has to be absolutely watertight. If the sensor was immersed into a solution with-out correct interfacing, the sensor and/or the electronic device may be damaged. In this case the repair isn't covered by the guarantee.

For **switching on**, please use a stabilised 9-30 V DC power supply unit. With switching on you start automatically the polarisation of the sensor. It takes approximately 10 to 20 minutes to reach the **residual current** in hydrogen peroxide free solution.

After this the sensor is ready for use in principle. But before starting with the measurements you have to determine the residual current  $U_G$  in  $H_2O_2$ -free water (never on air). Write down this value.

Now you can start with your measurements.

### 3.2 Measurement

Measurements are possible in flow through systems with the AMT flow through cell or in-situ by immersing the sensor into the analyte solution (in-situ measurements):

#### 1. *in-situ measurement*

Immerse the sensor/sensor tip into the solution and read the concentration at the display of the voltage measuring instrument.

#### 2. flow through measurement

Insert the sensor into the flow through cell (please order extra) in a manner, that the long hole of the micro-sensors protection cage is across to the fitting at the side of the flow through cell. If the O-ring is lost in the flow through cell, the seal is sufficient. Connect now the tube with the analyte solution with the tube at the bottom of the flow through cell, so that the sensor is streamed directly. Put the other tube end of the flow through cell into a waste bottle. Now start slowly with pumping the solution through the cell. As flow rate we recommend 1-3 ml/min. When filling the flow through cell the first time, take care, that no gas bubbles are enclosed in the flow through cell and that the output of the cell is working properly. Therefore turn round

the flow through cell for some seconds, so that the solution output is up. Please take note, that because of adsorption/desorption equilibriums at the vessel and tube walls it takes some minutes for an adjustment of the steady state. This adjustment time depends on the H<sub>2</sub>O<sub>2</sub> concentration, on the flow rate and on the measuring breaks.

### 3.2.1 Calibration and temperature compensation

#### Fundamental

For accurate measurements an accurate calibration is required. The frequency of calibration depends on the accuracy demands and on H<sub>2</sub>O<sub>2</sub> stress of the sensor. A check up of the calibration/sensor slope is recommended after 120 measuring hours.

The sensor is working temperature dependent. This means, that the signal for the same concentration at different temperatures is also different. Therefore the temperature has to be considered always when measuring. If you have been ordering a calibrated sensor, you will find at the end of this brochure the sensor slope  $a_{20^{\circ}\text{C}}$  and the factors  $a_{0...3}$  for the temperature compensation ( $E_T$ ).

#### Calibration

If your sensor is not calibrated, you have to determine the temperature coefficients  $a_{0...3}$  and the sensor slope  $a_{20^{\circ}\text{C}}$  before starting with measurements. So, the calibration procedure consists of two parts – the slope calibration ( $a_{20^{\circ}\text{C}}$ ) and determination of the temperature coefficients. First we recommend to determine the:

#### *Temperature coefficients*

For this purpose it is recommended to put the sensor into a flow through cell (available from AMT) and pump slowly (0,8...1,2 ml/min) the H<sub>2</sub>O<sub>2</sub>-solution with a constant concentration through the cell. If the flow through cell is immersed completely into ice water and heated slowly - a slow increase of the temperature is realised and you can read the values at any temperature for a constant concentration at the display of your display unit. Take 10-15 output (mV)/temperature (°C) values within a temperature range between 0-30°C. After this a simple calculation of  $E_T$  (=temperature correction factor) is possible when using an mathematical equation of third order:

$$E_T = f(T) = a_3 T^3 + a_2 T^2 + a_1 T + a_0 \quad [T \text{ in } ^{\circ}\text{C}] \quad (1)$$

The regression of third order delivers the coefficients  $a_{0...3}$ . Using the equation (1) in combination with your specific coefficients  $a_{0...3}$  allows you to calculate any temperature correction factor  $E_T$ .

