Galvanic Oxygen Micro-sensor

Determination of dissolved oxygen in aqueous solutions

The galvanic O_2 micro-sensor has been developed for the *insitu* determination of oxygen containing aqueous solution. Therefore the sensor is suitable for direct measurements in lakes, estuarines, rivers, oceans and sediments. Compared with all the other commercially available oxygen sensors this galvanic oxygen micro-sensor works with such a *low analyte consumption*, that streaming of the sensor membrane or stirring of the analyte is not necessary. Therefore an additional stirrer is not necessary for stationary measurements. The second main difference to other DO sensors is the *very fast response time* of the galvanic oxygen micro-sensor produced by AMT with $t_{90\%}$ down to 200 milliseconds compared with approximately 6 to 20 seconds in the case of the conventional sensors. The third advantage of the new micro-sensor is founded in the micro-sensor technology. Galvanic oxygen micro-sensors are working with a *high local resolution* and allow profiling with µm-steps. Therefore also measurements in soft sediments or mud became practicable.

The general working principle of the sensor

Because of the partial pressure of gaseous O_2 dissolved in the sample the analyte is separated by permeation through the membrane. The *membrane is only pervious to gases*, so that liquids, ions and solids are not able to reach the inner electrolyte of the sensor. Inside the sensor contains a buffered solution and 3 electrodes. The electrode materials are selected carefully to realize a *self polarization* for requested electrochemical reduction of oxygen at the working electrode surface. Therefore essential shorter times for putting into operation after switching on are observed compared with the normally delivered amperometric sensors. If the O_2 passes now the membrane, the oxygen is transported by diffusion to the working electrode followed by the electrochemically reduction of the O_2. This causes a current depending on the oxygen partial pressure/oxygen concentration of the analyte. The observed very small current within a range of some hundred picoamperes is converted into a voltage of 0...5 Volt (main working range: 0...1,500 mV) inside the integrated electronic device of the sensor. Besides, the current flow in the galvanic sensor leads to a rapid decrease of the analyte inside the sensor resulting in *very fast response times.* This is also observed, if a rapid change from high to very low concentration levels is necessary.

All electrochemically working oxygen sensors have to be combined with a temperature sensor. When ordering a complete AMT 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 sensor with temperature compensation data is ordered, the temperature correction of the signal is very easy by means of a factor or for more accurate measurements by means of a mathematical formula.

The advantages of the micro-sensor technology

For manufacturing the galvanic O_2 sensor a special geometric design has been selected to built a real **micro-sensor**. Electrode diameters below 25 µm, a very thin special membrane with small diameters, extreme short diffusion distances for the oxygen to the working electrode and a negligible analyte consumption on the electrodes are leading finally to *response times ($t_{90\%}$) of down to 200 milliseconds*. The *analyte consumption effects are negligible* too, so that s*treaming 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 or biofilms are required.

Technical data of all O_2 micro-sensor heads independent from the sensor design *)

- measuring principle: galvanic, selfpolarizing and membrane covered sensor
- 3 sensor electrodes
- ready for putting into operation immediately after switching on,
  waiting time only for adjustment of temperature and oxygen equilibriums
- streaming of the membrane or stirring of the analyte is not necessary because of very low analyte consumption
- usuable for profiling with a high local concentration resolution
- concentration range: 0...200% O_2 saturation (standard),
  other ranges on request
- accuracy: better than 2% of the measuring value
- concentration/saturation resolution: variable, e.g. 0,1% saturation
- temperature range: 0°C .... 30°C
- response times: $t_{90\%}$: down to 200 milliseconds
  (remarks: The response times noticed at the display of a following electronic or measuring device, could appear longer than the real response times of the sensor caused by electronic buffers. But nevertheless, the real response times of the sensor are not influenced by this fact.)
- average life time: approx. 9-18 months at 100% oxygen saturation
- no exchange of the membrane or re-filling of electrolyte
- pressure stability: up to 10 bar
- signal equivalents in presence of:
  - high CO_2 evolution (only if the membrane is streamed directly with high concentrated carbon dioxide gas): leads to local changes of the pH value in the sensor tip connected with increasing response times/equilibrium adjustments;
  - higher H_2S concentrations for long times lead to rapidly decreasing life times and sometimes to false results or to a damage of the sensor

*) Changes for technical improvement are reserved.

Sensor designs of galvanic O_2 micro-sensors

1.) Laboratory micro-sensor 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 oxygen sensor head (0...200%) and with the H_2S sensor heads type I (0,05...10 mg/l H_2S), type II (0,5...50 mg/l H_2S) and type III (0,01...3 mg/l H_2S). 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 micro-sensor for probe systems

The shallow water sensor has been developed for use in combination with so called CTD-probe systems up to depths of 100 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 oxygen sensor head (0...200%) and with the H_2S sensor heads type I (0,05...10 mg/l H_2S), type II (0,5...50 mg/l H_2S) and type III (0,01...3 mg/l H_2S). 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 galvanic O_2 micro-sensors

1. Laboratory use:

laboratory sensor with integrated electronic device
+ measuring device with cable
+ temperature sensor
+ conductivity sensor (for measurements in solutions with variable salt concentrations)

2. Field measurements (up to 1 m water depth):

a) laboratory sensor with integrated electronic device
+ measuring device with cable
+ temperature sensor
+ conductivity sensor (for measurements in solutions with variable salt concentrations)

b) O_2-probe with sensors for O_2 (shallow water version), conductivity, pressure (depth), temperature
+ multi-core sea-cable
+ notebook/personal computer
+ software

3. Online insitu measurements (up to 100 meter water depth)

a) O_2-probe with sensors for O_2 (shallow water version), conductivity, pressure (depth), temperature
+ multi-core sea-cable
+ notebook/personal computer
+ software

b) Interfacing of already existing probe systems with a O_2 shallow water sensor, provided that the probe system contains one more free channel and is equipped already with sensors for conductivity, temperature and pressure
+ integration of the mathematical formula for the calculation of the oxygen concentration/oxygen saturation into the probe's software