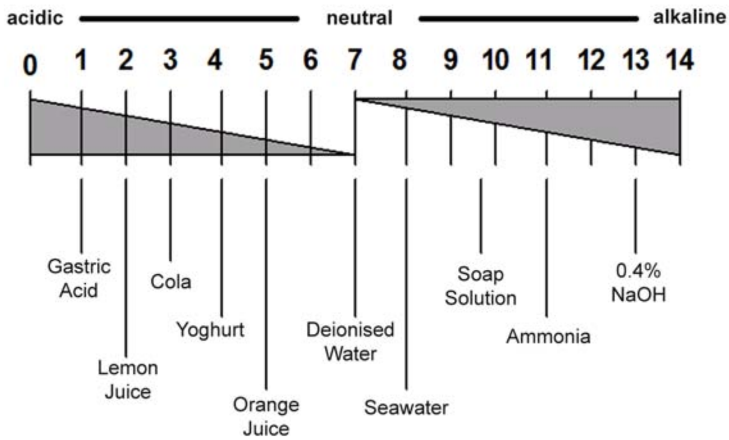
# 3.9 Chemical Probes

## 3.9.1 pH and Redox Probes

### 3.9.1.1 pH Measurement

The pH value is a logarithmic measure for the concentration of the H ions in a hydrous solution and indicates by a numerical value whether it has an acid, neutral or alkaline reaction. The pH scale ranges from pH0 to pH14, pH7 is neutral. Below are a few examples for pH values of typical substances:



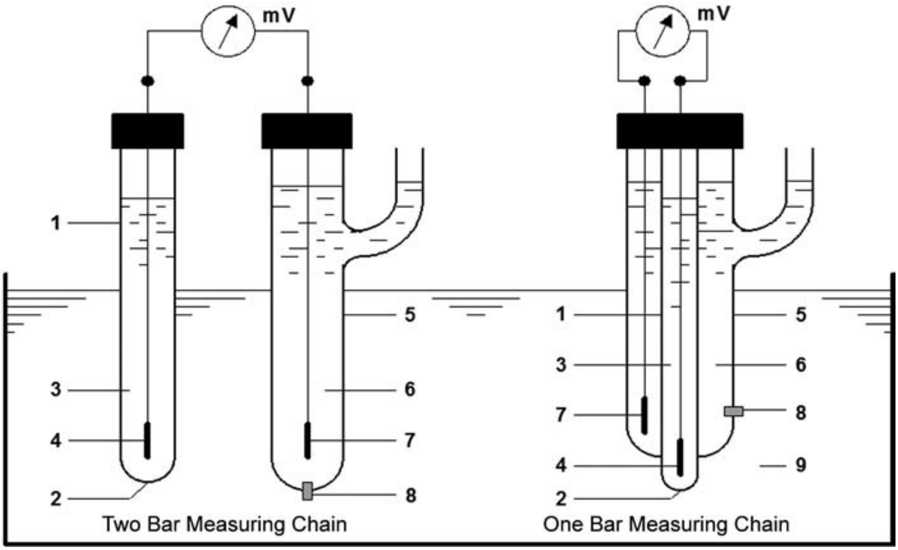

When measuring the pH value and the Redox potential the chain voltage between two electrodes is determined by potentiometric measurement.

**pH Measuring Chains**

A pH measuring chain for pH measurement always consists of a glass electrode (1) and a reference electrode (5) and is arranged either as a separated two-bar measuring chain (two single electrodes) or as a one-bar measuring chain with the latter being easier to handle.

The actual pH-sensitive sensor component is the glass membrane (2) of the glass electrode. A potential difference that occurs here corresponds to the difference in the pH value between the inner and outer side.

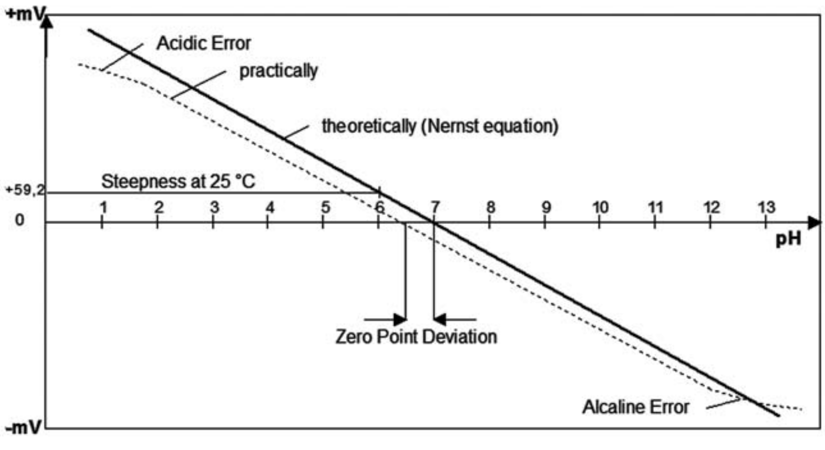
The glass electrode contains an inner electrolyte (3) that is buffered to pH7 and the inner conduction (4). The reference electrode consists of a reference electrolyte (6), the outer conduction (7) and a membrane (8), which provides the electrolytically conducting connection between the reference electrolyte (6) and the measuring solution (9).




| | | | |
|---|---|---|---|
| **pH meas. chains:** | 1 glass electrode | 5 reference electrode | 2 glass membrane |
| | 6 reference electrolyte | 3 inner electrolyte | 7 outside conduction |
| | 4 inner conduction | 8 membrane | 9 measuring solution |

**Measuring Signal**

The pH measuring signal of a pH measuring chain has its theoretical zero point at pH7 and changes at 25°C by 59.2mV if the pH of the measuring solution changes by one pH. The voltage is positive for acidic (pH0 to pH7) and negative for alkaline solutions (pH7 to pH14). The steepness increases by 0.2mV/K with rising temperatures. It decreases with decreasing temperatures.




In practice, the measuring signal of a pH measuring chain differs from the Nernst equation:

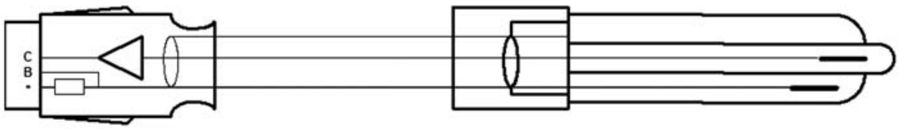
1. The real zero point slightly deviates from the theoretical pH7.
2. Due to ageing effects the steepness can be less than the theoretical value.
3. At very high pH values the steepness may decline. This is called the 'alkaline error' and depends on the glass type used for the membrane glass.
4. At very low pH values the 'acid error' may occur, i.e. the steepness may decline slightly.
5. Depending on the operating conditions, the measuring signal can be corrupted by many other influences, e.g. ageing, penetration of measuring solution into the reference electrode, depositions on the glass membrane.

☞ Because of manufacturing tolerances and various other influences, every measuring chain must be calibrated using special buffer solutions that have a defined pH value at the specified temperature.