### Slope $a_{20^{\circ}\text{C}}$

For the determination of the slope  $a_{20^{\circ}\text{C}}$  you can use hydrogen peroxide solutions produced by diluting any H<sub>2</sub>O<sub>2</sub> stock solution step by step. The H<sub>2</sub>O<sub>2</sub> content of the calibration solution has to be determined by titration (permanganate or iodometric method). Please start always with 0% H<sub>2</sub>O<sub>2</sub> (e.g. in water, could be used also as residual current) followed by a hydrogen peroxide concentration near the end of the measuring range (e.g. 10% H<sub>2</sub>O<sub>2</sub> for the standard sensor type I). Write down the concentration – voltage output pairs. And don't forget to measure the temperature in order to be able to calculate the  $E_T$  temperature correction factor.

If you have determined the sensor slope  $a_{T_m}$  at the measuring temperature using the linear regression of any calculation program (e.g. Excel), you have to lead back this slope to 20°C. Using the following formula.

$$a_{20^{\circ}\text{C}} = a_{T_m} / E_T$$

$a_{T_m}$  = sensor slope at measuring temperature

$a_{20^{\circ}\text{C}}$  = sensor slope at 20°C.

The result is the sensor slope  $a_{20^{\circ}\text{C}}$  in „%/pA“. On request we offer the determination of the sensor slope  $a_{20^{\circ}\text{C}}$  also as service.

For a check up of the sensor slope  $a_{20^{\circ}\text{C}}$  act as described before.

### 3.2.2 Calculation of the H<sub>2</sub>O<sub>2</sub> concentration

The calculation of the hydrogen peroxide concentration has to be done by using the following equation:

$$c_{\text{H}_2\text{O}_2} = a_{20^{\circ}\text{C}} \times (U - U_G) \times E_T$$

$c_{\text{H}_2\text{O}_2}$             hydrogen peroxide concentration (%)

$a_{20^{\circ}\text{C}}$                 sensor slope at 20°C (% : mV)

$U - U_G$              measuring value (measuring signal minus residual current in mV)

$E_T$                     temperature correction coefficient (see calibration sheet)

### 3.2.3 Errors and troubles during measurements

If the sensor is used as described before and, if the sensor is not stressed with H<sub>2</sub>O<sub>2</sub> without polarizing the sensor, there should be no trouble during measurements.

But if it is observed, that it takes the sensor much too long for adjustment of the residual current (more than 10-15 minutes without any traces of H<sub>2</sub>O<sub>2</sub> around the sensor tip), this is caused by the fact, that H<sub>2</sub>O<sub>2</sub> has passed the sensor membrane without polarising the sensor or, that the measured concentration was much too high. Another characteristic after long H<sub>2</sub>O<sub>2</sub>-uptake is an essential higher residual current.

Caused by natural aging and H<sub>2</sub>O<sub>2</sub> stress the sensor slope decreases within the sensor's life. Therefore we recommend calibration intervals depending on your demands regarding the accuracy.

If the sensor is used for *in-situ* measurements, do not forget to check up the link between sensor head and sensor housing (waterproof ?) as well as sensor housing and cable before starting with measurements. This is necessary after long breaks and of course after the exchange of the sensor tips. If water comes between sensor/sensor head and/or sensor/cable this may lead to short circuits and may destroy the sensor or its electronic device. Nevertheless, if this has happened, the sensor should be stored and dried on air (not in a drying chamber, not more than 30°C !). Please check the residual current from time to time and decide, if the sensor can be used again.

Although the sensor contains an integrated electronic device to minimize influences caused by electric fields and magnetic effects, some smaller troubles may appear occasionally in the near of strong magnetic or electric fields. If these troublemakers are well known, please switch off, if possible.

Most of the "troubles" during measurements are not caused by the sensor itself, but more by the high reactivity of H<sub>2</sub>O<sub>2</sub> solutions, by local concentration gradients or by formed oxygen bubbles due to the decomposition of hydrogen peroxide.

