Amperometric Hydrogen Microsensor for external interfacing to probe systems

- Operating Instruction 100 m/100 dbar version -

Exclusively Distributed & Supported By:

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1 Preface

This amperometric AMT-H_2-microsensor has been developed above all for the very fast *in-situ* and *online* measurement of dissolved hydrogen and for watching hydrogen concentrations in industrial applications. For measuring the hydrogen concentration the sensor has to be combined with a temperature measurement, which is not included in the delivery. Interfacing cables (IL4F) are available in several lengths on customers request.

The working principle of the sensor could be explained simlpy as follows: Because of the partial pressure of the gaseous H_2, the analyte is separated by permeation through the membrane. Inside the sensor the hydrogen reacts electrochemically at the working electrode. This causes a current corresponding to the partial pressure of the dissolved hydrogen.

The sensor has very short response times of approx. 2 seconds for $t_{90\%}$. So, the response times depend above all on the concentration exchange time near the sensor membrane. Streaming of the membrane - as it is well-known from all the other membrane covered electrochemical sensors - is not necessary. Due to the microsensor technology measurements with high local resolutions of some micrometers are possible. Both turbid and coloured solutions do not interfere with the signal.

The hydrogen microsensor can be used in water depths of up to 100 m resp. 100 dbar pressure. The sensor includes an integrated electronic device for the transformation of the sensor current into a voltage of 0...+ 3 V (DC). The required power supply is 9...30 V DC.

All sensors are delivered with sensor slope, temperature compensation data and mathematical formulas for calculating the hydrogen concentration. The exchange of sensor heads is very easy and could be done by the customer itself. The alternative exchange tip for dissolved oxygen extends the sensors flexibility.

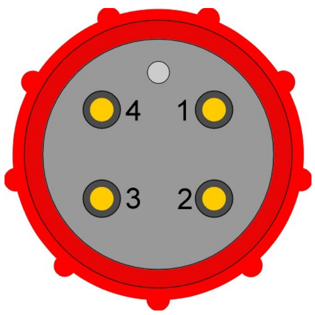
The perfect functioning and operational safety of the sensor can only be ensured if the user observes the safety precautions as well as the specific safety guidelines stated in the present operating instruction.

2 Technical Data*)

sensor type:	amperometric membrane covered microsensor
power supply:	9 ... 30 V DC (not included)
polarisation time:	approx. 60 minutes first time after switching on, less in case of only short brakes
streaming of the membrane:	not necessary
stirring of the analyte:	not necessary
output:	0 ... + 3 V DC
connector:	Subconn BH4MP (= standard, others on request)
materials:	titanium (housing), silicone (membrane), glass (sensor), epoxy resin
dimensions:	total length (incl. connector): 262 mm diameter housing with electronic device: 20 mm outer diameter nut: 24 mm outer diameter sensor head: 13 mm (without o-ring)
concentration range:	0-0.5 mg/l H_2 or 0-1 mg/l H_2 or 0-2 mg/l H_2 or 0-3 mg/l H_2 as selected when ordering
accuracy:	± 2% (measuring value)
pressure range:	up to 100 dbar
temperature range:	0°C ... 30°C (standard for measurement and storage) 0°C ... 40°C (on special request)
response time ($t_{90\%}$):	approx. 2 seconds
life time:	approx. 6-10 months depending on the application
signal interferences:	H_2S (sensor may be destroyed)
special features:	exchangeable sensor head (hydrogen or oxygen), integrated electronic device for transformation of pA-currents into 0 ... + 3 V DC

*)Changes for technical improvement are reserved.