**ALMEMO® pH Measuring System**

To avoid an invalidation of measuring signals caused by the measuring instrument, it is necessary to use measuring amplifiers with extremely high impedance (>500GΩ) for pH measuring chains. A special connecting cable (ZA 9610-AKY4, Cable with spray-coated ALMEMO® connector ), which has the required measuring amplifier integrated into the ALMEMO® connector, is available to connect all popular measuring chains with plug-on head type S7, SN6 to ALMEMO® measuring instruments. By impedance transformation and differential measurement it is also possible to acquire data from several probes that have different potentials and to transmit the data over longer distances free from disturbances.




Connecting Cable ZA9610-AKY     Coaxial Connector     Probe

The measurement is performed in the measuring range 2.6000V. For displaying the pH value with 2 digits it is necessary, according to the Nernst equation, to program the connector with the following parameters.

The connecting cables ZA 9610-AKY4 are, as standard, configured as follows:

| | | |
|---|---|---|
| Measuring range: | d2600 | |
| Dimension: | PH | |
| Slope correction: | -0.1689 | 100 (1.00pH) : 592 (59.2mV) |
| Base value: | -7.00 | |
| Exponent: | 2 | |
| Locking mode: | 5 | |

**Connection of the pH Probes**

As the system uses high-impedance signals, ensure that NO moisture can penetrate into the connector head or the transducer when screwing the pH probe to the connector head.

On connecting pH probes (dimension 'PH') to hand-held devices the following functions will be additionally activated under the function key F2:

- zero point correction
- slope correction
- temperature compensation.

By means of these functions the sensors can, by using buffer solutions, be individually calibrated in zero point and slope. If the temperature of the medium under test is different from the temperature of the buffer solution, a temperature compensation is possible. Similar to all other ALMEMO® sensors these parameters are also stored in the connector so that different pH probes with own connecting cables, can be interchanged without re-calibration.

**Calibration**

The system is operational after the ALMEMO® connector has been connected to the instrument. However, depending on the operating conditions, the probe should be re-calibrated at regular intervals. For calibrating pH probes three buffer solutions are available as accessories. The measuring accuracy is practically determined by the accuracy and purity of the buffer solution.

1. ZA 98PH-PL4: pH 4 (±0.05pH at 25°C)
2. ZA 98PH-PL7: pH 7 (±0.05pH at 25°C)
3. ZA 98PH-PL10: pH 10 (±0.05pH at 25°C)

For sensors with the dimension ´PH´ or ´pH´ an automatic zero point correction and an automatic slope correction is available. For calibration purposes the locking mode for the correction values must not be set any higher than 3. On many devices, for manual operation, the functions “zero-point” and “gain” must also be activated.

Each device has a special key combination assigned for quickly and easily activating this adjustment mode and carrying out adjustment; (see device operating instructions, “Sensor adjustment”).

*The zero point correction is always the first step, using the buffer solution pH7 !*

**Zero Point Correction:**

1. Hold pH probe in buffer solution pH7.
2. Allow for the measured value to stabilise.
3. Perform the zero point alignment (see device operating instructions).
   The zero point error is automatically stored in the connector.
   The device will display exactly " 7.00 PH".
4. Rinse the probe using distilled water, if possible.
5. Wipe the probe with a soft, 'fluff-free' paper cloth.

Do NOT rub the probe! This could lead to electrostatical charging and, consequently, to measured values being invalidated.

**Slope Correction:**

1. Hold pH probe in buffer solution pH4 for acidic or in pH10 for alkaline measuring solutions.
2. Allow for measured value to stabilise.
3. In the event of deviation from the setpoint the procedure “zero-point adjustment” should be repeated. (see device operating instructions). The slope is re-calculated and stored and the probe is then accurately adjusted.
4. Rinse and wipe the probe (see above).

If wrong buffer solutions or worn-out probes are used, the alignment might not provide accurate correction values anymore. In such cases the function 'Set measured value to zero' (see device operating instructions) can be used to re-establish the default values (slope correction -0.1689, base value -7.00).

**Measurement**

1. Immerse the probe into the measuring solution and slightly turn it.

The electrode must be immersed far enough so the membrane is well covered with measuring solution.

2. Read out and record when a stable measured value has been achieved.
3. Rinse the probe and store it wet in KCl solution.

**Temperature Compensation**

pH values are calculated based on the electrode steepness at 25°C or, after a calibration, on the steepness of the buffer solution temperature. All ALMEMO® instruments allow for a temperature compensation when the temperature of the medium under test is largely varying from the nominal temperature. With the aid of the reference channel any temperature sensor with a resolution of 0.01°C (NTC or P204) can be used for compensation purposes. However, for long-term measurements continuous updating of the measured temperature value must be ensured by a measuring point scan (cyclic or continuous).
On most devices the compensation temperature can also be entered manually; (see device operating instructions). The pH value is then compensated based on the temperature entered. The programming is described in the operating instructions of the corresponding device.

### 3.9.1.2 Redox Measurement

The level of the Redox potential (measured in mV) indicates the strength of an oxidizing or reducing reaction of a measuring solution. It allows for monitoring a variety of chemical processes (e.g. cyanide oxidation or chromate reduction). As the extermination of microorganisms (disinfection) is directly related to the strength of the oxidation (e.g. of chlorine) the Redox potential is successfully being used for monitoring disinfection processes.
The measurement is based on measuring the voltage potential of a precious metal electrode (platinum or gold) against a reference electrode. One-bar measuring chains are used as they are easier to handle than two-bar chains.
ALMEMO® Redox Measuring System
The connection cable ZA 9610-AKY5 can also be used as a transducer between Redox probes (e.g. FY96RXEK) and ALMEMO® measuring instruments. As voltages are only measured in the range ±1000mV the programming of the connectors is quite simple:

| | |
|---|---|
| Measuring range: | D2600 |
| Dimension: | mV |
| Exponent: | 3 |
| Locking mode: | 5 |

**Measurement**
After connecting the probe to the instrument, the probe is immersed in a Redox buffer solution, e.g. 220mV (Order No.: ZB98RXPL2). The value of the buffer solution should be reached or exceeded within 30 seconds. The probe must be cleaned (see 3.8.1.3) if the value is not reached within this time or if it remains more than 20mV below the reference value. If false values are still displayed after cleaning the probe, it must be replaced.

### 3.9.1.3 Handling pH and Redox Probes

**Storage of pH and Redox Probes**
The pH and Redox one-bar electrodes must only be stored in humid conditions. To ensure humid storage, fill 3-molar KCl solution into the protection cap and put it back on the probe.

**Life**
The measuring probes are subject to natural ageing, even if they are handled properly. Depending on the application, the probe life can vary between six months and three years. Certain applications, especially when extreme operating conditions are involved, can reduce the probe life to a few days.

**Cleaning and Service**
Measuring probes should be visually inspected regularly (approx. once per month) and cleaned, if necessary. If contaminations on the glass membrane cannot be removed with a damp cloth, the cleaning agents listed below may be used:

| Type of Contamination | Detergent / Effective Time |
|---|---|
| General deposits | NO domestic scouring powder |
| Lime or metal hydroxide | Aqueous hydrochloric acid (approx. 0.1% - 3%) / 1 to 5 minutes |
| Oil, grease | Solvents such as alcohol or acetone |
| Biological coating | Solution of aqueous hydrochloric acid and pepsin / several hours |

☞ In principle, the probes must be thoroughly rinsed after each cleaning process.



