
Amperometric Hydrogen micro-sensor

Determination of dissolved hydrogen in aqueous solutions

The amperometric H₂ micro-sensor has been developed for the *insitu* determination of hydrogen containing aqueous solutions. Therefore the sensor is suitable for direct measurements in coloured and turbid solutions and in sediments. Special applications of the sensor are the measurement in deep sea volcanic areas, measurements 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 microsensor 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 H₂ sensors is the *very fast response time* of the AMT hydrogen microsensor with $t_{90\%}$ 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 new micro-sensor is based on the micro-sensor technology. The signal stability of amperometric hydrogen microsensors 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.

The general working principle of the sensor

Because of the partial pressure of the gaseous H₂ dissolved in the sample, the analyte is separated from the inner electrolyte by the membrane. The *membrane is only pervious to gases*, so that liquids, ions and solids are not able to reach the inner electrolyte or the electrodes of the sensor. The sensor contains inside a special electrolyte and 3 electrodes. The electrode materials have been chosen and prepared very carefully to realize ideal electrochemical conditions. The time for the polarization, realized by means of the sensors integrated electronic device, is approximately 15 to 30 minutes after the first switching or long breaks. If the hydrogen has passed now the membrane, it is transported by diffusion to the working electrode followed by the electrochemically oxidation of the H₂. This causes a current depending on the hydrogen partial pressure/hydrogen concentration of the sample. The observed current within a range of 0...400 picoamperes is converted into a voltage of 0...5 Volt inside the integrated electronic device of the sensor. Besides, in opposite to other measuring principles, the current flow in the amperometric sensor leads to a rapid decrease of the analyte inside the sensor resulting in *very fast response times* even though there is a concentration jump from high to low concentrations.

All electrochemically working sensors have to be combined with a temperature measurement and the amperometric hydrogen sensor too. When ordering a multisensor measuring system for laboratory use or a complete submersible probe system, the temperature measurement and the temperature correction of the sensor signal is already included. If measurements in a flow through system are required, special temperature sensors for the integration in AMT flow through cells are offered. When measuring in opened vessels or beakers in the laboratory, the customers have to realize the temperature measurement themselves. If a calibrated sensor is ordered, the temperature correction is very easy by means of a factor or for more accurate measurements by means of a mathematical formula, delivered with the sensor.

The advantages of the micro-sensor technology

For manufacturing the amperometric H₂ sensor a special geometric design has been chosen to build a real **micro-sensor**. Electrode diameters below 25 µm, a very thin special membrane with small diameters, extremely short diffusion distances for the hydrogen to the working electrode and a negligible analyte consumption at the electrodes leading finally to *response times (t_{90%}) of less than 2 seconds*. The *analyte consumption effects are negligible* too, so that *streaming of the sensor membrane and stirring is not necessary*. Besides, the dimensions of the sensitive tips within a range of some micrometers allow *insitu* measurements without destroying equilibriums, concentration gradients and geometrical structures. This is very important, if measurements in muddy sediments are required.

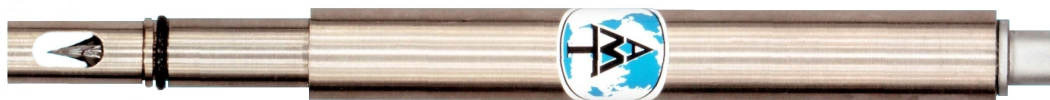
Technical data for all H₂-micro-sensor heads independent from the sensordesign *)

- ☞ measuring principle: amperometric membrane covered microsensor
- ☞ 3 sensor electrodes
- ☞ exchangeable sensor head
- ☞ necessary time for the first polarization: approx. 15-30 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: 0,0002.....3 mg/l H₂
others on request
- ☞ accuracy of the sensor:: better than 2% of the measuring value
- ☞ temperature range: 0°C to 30°C
- ☞ response times: t_{90%}: below 2 seconds
- ☞ average life time: approximately 6-10 months, may be influenced by the samples matrix
- ☞ pressure stability: laboratory sensor or
shallow water version for pressures of up to 10 bar or
- ☞ housing: all housings made of titanium

*) Changes for technical improvement are reserved.

Sensor designs of amperometric H₂ micro-sensors

1.) *Laboratory microsensor with integrated electronic device*



This sensor has been developed for the laboratory and simple field use and has to be combined with one of the offered measuring devices. The sensor consists of a titanium housing, a waterproof connection with the cable (IP 68), an exchangeable sensor head and a removable protection cage (on your own risk - no guarantee in the case of mechanical destruction). This sensor could be equipped both with the hydrogen sensor head and with a galvanic oxygen sensor head. Other concentration ranges can be delivered on request. The exchange of the sensor head is very easy by pull off and push on. Please take note, that no liquid can get in to the plug connection when changing the sensor head.

2.) *Shallow water microsensor for probe systems*



The shallow water sensor has been developed for use in combination with so called CTD-probe systems up to depths of 70 meters. Therefore every shallow water sensor is equipped with a special underwater connector, type wet con BH-4-MP. Further characteristics are the integrated electronic device, the titanium housing and the exchangeable sensor head. This sensor could be equipped both with the hydrogen sensor head and with a galvanic oxygen sensor head. Other concentration ranges can be delivered on request. The exchange of the sensor head is very easy by pull off and push on. Please take note, that no liquid can get in to the plug connection when changing the sensor head.

Use of amperometric H₂ micro-sensors

1. Laboratory use:
 - laboratory sensor with integrated electronic device
 - + measuring device with cable
 - + temperature sensor

2. Field measurements
(up to 1 m water depth):
 - a) laboratory sensor with integrated electronic device
 - + measuring device with cable
 - + temperature sensor
 - b) H₂-probe with sensors for H₂ (shallow water version), pressure (depth), temperature
 - + multi-core sea-cable
 - + notebook/personal computer
 - + software

3. Online insitu measurements
(up to 100 meter water depth)
 - a) H₂-probe with sensors for H₂ (shallow water version), pressure (depth), temperature
 - + multi-core sea-cable
 - + notebook/personal computer
 - + software or
 - b) Interfacing of a H₂ shallow water sensor to already existing probe systems, provided that the probe system contains one more free channel and is quipped already with sensors for temperature and pressure
 - + integration of the mathematical formula for the calculation of the dissolved hydrogen amount into the probe's software