

**Amperometric micro-sensor for the *in-situ*  
determination of dissolved hydrogen**

**H2-L**



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## 1 Preface

The amperometric H<sub>2</sub> micro-sensor has been developed for the *in-situ* determination of dissolved hydrogen containing aqueous solutions. Therefore the sensor is suitable for direct measurements in coloured and turbid solutions. Special applications are the measurement in the condensate of compost factories and in power stations, but also in the chemical industry to follow chemical reactions. Compared with all the other commercially available hydrogen sensors this amperometric hydrogen micro-sensor works with such a *low analyte consumption*, that streaming of the sensor membrane or stirring of the analyte is not necessary. And, an additional stirrer is not necessary for stationary measurements. The second advantage of the micro-sensor compared to other H<sub>2</sub> sensors is the *very fast response time* of the AMT hydrogen microsensor with t<sub>90%</sub> below 2 seconds compared with a minimum of approximately 30 to 120 seconds in the case of the conventional sensors. The third advantage of the micro-sensor is based on the micro-sensor technology itself. The signal stability of amperometric hydrogen micro-sensors is essential better. And the *high local signal resolution* allows some new applications, as for instance the profiling in µm-steps. Besides, measurements in soft sediments or muds became also practicable. But such measurements are on your own risk. Mechanical damage of the sensor tip is not covered by the guarantee.

Please take note, that the sensor delivers only the raw data (mV) and that you have to use a temperature sensor for temperature measurements in order to compensate the H<sub>2</sub> sensor's temperature dependence.

**Note: This manual may vary in details depending on the special OEM-version you have ordered !**

**The perfect functioning and operational safety of the sensor can only be ensured if the user observes the safety precautions as well as the specific safety guide-lines stated in the present operating instruction.**

## 2 Technical Data

### Amperometric Hydrogen Micro-sensor

- ☞ measuring principle: amperometric membrane covered micro-sensor
- ☞ 3 sensor electrodes
- ☞ exchangeable sensor head
- ☞ necessary time for the first polarisation: approx. 45-60 minutes
- ☞ streaming of the membrane or stirring is not necessary, low analyte consumption
- ☞ suitable for the determination of concentration gradients with high local resolution
- ☞ measuring ranges: 0,0005....1 mg/l H<sub>2</sub>  
others on request
- ☞ accuracy of the sensor: better than 2% of the measuring value
- ☞ temperature range: 0°C to 30°C (for storage and measurement)
- ☞ response times: t<sub>90%</sub>: below 2 seconds
- ☞ average life time: approximately 6-10 months, influenced by the samples matrix
- ☞ pressure stability: up to 10 bar (if connector is not integrated in the pressure system)
- ☞ housing: made of titanium

\*) Changes for technical improvement are reserved.

## 3 Operation

### 3.1 Putting into operation, residual current

Please check up the link between sensor head and the housing always before every putting into operation. This link has to be absolutely watertight. If the sensor was immersed into a solution without correct interfacing, the sensor and/or the electronic board may be damaged. In this case the repair isn't covered by the guarantee.

For putting into operation first realise all the electrical connections. Please be carefully and check up, if the link between the sensor socket and plug is waterproof. If you switch on the power supply, the sensor will be polarised automatically and it will take the first time (or after long breaks) up to 60 minutes to reach the residual current. Put the sensor into a hydrogen free solution at room temperature and wait for the adjustment of the residual current (U<sub>G</sub>). Do never forget to subtract the residual current U<sub>G</sub> from the measuring value. The determination of the U<sub>G</sub> on air is not recommended !

## 3.2 Measurement

### General

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 “measuring current” at the display (U)
- subtract the residual current (U<sub>G</sub>), which has to be determined in water (not air) before starting with measurements
- calculate the concentration as follows:

$$c_{H_2} = a_{20^\circ C} \times (U - U_G) \times E_T$$

$c_{H_2}$  dissolved hydrogen amount (unit depends on unit for  $a_{20^\circ C}$ )

$E_T$  temperature correction factor (see calibration sheet last page)

$a_{20^\circ C}$  sensor slope at 20°C (mg/l : mV)

$U - U_G$  measuring value – residual current

#### 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 on 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. Now start slowly with pumping the solution through the cell. As flow rate we recommend 1-5 ml/min. When filling the flow through cell the first time, take care, that no gas bubbles are enclosed in the flow through cell. Therefore turn round the flow through cell for some seconds, so that the solution output is up. Please take not, 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> concentration, on the flow rate, on the wall saturation with hydrogen and on the measuring breaks.

Calculate now the concentration as follows:

$$c_{H_2} = a_{20^\circ C} \times (U - U_G) \times E_T$$

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$c_{H_2}$	dissolved hydrogen amount (unit depends on unit for $a_{20^\circ\text{C}}$ )
$E_T$	temperature correction factor (see calibration sheet last page)
$a_{20^\circ\text{C}}$	sensor slope at 20°C (mg/l : mV)
$U-U_G$	measuring value – residual current
3.3	Calibration

### Fundamental

For accurate measurements an accurate calibration is required. The frequency of calibration depends on the demands concerning accuracy. We offer calibration as service by means of an electrochemical generator for the online generation of dissolved hydrogen standard solutions. Apart from this, every delivered new sensor is calibrated, provided that a calibrated sensor was ordered. A check up of the calibration/sensor slope is recommended after 120 measuring hours, or after long breaks of some weeks.

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 for the temperature compensation ( $E_T$ ).