The metal surfaces of Redox probes can also be cleaned by grinding and polishing. If the ceramic membrane, mounted at the side of the reference electrode, is blocked due to deposits, it can be cleaned in the same way as the glass membrane. Furthermore, it can be cleaned by carefully scraping the membrane with a fingernail, razor blade or a fine file.

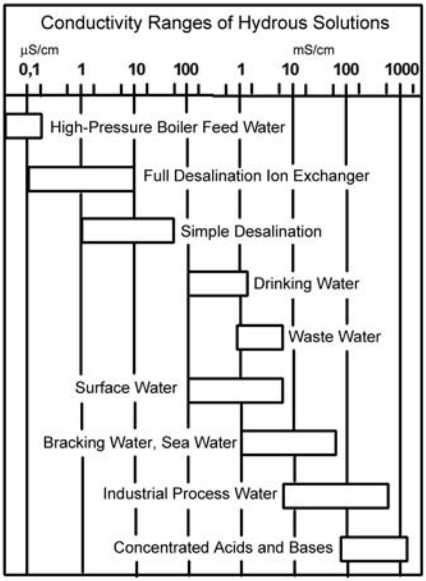
☞ The glass membrane must not be scratched during cleaning.

| **Product Overview** | | **Order No.** |
|---|---|---|
| Gel-filled, non-refillable pH electrode with shaft of synthetic material, glass fiber diaphragm,<br>Typical applications:<br>manual measurements e.g. swimming pools, drinking water | | FY96PHEK |
| Polymer-filled, non-refillable pH electrode with glass shaft, PTFE ring diaphragm, screw connection thread PG13.5<br>Typical applications:<br>Waste water, drinking water, industrial water | | FY96PHER |
| KCl-refillable pH probe with glass shaft, refill stud, ceramik diaphragm<br>Typical applications: manual measurements in the laboratory | | FY96PHEN |
| KCl-refillable pH insertion electrode with glass shaft, ceramic diaphragm<br>Typical applications: food, for example, meat, cheese | | FY96PHEE |
| Non-refillable Redox electrode with shaft of synthetic material, glass fiber diaphragm<br>Typical applications:<br>manual measurements e.g. swimming pools, drinking water | | FY96RXEK |
| KCl solution, 3-molar | ZB 98PH-NL | |
| Buffer solution, pH 4.0, coloured red | ZB 98PH-PL4 | |
| Buffer solution, pH 7.0, coloured green | ZB 98PH-PL7 | |
| Buffer solution, pH 10.0, coloured blue | ZB 98PH-PL10 | |
| Redox buffer solution 220 mV against Pt-Ag/AgCl | ZB 98RX-PL2 | |
| ALMEMO® Connecting Cable with Transducer for probes with plug-on heads S7, SN6 | | |
| programmed for pH | ZA 9610-AKY4 | |
| programmed for Redox | ZA 9610-AKY5 | |
| Technical Data of the Transducer | | |
| Input resistance: | > 1000GΩ | |
| Amplification: | 1 | |
| Potential of the reference electrode to GND: | < 2V | |
| Current consumption: | < 1mA | |
| Line length: | < 100 m | |

## 3.9.2 Conductivity Probe

### Basic principles

The conductivity (unit S/m = Siemens/meter) is a measure for the ion concentration in a measuring solution. It is proportional to the salt, acid or base content in the measuring solution. High-purity waters have a conductivity of approx. 0.05 µS/cm (at 25°C), natural waters approx. 100 to 1000 µS/cm, some bases (e.g. potassium hydroxide solutions) up to slightly more than 1200 mS/cm.
The diagram on the left shows further examples of aqueous solutions relevant for measurements

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### Standardization

The method for determining the electrical conductivity of water is defined in DIN EN 27 888.

### Temperature compensation

Conductivity is a temperature-dependent variable. For most diluted, aqueous salt solutions and natural water within a certain temperature range conductivity is a virtually linear function of temperature T.

$$\kappa_T = \kappa_{25}\left(1 + \alpha \frac{(T - 25\,°C)}{100}\right)$$

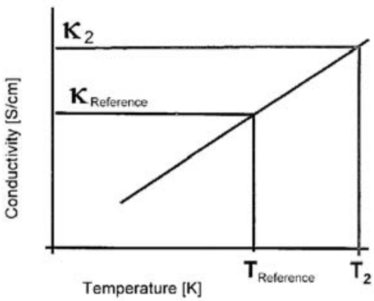
Conductivity, at reference temperature 25°C κ25, is calculated as follows:

$$\kappa_{25} = \frac{\kappa_T}{1 + \alpha \frac{(T - 25)}{100}}$$

The temperature coefficient. describes the relative change in conductivity as the temperature changes with respect to the reference temperature of 25°C.

Definition of α [ %/K ]:

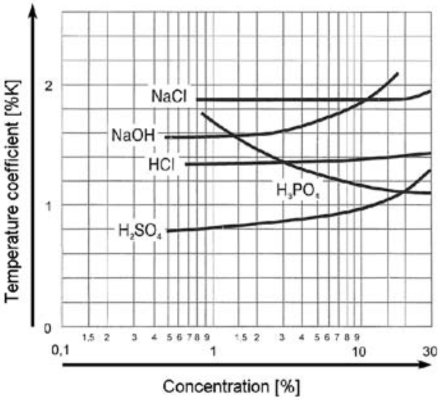
- Change in conductivity in % as the temperature increases by 1K, with respect to reference temperature 25°C.



$$\alpha = \left(\frac{\kappa_T - \kappa_{25}}{T - 25}\right)\frac{1}{\kappa_{25}} * 100\,\%$$

Temperature coefficient α depends on

- the chemical composition of the solution
- the concentration of the electrolytes
- the temperature, especially at low conductivity levels of <1 µS and very high conductivity levels




If the temperature coefficient of a sample is not known, α can be defined experimentally. Electrical conductivity values at 25 (±0.1) °C and at some other known temperature T2 (±0,1) °C are averaged and then entered in the above equation. If measuring is performed without temperature compensation, the conductivity measured at a known temperature can be converted using a correction factor to 25°C.

**Measuring principle**

The conductivity in electrolytes is obtained via an electro-chemical resistance measurement using a 2-electrode or a 4-electrode measuring cell. A sinusoidal voltage with a frequency of approx. 1 kHz is applied to the electrodes. The current flowing through the test object is converted into a voltage. This voltage is rectified in phase-synchronous form, smoothed, and then displayed as the measured value.

**ALMEMO® conductivity probe**

For the purposes of measuring conductivity in electrolytes the spectrum of ALMEMO® sensors includes 5 conductivity probes with integrated NTC temperature sensors for altogether 4 measuring ranges : 0 to 200.0 µS/cm (FYA641-LFP2/LFL2),0 to 10.00 mS/cm (FY A641-LFL1), 0 to 20.00 mS/cm (FY A641-LFP1), and 0 to 200.0 mS/cm (FY A641-LFP3).