Sensor's pin assignment (=sensor's plug view):



Pin 1: ground

Pin 2: not connected

Pin 3: H_2-signal output: 0 ... +3 V DC

Pin 4: power supply 9 ... +30 V DC

3 Structure of the H_2 micro-sensor

Subconn Connector

Titanium Housing with Electronics

Screw

Sensor Head with Titanium Housing
(=replacement part)

Sensitive Part for Measuring

4 Putting into operation

For putting into operation please act as follows:

1. Check your plug connections at your probe system/pig tail and compare with the plug connections of the sensor as described in chapter 2.
2. Moisten the sensor plug and link it with your probe system or pig tail adapter.
3. Switch on the power supply and dive the sensor into hydrogen-free water (e.g. Tap water or destilled water)
4. Please follow the polarisation for approximately 45-60 minutes and write down the “zero-voltage”, called U_G. The sensor is now ready for measurements.

Attention ! Make sure that the glassy tip will not be destroyed mechanically by handling.

5 Measurement and calibration

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 "measuring value" at the display (=U)
- Subtract the residual current (U_G), which has to be determined in water (not air) before starting with measurements (see chapter 4: Putting into operation)
- Calculate the hydrogen concentration as follows:

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

c_{H_2} dissolved hydrogen concentration (unit depends on unit for $a_{20°C}$)
E_T temperature correction factor (see calibration sheet last page)
$a_{20°C}$ sensor slope at 20°C
U-U_G measuring value minus "zero voltage"

2. flow through measurement

Insert the sensor into the flow through cell (please order extra) in a manner, that the long hole of the microsensor's 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 a steady state. This adjustment time depends on the H_2 concentration, on the flow rate and on the measuring breaks. A general rule is, that you have to change the volume of the cell 5 times until the adjustment. In case of trace amounts it may take some more time.

Calculate now the hydrogen concentration as follows:

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

c_{H_2} dissolved hydrogen concentration (unit depends on unit for $a_{20°C}$)
E_T temperature correction factor (see calibration sheet last page)
$a_{20°C}$ sensor slope at 20°C
U-U_G measuring value minus "zero voltage"

Calibration

For accurate measurements an accurate and periodical calibration is required. The frequency of the 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, new sensors are delivered 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 ordered a calibrated sensor, you will find at the end of this brochure the sensor slope $a_{20°C}$ and the factors for the temperature compensation (E_T). There is also a formula which allows to calculate any E_T at any temperature.

Self calibration – temperature/slope

If your sensor is not calibrated, first you have to determine the sensor slope $a_{20°C}$ 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_2-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 with time (or by means of very slow heating) is realised. You can read the measuring value at any temperature for a constant concentration at the display. After this a simple calculation of E_T is possible.

For determining the sensor slope please act as follows:

- 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 calibration solution through the cell (recommended: 1-3 ml/min)
- read about 5 different current-concentration pairs (within the range 0...800 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_{Tm}) 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 $a_{20°C}$ - value by means of equation 1:

$$a_{20^\circ C} = \frac{a_{Tm}}{E_T} \qquad (1)$$

a_{Tm} = sensor slope at measuring temperature; $a_{20°C}$ = sensor slope at 20°C.

For a check up of the sensor slope $a_{20°C}$ act as described before.

Calibration as service is also available from the manufacturer within 1-3 days (plus shipment time).

6 Maintenance

Mechanical stress of the sensor tip, especially cross forces, unintentional touch downs or strong vibrations have to be avoided. The sensor tip is very weak. Do not touch it. Mechanical damage of the sensor tip excludes that the repair is covered by the guarantee.

For cleaning the sensor head rinse it in destilled water (if not available, you can take also tap water) only. Do not use organic solvents like aceton or anything like this. If there should be any bio fouling at the sensor tip, it is recommended to clean the sensor tip by immersing it into diluted H_2SO_4 (less than 0,5 mol/l) or diluted NaOH (less than 0,02 mol/l) up to maximum of 24 hours.

Protect the sensor tip with the wetting cap during long breaks. Fill the wetting cap with less than ¼ with distilled water. This saves time, if you start the measurements again, because the membrane has to be conditioned in water for some minutes, if it was dryed out.