If your sensor is not calibrated, first you have to determine the sensor slope  $a_{20^\circ\text{C}}$  before starting with measurements. In addition - if it's not possible for you to calibrate at the measuring temperature, the temperature correction factors ( $E_T$ ) for your special temperature range have to be determined. For that 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) an H<sub>2</sub>-solution with a constant concentration through the cell. If the flow through cell is immersed completely into cold water or ice water - a slow increase of temperature is realised and you can read the value at every temperature for a constant concentration at the display. After this a simple calculation of  $E_T$  is possible.

### Calibration

- insert the sensor into the flow through cell (please order extra)
- connect 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 into a waste bottle
- pump the solution through the cell (recommended: 0,8...1,2 ml/min)
- read about 5 different current-concentration pairs (within the range 0...1,000 mV)
- Do not forget to subtract the residual current from the measured current !
- read the value for the temperature of the solution
- calculate the slope at the measuring temperature (mg/l : mV =  $a_{T_m}$ ) after linear regression
- use the correct  $E_T$  (= temperature correction factor according to the enclosed table or to the determined  $E_T$ 's)
- calculate the  $a_{20^\circ\text{C}}$  - value by means of equation 1:

$$a_{20^{\circ}\text{C}} = \frac{a_{T_m}}{E_T} \quad (1)$$

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

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

### 3.4 Temperature dependence

Every electrochemical sensor shows a dependence of temperature. That means, that the sensor signal changes with temperature changes too, although the concentration is still the same. The amperometric H<sub>2</sub> sensor works at temperature ranges of 0 ... 30°C. Please note, that temperature changes of some degrees may lead to some short troubles caused by equilibrium interferences inside the sensor. In this case please wait some seconds and go on after a new adjustment. The temperature has to be measured or has to be known for every H<sub>2</sub> determination.

If a calibrated sensor has been ordered, for every temperature you will find a temperature correction factor ( $E_T$ ) on the last page of this operating instructions. On this calibration sheet you will also find a mathematical equation with the coefficients  $a_{0...3}$ , which you have to use to calculate  $E_T$  accurately. For lower demands you can also use the  $E_T$  table on the calibration sheet.

### 3.5 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> without polarising 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 60 minutes without any traces of H<sub>2</sub> around the sensor tip), this is caused by the fact, that H<sub>2</sub> has passed the sensor membrane without polarising the sensor. Another characteristic after long H<sub>2</sub> uptake is an essential higher residual current.

Caused by natural aging the sensor slope decreases within the sensors life. Therefore we recommend calibration intervals depending on the demanding of 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 ?) and sensor housing and cable before starting with measurements. This is necessary after long breaks and of course after exchange of the sensor head. If water comes between sensor/sensor head and/or sensor/cable this may lead to short circuits of the electrodes 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 device, no more than 30°C). Please check the residual current from time to time and decide, if the sensor could be used again.

Although the sensor contains an integrated electronic device to minimise 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 them if possible. Please note too, that measurements in air or in other gases are impossible because the signals become very instable caused by the moist sensor tip.

Most of the "troubles" during measurements are not caused by the sensor itself, but more by the high reactivity of H<sub>2</sub> solutions. Some "troubles" are due to the fact of inhomogeneous solutions (e.g. concentration gradient in beakers, hydrogen springs). Please avoid too the existence of a gaseous phase above your analyte solution

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 --> could leading to fast decreasing signals, negative values are possible !; cold --> warm leading to fast increasing signals). It will take the sensor now some minutes to return to the real value because the equilibriums inside the sensor adjust again.

## 4 Switching off

After measurements have been finished rinse off the sensor tip with distilled water. Dive the still polarised sensor with its sensor head tip after this approximately 5 minutes in a H<sub>2</sub> free solution (e.g. distilled water). Check up, if the sensor has reached again the residual current. If necessary, rinse the sensor again with distilled water. Now you can pull off the flow through cell, if it has been used. Then you can switch off the power supply.

**Attention ! If H<sub>2</sub> permeates through the membrane without polarising the sensor, a decrease of the sensors slope and signal resolution may appear. A damage of the sensor is also possible ! Repair work caused by this is not covered by the guarantee !**

## 5 Exchange of sensor heads

This sensor allows a very simple exchange of the sensor head. But not only H<sub>2</sub> measurements are possible. If you order an AMT-oxygen-sensor head too, you have the possibility to change between O<sub>2</sub> and H<sub>2</sub> sensor head without any new electronic or mechanic adjustments.

For exchanging the sensor head please act as follows:

Dry the sensor (**not the glassy sensor tip, do never touch the glassy tip**) first some minutes on air. Pull off the old sensor head (not screw !) carefully and avoid the get in of water into the plug and socket. Plug in the new sensor head considering that the red points on plug and socket are faced each other. Take care that there is a noticeable click in to place. Otherwise there is a danger of getting in of water (sensor may be damaged !). This leads to a loss of guarantee.



## **6 Maintenance**

Mechanical stress of the sensor body and of the sensor tip, especially cross forces have to be avoided. That's why the sensor body is protected by a titanium safety cap with three holes.

The integration of the sensor or the measuring device into other measuring systems is possible only by one's own risk. There is no warranty for electrical and mechanical damages.

The sensor is maintenance-free, if it is carefully rinsed with distilled water after every measurement. But you should store the sensor protected, if it is not used for a longer time. Make sure, that no H<sub>2</sub> or vapours of organic compounds can permeate into the sensor.