*For the two measurable variables, temperature and conductivity, two channels are programmed in the connector for each:*

| Sensor | Cha | Meas.val. | Range | Resol. | Units | R | Factor | Exp |
|---|---|---|---|---|---|---|---|---|
| FYA641LFP1<br>FYA641LFL1 | 1 | temperature T | -5...70 °C | 0.01 | °C | Ntc | - | 0 |
| FYA641LFP1 | 2 | conductivity κ | 0.0...20.00 mS | 0.01 | mS | LF | 0.1 | 1 |
| FYA641LFL1 | | | 0.0...10.00 mS | 0.01 | mS | LF | 0.1 | 1 |

| Sensor | Cha | Meas.val. | Range | Resol. | Units | R | Factor | Exp |
|---|---|---|---|---|---|---|---|---|
| FYA641LFP2 | 1 | temperature T | -5...70 °C | 0.01 | °C | Ntc | - | 0 |
| FYA641LFP2<br>FYA641LFL2 | 2 | conductivity κ | 0.0...200.0 µS | 0.1 | µS | LF | 0.1 | 2 |
| FYA641LFP3 | 1 | temperature T | -5...70 °C | 0.01 | °C | Ntc | - | 0 |
| FYA641LFP3 | 2 | conductivity κ | 0.0...200.0 mS | 0.1 | mS | LF | 0.1 | 2 |

*The units and exponent in the ALMEMO® connector must not be altered; they are used for identifying device-internal calculation functions !*



The sensor is already adjusted on delivery and ready for use. In the measuring operation the sensor must be lowered at least 30 mm in the liquid so that the electrodes are completely immersed in liquid.
Probe FY A641-LFL1 (measuring range 0 to 10.00 mS/cm), probe FY A641-LFP1 (measuring range 0 to 20.00 mS/cm), and probe FYA641-LFP2/LFL2 (measuring range 0 to 200.0 µS/cm) continuously measure medium temperature T and thus calculate and display conductivity $\kappa 25$ at reference temperature 25°C.
On probe FY A641-LFP1/LFL1 and probe FYA641LFP2/LFL2 the device-internal temperature coefficient is $\alpha 25 = 1.9\% / K$.
On probe FY A641-LFP3 (measuring range 0 to 200.0 mS) temperature compensation is not performed because at high conductivity levels the temperature coefficient may vary widely; (see basic principles).

**Important !**
*Irrespective of which type of temperature compensation is used for measuring electrical conductivity at temperatures other than standard conditions, the result will always be less exact than that actually measured at reference temperature 25°C.*
*When performing routine work on site it may possibly not be necessary to convert values measured at the prevailing temperature to 25°C. However, such measured values should be interpreted with a measure of caution; comparison with other values is usually difficult and often even impossible !*

**Routine servicing and care**
Minor dust and dirt can be removed using a soft brush. Cleaning on a more intensive scale, as required if the electrodes are very dirty, may result in the distances between electrodes being slightly altered; this may have an adverse effect on results.

**Checking**

It makes good sense to check the probe in the following circumstances:

- in the event of the geometry changing (e.g. electrode spacing)
- after use in extreme conditions (e.g. high temperatures)
- if the probe produces measured results that are not plausible

**Adjusting a conductivity probe**

Throughout the adjustment procedure the solution must be kept at a constant temperature (±0,1)°C.

**Adjusting a conductivity probe that is temperature-compensated**
*(FYA641LFP1/LFL1, FYA641LFP2/LFL2)*

Automatic adjustment of a conductivity probe of this type is performed at two measuring points

1. at 0 mS/cm in a dry state
2. at 2.77 mS/cm - 0.02 mol KCl reference solution at 25 (±0.1) °C
   or at 147 µS/cm - 0.001 mol KCl reference solution at 25 (±0,1) °C

Correction is performed at both points (zero-point and gain) with the same sensor adjustment procedure.
(See device operating instructions, “Sensor adjustment” or Manual 6.3.10).

**Adjusting a conductivity probe that is not temperature-compensated**
*(FYA641LFP3)*

Adjustment of a conductivity probe of this type is performed at two measuring points

1. at 0 mS/cm in a dry state
2. at 111.8 mS/cm - 1 mol KCl reference solution at 25 (±0.1) °C

In standard conditions, 25 (±0,1) °C, correction is performed at both points with the same sensor adjustment procedure.
(See device operating instructions, “Sensor adjustment” or Manual 6.3.10)

When using the automatic adjustment procedure, standard conditions, 25 (±0.1) °C, must be ensured.

This probe can also be adjusted outside of standard conditions, 25 (±0.1) °C:

Zero-point adjustment is performed in the same way as automatic adjustment.
For the purposes of gain adjustment the value of the reference solution at a known solution temperature (see Table 1) is compared with the deviating value determined on site; this ratio is manually entered as correction value in the ALMEMO® connector under “gain correction” (SK)
(See device operating instructions, “Correction values” or Manual 6.3.10).

Example
adjusting probe FYA641LFP3 using 1 mol KCl reference solution at measured solution temperature 20.0 °C
*Value for reference solution at solution temperature 20.0 °C: 102.09 mS/cm (Table 1)*
Measured value at solution temperature 20.0 °C : 98.72 mS/cm

$$SK = \frac{(\text{Value for reference solution at solution temperature } 20°C)}{(\text{Measured value at solution temperature } 20°C)} = \frac{102{,}09}{98{,}72} = 1{,}034$$

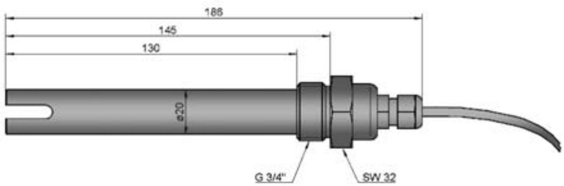
Table 1
*Electrical conductivity κ in mS/cm of KCL standard solution*
*as a function of temperature t and concentration:*

| t [°C] | κ[ mS/cm ] 0,001 mol/l | κ[ mS/cm ] 0,01 mol/l | κ[ mS/cm ] 0,02 mol/l | κ[ mS/cm ] 1,00 mol/l |
|---|---|---|---|---|
| 0 | | 0,776 | 1,521 | 65,41 |
| 1 | | 0,800 | 1,566 | 67,13 |
| 5 | | 0,896 | 1,752 | 74,14 |
| 10 | | 1,020 | 1,994 | 83,19 |
| 15 | | 1,147 | 2,243 | 92,52 |
| 16 | | 1,173 | 2,294 | 94,41 |
| 17 | | 1,199 | 2,345 | 96,31 |
| 18 | 0,127 | 1,225 | 2,397 | 98,24 |
| 19 | 0,130 | 1,251 | 2,449 | 100,16 |
| 20 | 0,133 | 1,278 | 2,501 | ***102,09*** |
| 21 | 0,136 | 1,305 | 2,553 | 104,02 |
| 22 | 0,138 | 1,332 | 2,606 | 105,54 |
| 23 | 0,141 | 1,358 | 2,659 | 107,89 |
| 24 | 0,144 | 1,386 | 2,712 | 109,84 |
| ***25*** | ***0,147*** | ***1,413*** | ***2,765*** | ***111,8*** |

These reference solutions are available as accessories specific to each conductivity probe. (See our Catalog. pages 16.06 and 16.07.).

