Amperometric Ozone micro-sensor

Determination of dissolved ozone in aqueous solutions

The amperometric O_3 micro-sensor has been developed for the *insitu* determination of ozone containing aqueous solutions. Therefore the sensor is suitable for direct measurements in coloured, turbid and solid containing solutions. Compared with all the other commercially available ozone sensors this amperometric ozone micro-sensor contains a redox catalyst and works *with a very 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 ozone sensors is the *very fast response time* of the AMT ozone micro-sensor with $t_{90\%}$ below 4,5 seconds compared with a minimum of approximately 80 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 itself. The signal stability of amperometric ozone 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.

The general working principle of the sensor

Because of the partial pressure of gaseous ozone dissolved in the sample, the analyte is separated by permeation through the membrane. The membrane is only pervious for gases, so that liquids, ions and solids are not able to reach the inner electrolyte of the sensor. The sensor contains inside an electrolyte with a redox catalyst (= redox mediator) and 3 electrodes. The electrode materials have been choosen and prepared very carefully to realize ideal electrochemical conditions. At the electrodes a special polarization voltage is adjusted to realize a well-defined concentration ratio of the oxidized and of the reduced form of the redox catalyst. The time for the polarization, realized by means of the sensors integrated electronic device is approximately 5-10 minutes. If the ozone passes now the membrane, it reacts first chemically with the redox catalyst to form a reaction product followed by the electrochemically reduction of the reaction product at the working electrode. Caused by the polarization voltage the system is now endeavoured to adjust the former concentration ratio. This causes a current similar to the dissolved ozone amount of the sample. Besides, the current flow in the amperometric sensor leads to a rapid decrease of the analyte inside the sensor resulting in *very fast response times* also, if a rapid change from high to very low concentration levels is necessary.

All electrochemically working sensors have to be combined with a temperature measurement and the amperometric ozone 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 has 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 O_3 sensor, a special geometric design has been choosen to built a real **micro-sensor**. Electrode diameters below 25 µm, a very thin special membrane with small diameters, extremly short diffusion distances to the working electrode and a negligible analyte consumption at the electrodes leading finally to *response times ($t_{90\%}$) of less than 5 seconds.* The *analyte consumption effects are negligible* too, so that s*treaming of the sensors 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 solutions are required.

Technical Data for all O_3-micro-sensor heads independent from the sensordesign *)

- measuring principle: amperometric membrane covered microsensor with redox catalyst
- 3 sensor electrodes
- exchangeable sensor head
- measuring range: 20 µg/l...10 mg/l O_3 (linear range)
  others on request
- accuracy of the sensor:: better than 2% of the measuring value
- resolution: > 2 µg/l per digit
- response times: $t_{90\%}$: below 4,5 seconds
  $t_{90\%}$: below 9 seconds
  (If the sensor is used the first time or after long breaks, a short 2 minutes long activation with a ozone concentration of approximately 0,5 mg/l is necessary.)
- pressure stability: laboratory sensor or
  shallow water version for pressures of up to 10 bar
- average life time: approximately 5-10 months, may be influenced by the samples matrix
- housing: all housings made of titanium
- polarization: necessary, switching on is realized automatically with sensor switching on
- necessary time for polarization: 5-10 minutes
- residual current: approx. 1-5 pA, temperature independent,
  changes not within the sensors life
- temperature range: -2°C to 30°C
- signal interferences: not against oxygen and chlorine, but signal interferences against H_2O_2 if the concentration is more than 2 Vol.%
- streaming of the membrane or stirring is not necessary, low analyte consumption
- suitable for the determination of concentration gradients with high local resolution

*) Changes for technical improvement are reserved.

Sensor designs of amperometric ozone micro-sensors

1.) Laboratory microsensor with integrated electronic device

This sensor has been developed for 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 ozone 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 100 meters and for applications with up to 10 bar pressure. 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 ozone 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 ozone micro-sensors

1. Laboratory use: laboratory sensor with integrated electronic device
+ simple or multisensor measuring device with cable
+ temperature sensor

2. Field measurements (up to 1 m water depth):
a) laboratory sensor with integrated electronic device
+ simple or multisensor measuring device with cable
+ temperature sensor or
b) submersible probe with sensors for O_3 (shallow water version), temperature, pressure (depth)
+ cable
+ notebook/personal computer
+ software

3. Online insitu measurements (up to 100 meter water depth)
a) submersible probe with sensors for O_3 (shallow water version), pressure (depth), temperature
+ cable
+ notebook/personal computer
+ software
b) Interfacing of already existing probe systems with a O_3 shallow water sensor, provided that the probe system contains one more free channel and is equipped already with sensors for temperature and pressure
+ integration of the mathematical formula for the calculation of the hydrogen concentration into the probe's software