Inhomogeneous standard solutions may also lead to rapid changing concentrations and of course to rapid changing measuring values (visible only because of the very fast response time of the micro-sensor).

**Please take note, that when rapid changing temperatures are observed, the sensor is shocked for some seconds (warm --> cold: leading to fast decreasing signals, negative values are possible !; cold --> warm: leading to fast increasing signals). It will take the sensor now some seconds or minutes depending on the kind of shock to return to the real value. This is because the equilibriums inside the sensor have to be adjusted again.**

### 3.2.4 Switching off

After the measurements have been finished, rinse the sensor tip carefully with distilled or tap water. Dive in the still polarised sensor with its sensor tip for approximately 5 minutes into a H<sub>2</sub>O<sub>2</sub> free solution (e.g. distilled water). Check up by means of the display, if the sensor has reached again a concentration value of around 0,000 % (or around its starting residual current if the current display is used). If necessary, rinse the sensor again with distilled water and wait a moment. Now you can pull off the flow through cell if it has been used. Take care, that an unintentional pull off of the sensor tip is impossible. After this you can switch off the power



supply. If requested, now you can also disconnect the cables. Don't forget to protect the sensor tip with the plastic cap for the storage .

Table 1: troubles and errors: short description, causes and possibilities of action

Problem	cause	action
adjustment of residual current takes too much time	$H_2O_2$ has passed the membrane without polarising the sensor, natural aging process	wait some more minutes for adjustment or exchange the sensor head
high residual current	organic solvent in high concentration (>20%Vol.) has passed the membrane as a gas or natural aging or overstress	compensate the offset and/or exchange the sensor tip
decreasing signal resolution	natural aging or precipitations at the membrane	rinse the sensor carefully with distilled water, if necessary dive in the sensor for 1 hour into 0,5 M acidic acid, new calibration or exchange the sensor tip
overflow at the display	short circuit sensor tip damaged concentration is much to high	dry the plug and socket on air at temperatures below 30°C and check the residual current, if the residual current is to high exchange cable and connectors exchange the sensor head dilute with water
fast signal drift	concentration gradients in the solution, natural aging of the sensor, electric fields or magnetic effects, glass body inside destroyed	use a stirrer or mixing unit exchange the sensor tip, switch off interfering devices, exchange the sensor tip

**Attention ! If  $H_2O_2$  permeates through the membrane without polarising the sensor, a decrease of the sensors slope and signal resolution may appear. Avoid a mechanical damage of the sensor tip ! Repair work caused by this is not covered by the guarantee !**

### 3.2.5 Exchange of sensor tips

This sensor allows a very simple exchange of sensor tips and therefore the use of a sensor with an optimised concentration range. The standard type is:

type I: 0,02...10%  $H_2O_2$

But not only  $H_2O_2$  measurements are possible. If you order an AMT-oxygen-sensor tip too, you have the possibility to change between the analyte  $O_2$  and  $H_2O_2$  without any new electronic or mechanic adjustments. Additionally you can also order  $H_2S$  sensor tips.

For exchanging the sensor tips please act as follows:

Dry the sensor first some minutes on air. Pull off the old sensor tip (not screw !) carefully and avoid the get in of water into the plug or socket. Plug in the new sensor tip considering the two red points on the socket and on the plug (have to be opposite to each other). Take care that there is a noticeable click in to place. Otherwise there is a danger of get in of water (sensor may be damaged !) leading to a loss of the guarantee.

## 4 Maintenance

The sensor is maintenance-free, if it is carefully rinsed with distilled water after every measurement. But you should store the sensor protected with the plastic cap, if it is not used for a longer time. Make sure, that no  $H_2O_2$  or vapours of organic compounds can permeate into the sensor.

Mechanical stress of the sensor body and of the sensor tip, especially cross forces have to be avoided to avoid mechanical damages.

The integration of the sensor or the measuring device into other measuring systems is possible only on own risk.