**Dimensions**

FYA641LFP1,
FYA641LFP2,
FYA641LFP3




FYA641LFL1,
FYA641LFL2

## Technical data FYA641LFP1/LFL1, FYA641LFP2/LFL2

| Probe: | FYA641LFL1 | FYA641LFP1 | FYA641LFP2/ LFL2 |
|---|---|---|---|
| Measuring range | 0.01 to 10 mS/cm | 0.01 to 20 mS/cm | 1 to 200 µS/cm |
| Temp. compensation | 0 to +70 °C, automatic | | |
| Compensation coefficient | 1.9 % /K linear | | |
| Cell constant | approx. 1 $cm^{-1}$ | | |
| Electrode material | Special carbon | | |
| Accuracy | 0.01 to 5 mS/cm: ± 1% of meas. val. ± 0.05 mS | | ± 2% of meas. val. ± 0.5 µS |
| | 5 bis 20 mS/cm: ± 2% of meas. val. ± 0.05 mS | | |
| Nominal temperature | 25 °C ± 3 °C | | |
| Operating temperature | -5 to 70 °C | | |
| Minimum immersion depth | 30 mm | | |
| Shaft material | PVC - C | | |
| Shaft length / Shaft diameter | LFPx: 130 mm / 20 mm<br>LFLx: 130 mm / 10 mm | | |
| Fitting length / thread | nur LFPx: 145 mm / G3/4" | | |
| Maximum pressure | LFPx: 16 bar at 25°C<br>LFLx: unpressurized | | |
| Cable length | 1.5 m | | |
| Power supply | 6 bis 12 V via measuring instrument | | |
| Current consumption | approx. 3 mA | | |

## Technical data FYA641LFP3

| Probe | FY A641 LFP3 |
|---|---|
| Measuring range | 1 to 200 mS/cm |
| Accuracy | 1 mS / cm ±1,5% of meas. val. |
| Working electrode | 4 electrodes, special carbon |
| Temperature range | 0 to +70 °C |
| Minimum immersion depth | 30 mm |
| Power supply | 6 to 12 V via measuring instrument |
| Current consumption | approx. 15 mA |
| Temperature sensor | NTC Typ N 10k at 25 °C |
| Shaft material | PVC-C |
| Dimensions | 130 mm long, 20 mm diameter |
| Fitting length / thread | 145 mm / G3/4" |
| Maximum pressure | 16 bar at 25°C |
| Cable length | 1.5 m |

## 3.9.3 Sensor for gases
## $C_2H_4O$- / $Cl_2$- / CO- / $H_2S$- / $NH_3$- / $NO_2$- / NO- / $SO_2$

**Basic principles of electrochemical sensors**

Of decisive importance for the function of electrochemical sensors are so-called redox processes (reduction - oxidation). The chemical reaction between two substances usually involves the transfer of electrons between them. While one partner in the reaction is oxidized, losing electrons (increase in oxidation number), the other partner is reduced, gaining electrons (decrease in oxidation number). If the oxidation and reduction processes can be physically separated by means of "half cells" (anode, cathode) in such a way that electrons are transferred not directly between the molecules but via an external circuit, this electron flow can be used as a measure of the reaction's intensity. This can be achieved by having the processes take place on electrodes immersed in an electrolyte thus permitting ion exchange.

3

The process becomes more easily comprehensible if we look at the examples of the electrode reactions of a CO sensor and of a $H_2S$ sensor:

| Reaction | $H_2S$ sensor (hydrogen sulfide) | CO-Sensor (carbon monoxide) |
|---|---|---|
| Oxidation - anode | $H_2S + 4\,H_2O \rightarrow H_2SO_4 + 8H^+ + 8e^-$ | $CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$ |
| Reduction - cathode | $2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O$ | $½\,O_2 + 2H^+ + 2e \rightarrow H_2O$ |

**Physical concentration units**

When it comes to measuring gases the most important units are volume percent or parts per million (ppm). Actually in the latest standards the term "ppm" is no longer used. The exact form is "ml/m$^3$" or "mg/kg" (although these do in reality mean the same). The proportions of gases measured in the ambient air using these various units of concentration are shown in the following table:

| | | |
|---|---|---|
| 1 percent (%) is one part per hundred | 10 grams per kilogram | 10 g/kg |
| 1 permil (‰) is one part per thousand | 1 gram per kilogram | 1 g/kg |
| 1 ppm is one part per million | 1 milligram per kilogram | 0.001 g/kg |
| 1 ppb is one part per billion | 1 microgram per kilogram | 0.000001 g/kg |
| 1 ppt is one part per trillion | 1 nanogram per kilogram | 0.000000001 g/kg |
| 1 ppq is part per quadrillion | 1 picogram per kilogram | 0.000000000001 g/kg |

**Measuring principle**

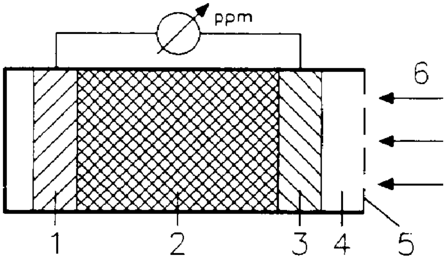
An electrochemical sensor comprises a housing, usually designated the measuring cell, whose two ends are covered with gas-permeable membrane. This housing contains an electrolyte, the measuring electrode, and the counter electrode. The electrolyte itself can be a liquid or a paste or a porous, impregnated solid. The electrolyte comprises a strongly alkaline or acidic solution whose constituents are ionized.

The air to be analyzed diffuses in the measuring cell and at the electrode the positive hydrogen ions ($H^+$) and the negative electrons that are released are consumed in a cathode reaction. The amount of current thus generated

between anode and cathode is then directly proportional to the level of gas concentration in the air being analyzed.
Schematic structure of an electrochemical sensor.

**Sensor measuring principle**

1- Cathode
2- Electrolyte
3- Anode
4- Diffusion Path
5- Membrane
6- Measured Air




**Uses**
ALMEMO® gas sensors can be used a wide variety of applications especially in the industrial and environmental sectors:

1. Workplace monitoring
   - ➔ Monitoring room air quality with respect to the MAK levels ( = maximum admissible concentrations of toxic gases in the workplace)
   - ➔ Monitoring for laboratories and engine test benches
2. Measuring emissions / immisions
   - ➔ Measurement, control, and warning systems, e.g. in underground car parks, power stations
   - ➔ Monitoring of outside air or of protected air systems in domestic shelters and large public shelters
3. Process control
   - ➔ Bioreactors
   - ➔ Chemicals industry

Each of these measuring tasks makes specific demands of the devices and sensors used. Workplace monitoring often requires long measuring periods with summation and evaluation of measured values with a view to assessing possible health risks. Since many substances - even in relatively low concentrations - may harm the human organism, the sensors used must be capable of registering low concentrations as exactly as possible.

