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

O3-L Manual

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1 Preface

This amperometric AMT ozone micro-sensor has been developed above all for the very fast *in-situ* and *online* measurement of ozone and for watching ozone concentrations in industrial applications. For measuring the ozone concentration the sensor has to be combined with a temperature measurement, which is not included in the delivery. Interfacing cables 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 ozone, the analyte is separated by permeation through the membrane. Inside the sensor the ozone reacts electrochemically at the working electrode. This causes a current corresponding to the partial pressure of the dissolved ozone.

Streaming of the membrane - as it is well-known from all the other membrane covered electrochemical sensors - is not necessary. Due to the micro-sensor technology measurements with high local resolutions of some micrometers are possible. Both turbid and coloured solutions do not interfere with the signal.

The ozone micro-sensor 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 main working range is mostly between 0 and 1 V DC output. The required stabilized power supply is 9...30 V DC.

All sensors are delivered with sensor slope, temperature compensation data and mathematical formulas for calculating the ozone concentration. The exchange of sensor tips is very easy and could be done by the customer himself. The alternative measurement of dissolved oxygen with a separate DO sensor tip extends the sensors flexibility.

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 O_3 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 ozone Micro-sensor

sensor type:	amperometric membrane covered micro-sensor
power supply:	9 ... 30 V DC (not included)
polarisation time:	approx. 10-20 minutes after switching on, less in case of only short brakes, more in case of natural aged sensors
streaming of the membrane:	not necessary
stirring of the analyte:	not necessary
output:	0 ... + 3 V DC (main working range approximately 0...1 V DC)
materials:	titanium (housing), silicone (membrane), glass (sensor), epoxy resin
concentration range:	0,02....10 mg/l ozone (standard, others on request)
accuracy:	± 2% (measuring value)
pressure range:	up to 100 dbar
temperature range:	0°C ... 30°C (for measurement and storage)
life time:	approx. 6-10 months depending on the application
signal interferences:	H_2S
special features:	exchangeable sensor tip (dissolved oxygen), integrated electronic device for transformation of pA-currents into 0 ... + 3 V DC
temperature dependence:	additional temperature measurement required

*) 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. Use the additional sheet delivered with the sensor. Please be carefully and check, 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 20 minutes to reach the residual current. Put the sensor into an ozone-free solution at room temperature and wait for the adjustment of the residual current (U_G). Do never forget to subtract the residual current U_G from the measuring value. The determination of the U_G 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_G), which has to be determined in water (not air) before starting with measurements
- calculate the concentration as follows:

$$c_{O_3} = a_{20^\circ C} \times (U - U_G) \times E_T$$

c_{O_3}	dissolved ozone amount (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 (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 ozone concentration, on the flow rate, on the wall saturation with ozone and on the measuring breaks.

Calculate now the concentration as follows:

$$c_{O_3} = a_{20^\circ C} \times (U - U_G) \times E_T$$

c_{O_3} dissolved ozone 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 (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 ozone 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 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).

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 (1...5 ml/min) an ozone solution with a constant or well-known 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: 1...5 ml/min)
- read about 5 different voltage-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_{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.

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 O_3 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 O_3 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 ozone 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 the adjustment of the residual current (more than 60 minutes without any traces of ozone around the sensor tip), this is caused by the fact, that O_3 has passed the sensor membrane without polarising the sensor. Another characteristic after long O_3 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 the sensor head and the sensor housing (waterproof ?) and between the housing and the cable before starting with measurements. This is necessary after long breaks and of course after the 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, not 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 O_3 solutions. Some “troubles” are due to the fact of inhomogeneous solutions (e.g. concentration gradient in beakers, ozone 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 in the still polarised sensor with its sensor tip for approximately 5 minutes into an ozone-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 ozone 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 O_3 measurements are possible. If you order an AMT-oxygen-sensor head too, you have the possibility to change between O_2 and O_3 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 body with three holes.

The integration of the sensor or the measuring device into other measuring systems is possible only on customer's risk. There is no warranty for electrical and/or 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 ozone or vapours of organic compounds can permeate into the sensor.