*Example Carbon monoxide (CO):*
CO is produced when carbon is only partially combusted (fuel). CO is very dangerous for humans because it is at the same time highly toxic - and invisible and odorless. Reasons for the production of CO in various combustion processes:

➔ deficiency of air; ➔ too high an excess of air; ➔ flame cooling down too early

Effects of CO in the ambient air on the human body

| **CO concentration** | | **Inhalation period and consequences** |
|---|---|---|
| 30 ppm | 0,0003% | Maximum concentration in the workplace per 8-hour shift (German MAK value) |
| 200 ppm | 0,02% | Slight headache within 2 to 3 hours |
| 400 ppm | 0,04% | Headache within 1 to 2 hours, first in the forehead and temples, then spreading to the whole head |
| 800 ppm | 0,08% | Dizziness, nausea, and twitching limbs within 45 minutes, unconsciousness within 2 hours |
| 1600 ppm | 0,16% | Headache, dizziness, nausea within 20 minutes, death within 2 hours |
| 3200 ppm | 0,32% | Headache, dizziness, nausea within 5 to 10 minutes, death within 30 minutes |
| 6400 ppm | 0,64% | Headache and dizziness within 1 to 2 minutes, death within 10 to 15 minutes |
| 12800 ppm | 1,28% | Death within 1 to 3 minutes |



**ALMEMO® Sensor CO**

Carbon monoxide gas sensor FY A600 CO Bx is suitable for continuous measuring of the carbon monoxide concentration in air in the measuring range 0 to 150 ppm up to 0 to 5 volume %. The sensor current is amplified and output via a 2-conductor 4 to 20 mA interface. Important parameters, e.g. measuring range and scaling, are stored in the ALMEMO® connector on the connecting cable; the measured value for CO is displayed in ppm.

**ALMEMO® Sensor $C_2H_4O$-/$Cl_2$-/$H_2S$-/$NH_3$-/$NO_2$-/NO-/$SO_2$**

Gas sensors ALMEMO FYA600 Axxxxxxx are suitable for continuous measuring of toxic gas concentrations in air in the measuring range 0 to 20 ppm up to 0 to 1000 ppm. Various types of electrochemical sensor element are available so that gases such as ammonia ($NH_3$), nitrogen dioxide ($NO_2$), nitrogen oxide (NO), chlorine gas ($Cl_2$), sulfur dioxide, ($SO_2$) hydrogen sulfide ($H_2S$), and ethylene oxide ($C_2H_4O$) can all be measured quickly and easily. The sensor current is amplified and output via a 2-conductor 4 to 20 mA interface.
Important parameters, e.g. measuring range and scaling, are stored in the ALMEMO® connector on the connecting cable; the measured value for the gas in question is displayed in ppm.

**General handling and safety advice**

Given the strongly alkaline or acidic composition of the electrolyte great care is advised when handling measuring cells; even slight leaks cause burns to the skin and mucous membrane.

Operation with the device in SLEEP mode is not possible.

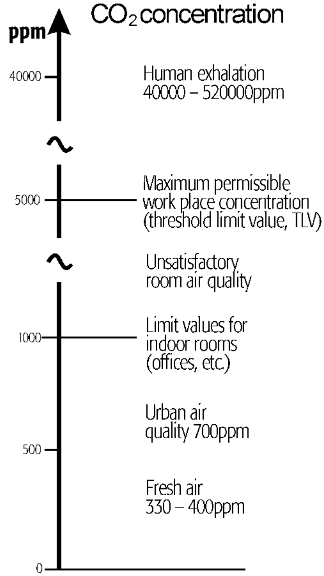
## Technical data

| Gas | CO | C2H4O / Cl2 / H2S / NH3 / NO2 / NO / SO2 |
|---|---|---|
| Measuring principle | Electrochemical reaction | |
| Measuring range | 0 to 150 ppm,<br>0 to 300 ppm,<br>0 to 5000 ppm | 0 to 250 ppm<br>depending on version |
| | 0 to 5.000 volume % | |
| Zero-point error | < 10 ppm CO | |
| Gauge reading balance | < 3 ppm CO | |
| Error in measured value | ±3% of the end value of the measuring range | |
| Zero point drift | < 2% (1 year) | |
| Reproducibility | < 2% (1 year) | |
| Linearity | < 2% of the end value of the measuring range | |
| Setting time t90 | < 60 seconds | |
| Cross sensitivities | < 2% by integrated filter | |
| Output | 4 to 20 mA on ALMEMO® connector | |
| Supply voltage | Via ALMEMO® device | |
| Ambient temperature | -10 to +40 °C | |
| | Sensor temperature-compensated in range | |
| Atmospheric humidity | 0 to 90% non-condensing | |
| Useful life of the measuring cell | approx. 2 years, typical | |
| Dimensions of measuring head | Diameter 80 mm, height 80 mm | |
| Weight | 600 g | |
| Connecting cable | 1.5 meters, with ALMEMO® connector | |

## 3.9.4 $CO_2$ Probe for Gases

### General remarks on $CO_2$ measuremen:

The $CO_2$ concentration is used as an indicator for the evaluation of the room air quality. A too high concentration of $CO_2$ in the room air (limit value 1000 ppm) is experienced as stale or stagnant air.

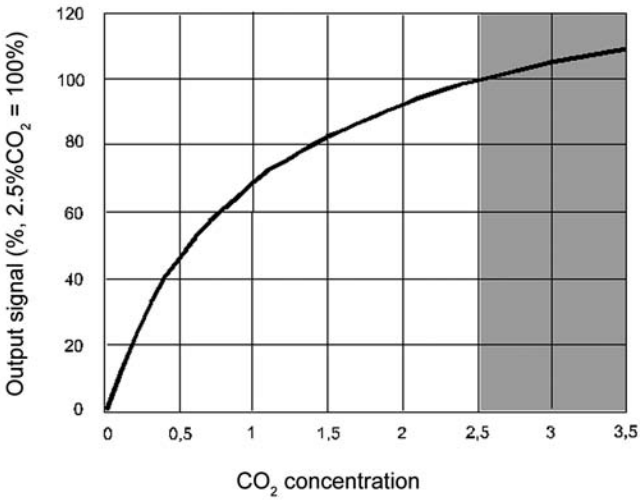



**Measuring Principle**

The operation of the carbon dioxide gas sensor module FY A600-CO2 is based on infrared optics. The sensor module utilises the light absorption of $CO_2$ in a narrow wave length range of the infrared spectrum.

The relation between the output signal of the module and the $CO_2$ concentration is substantially determined by the Lambert Beer absorption law. Due to further effects, the relation is not of a simple logarithmical character. The gas supply is realised, especially for air conditioning equipment via free convection. The sensor is not using any mechanically moving parts.





### 3.9.4.1 ALMEMO®-Carbon Dioxide Hand-Held Sensor

The sensor functions according to the 2-channel infrared absorption principle and is adapted to the ALMEMO® system via a digital interface.

**Handling:**
**These instructions must be strictly followed before initial operation:**

- Consider the operating range of the transducers! Overheating destroys the sensor!
- In case of a change of the ambient temperature (change of location indoor/outdoor) the measuring instrument requires a compensation period of a few minutes.
- The $CO_2$ sensor contains sensitive optical components. Please treat the sensor like you would treat your photo camera. Intensive shocks alter the adjustment of the sensor. Test the measured values with fresh air 350 ...450 ppm (city air to 700 ppm).
- Avoid any dewing of the sensor as this affects the long-term stability.
- Improper handling invalidates the guarantee!

**Initial Operation:**

- Connect the sensor to the ALMEMO® measuring instrument. For a safe measurement it is recommended to operate the ALMEMO® measuring instrument with the mains power supply adapter (high power consumption of the sensor!)
- Switch the device on.
- After switch on a 30 second heating-up time of the sensor follows.
- After 30 seconds the measuring instrument is operational.
- The $CO_2$ concentration within the sensor requires approximately 60 seconds to adjust to the environment.
- Slightly waving the sensor reduces the time required for the adjustment.
- In case of a ´bedewed´ sensor higher measured values can occur.

*To avoid any influences from the exhaled air the sensor should be kept as far away as possible from the body!*
*Operation with the device in SLEEP mode is not possible !*
*If more than one $CO_2$ probe is used with one ALMEMO® device an <u>external power supply</u> will be necessary for the $CO_2$ probes !*

Depending on your specific measurement setup we provide different power supply solutions on request

**Technical Data:**

| | |
|---|---|
| Sensor: | 2-channel infrared absorption principle |
| Measuring range: | 0 ...10 000 ppm (0...1 vol% $CO_2$ ) |
| Accuracy: | 0...5000 ppm ±(50 ppm+ 2% of m.) (at nominal conditions) |
| | 5000...10000 ppm ±(100 ppm +3% of m.) |
| Resolution: | 1 ppm or 0.0001 vol % |
| Nominal conditions: | 22°C ±2 °C / 50 % rF ± 10 % rF |
| Environmental temperature: | 0...+50 °C |
| Storage temperature: | -20...+50 °C |
| Environmental humidity: | 0... 90 % rF (non-condensing) |
| Temperature coefficient | 0.4% of m. / °C |
| Connector programming: | range: DIGI V24 instruction: B55 |
| Power supply: | 6.5 to 12 VDC from ALMEMO® device. |
| | Operation with mains power supply adapter is recommended! |
| Current consumption: | effective approx. 40 mA, max. approx. 80 mA |
| Connecting cable: | 1.5 m |



### 3.9.4.2 ALMEMO®- Sensor FYA600CO2

The sensor module FY A600-CO2 provides the output signal as a voltage between 0V (signal with absence of $CO_2$) and 2V (calibrated full scale value). The module is designed for a variable adjustment of the measurement range from 0,5% to 25% $CO_2$ and can, therefore, be used universally. As a standard, the present sensor version provides the output signal as a temperature-compensated signal.


**Handling**

Gas sensors are very delicate measuring devices.

Make sure that gas sensors are not exposed to shocks or jolts.
Mechanical stress may cause a misadjustment of the sensor.

A misadjustment of the sensor is usually related to the zero point (the curve character being maintained) In this case re-adjustment is necessary.
The response time is largely determined by the flow rate inside the sensor. COgas has a greater specific weight than air with the effect that it remains beneath air. The recommended position for installing the sensor is therefore upright (vertical).

*To avoid any influences from the exhaled air the sensor should be kept as far away as possible from the body!*
*Operation with the device in SLEEP mode is not possible !*
*If more than one $CO_2$ probe is used with one ALMEMO® device an <u>external power supply</u> will be necessary for the $CO_2$ probes !*

Depending on your specific measurement setup we provide different power supply solutions on request.

**Zero Point Verification in Ambient Air**

The verification of the zero point can be performed with sufficient accuracy in ambient air conditions. The average $CO_2$ content of non-polluted ambient air is 330 to 370 ppm. (approx. 0.03%) This value may be exceeded locally e.g. in urban or industrial areas.

**Calibration and correction**

The $CO_2$ sensor module, when delivered, is already adjusted to the appropriate range and can be used immediately.
For subsequent re-adjustment the zero point (offset) and gain (SPAN) can be set on the $CO_2$ sensor module. To do so you will need synthetic air (CO2-free!) and a test gas with a defined $CO_2$ concentration. A volume flow of at least 1 liter / minute must be set..

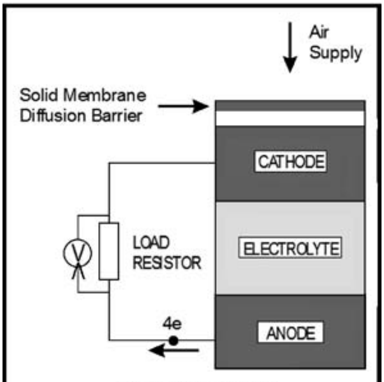
**Technical Data**

| | |
|---|---|
| Gas: | $CO_2$ |
| Measuring Principle: | IR optics |
| Meas. Ranges, nominal (% $CO_2$): | 0...0,500%, 0...2.5%, 0...10%, 0...25% |
| Accuracy: | ±2% of full scale value |
| Reproducibility: | ±1% of full scale value |
| Resolution (dep. on meas. range): | 50-100 ppm to 5000 ppm<br><200 ppm to 2.5% |
| Voltage Output: | 0 to 2V for selected measurement range |
| Supply Voltage: | 6.5 to 12V DC from the ALMEMO® measuring instrument, operation with mains power supply adapter is recommended |
| Current Consumption, effective: | 50mA |
| Current Consumption, maximum: | 70mA |
| Settling Time, t90: | <60s |
| Temperature Coefficient: | typically -0.4% signal/K |
| Temperature Range: | 5 to +40°C |
| Relative Humidity: | 0 to 95% |
| Dimensions: | 90 x 30 x 36 mm (WxHxD) |
| Weight: | 136g |
| Connecting Cable: | 1.5m with ALMEMO® connector |

## 3.9.5 $O_2$ Probe for Gases

### Measuring Principle

The oxygen measuring cell contains a lead-oxygen cell, a lead anode and a gold cathode and uses a special acid electrolyte. The oxygen molecules of the gas mixture flow through a non-porous membrane into the electrochemical cell and are absorbed by the gold electrode.



Measuring principle

3

The chemical process can be described by the following equations of reactions:

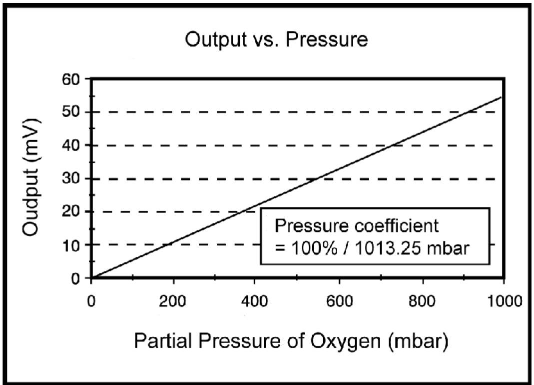
| | |
|---|---|
| $O_2$ reduction at the cathode: | $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ |
| Oxidation at the lead anode: | $2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^-$ |
| Reaction in the measuring cell: | $2Pb + O_2 \rightarrow 2PbO$ |

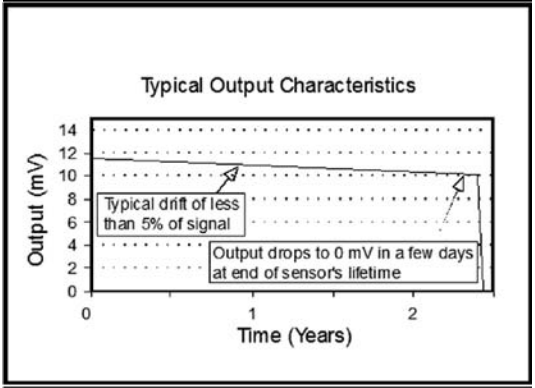
### ALMEMO® Oxygen Sensor

The oxygen sensor FY 9600-O2 can be used, for example, for measurements in air conditioning systems, air purifiers, oxygen rectifiers, greenhouses and oxygen incubators. The oxygen sensor is approved by PTB and is approved for exhaust gas measurements in the automotive industry.
The $O_2$ sensor contains a small circuit board, where measuring resistances and circuitry for the temperature compensation are located.
The response of the sensor is optimised by a compensating auxiliary probe. A correction value can be stored in the ALMEMO® connector plug to compensate for the natural ageing of the probes, so optimum output characteristics can be ensured for the whole operating life. For connecting the probe to ALMEMO® measuring instruments a standard jack connector (3.5mm) is used along with an adapter cable ZA 9600-AKO2.

**Output Signal**

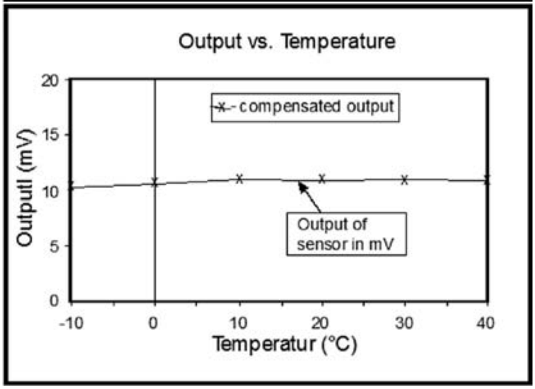
The current flow between the electrodes is proportional to the oxygen concentration in the gas mixture under test. For the temperature compensation the signals are measured as voltage drop over the resistance and the NTC. The change of the output voltage is proportional to the oxygen concentration, provided its penetration into the sensor is only limited by the diffusion. The sensor signal is determined by measuring the diffusion rate of the oxygen through the diffusion membrane. A plastic film is used as a diffusion membrane. At higher gas pressures the diffusion rate of the molecules increases. The output signal is, therefore, directly proportional to the oxygen partial pressure, which guarantees for a linear response at all concentrations.




**Operating Life**

The operating life of the sensor is dependent on the lead mass available for the oxygen reaction and of the oxidation rate. High oxygen partial pressures and high temperatures increase the output signal of the sensor and, therefore, shorten the life. At the end of the operating life the sensor signal quickly collapses to 0mV in air.




By screwing on the protective cap when the system is not used, oxidation can be avoided and the operating life is increased !

**Temperature Behaviour**
The integrated temperature compensation (NTC near the sensor electrode) stabilises the output signal of the sensor and is effective in the range -10°C to 40°C.

**Inspection and Adjustment**
The probes are, due to the electrochemical processes, subject to natural ageing. Therefore, the nominal value should be inspected and corrected before each measurement or at regular intervals, if necessary. The sensor must indicate 20.9% $O_2$ in fresh air. The sensor must be re-adjusted by programming a correction value if the measured value deviates from this nominal value.
Most ALMEMO® display devices also permit automatic setpoint programming. As soon as the final setpoint is entered, the correction factor is automatically calculated and saved as “Factor” in the connector EEPROM.
For all new devices the adjustment procedure using keys is described in the operating instructions under "Entering the setpoint"; the adjustment procedure via the interface is described in the Manual, section 6.4.2. For this purpose the locking mode must be set to 4!

3

In so doing the following working sequence must always be observed:
1. Take the sensor outdoors into the fresh air.
2. Set connector to locking mode 4.
3. Enter and adjust the setpoint to 20.9 %. The correction factor is saved as FACTOR and the measured value is now displayed as 20.9 %.
4. Set connector to locking mode 5.

On devices without setpoint entry the factor (setpoint value / actual value) can be calculated and programmed by the user. (see 6.3.11).

**Cross Sensitivity**
In many applications it is important to obtain very accurate oxygen measurements. For this reason, our oxygen probes meet the requirements of OIML R99 and PTB. Only small cross sensitivities occur in typical gas mixtures:

| Gas Mixture | Output Signal |
|---|---|
| 16% $CO_2$ / $N_2$- balance | <0.01% $O_2$ |
| 5% $H_2$ / $N_2$- balance | <0.001% $O_2$ |
| 2000ppm n-Hexan / $N_2$- balance | <0.01% $O_2$ |
| 6% CO / $N_2$- balance | <0.002% $O_2$ |
| 3000 ppm NO / $N_2$- balance | <0.002% $O_2$ |

Even if the sensor is used for longer periods in such gas mixtures, its output characteristics will not be affected:

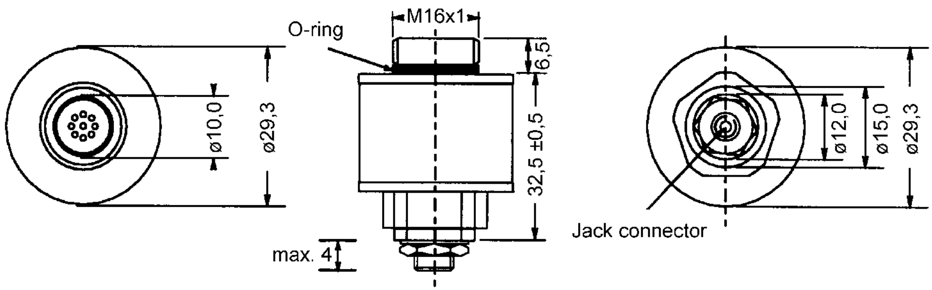
| Gas Mixture | Periods |
|---|---|
| 14.4% $CO_2$ / 3.6% CO / 2050ppm propane / $N_2$- balance | 16 weeks |
| 8% $CO_2$ / 10% $O_2$ / $N_2$- balance | 72 hours |
| 50% $CO_2$ / 10% $O_2$ / $N_2$- balance | 18 hours |

Although the measurement of the concentration is based on a capillary diffusion membrane, there is neither an increased $CO_2$ mass flow nor does a gas carrier effect occur. This means that the output signal of the oxygen sensor is only dependent on the oxygen partial pressure.

**Technical Data**

| | |
|---|---|
| Gas: | $O_2$ |
| Measuring principle: | electrochemical cell |
| Measuring range: | 1...100% $O_2$, linear |
| Accuracy: | 1% $O_2$ |
| Resolution: | 0.01% $O_2$ |
| Response time: | < 40s |
| Signal drift: | < 2% signal/month (typically <5% over lifetime) |
| Offset voltage at 20°C: | < 20µV |
| Operating life: | 2 years, at operation in 20.9% $O_2$ |
| Nominal conditions: | 20°C, 50%rH, 1013mbar |
| Temperature range: | -20 to +50°C |
| Temperature compensation: | effective in range -10 to +40°C |
| Pressure range: | atm. pressure ±10% |
| Relative humidity: | 0 to 99 % non-condensing |
| Connecting cable: | adapter cable 1.5m long with jack connector on ALMEMO® connector plug (ZA 9600-AKO2) |

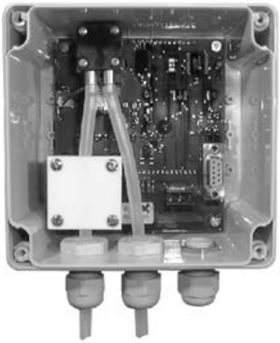
**Dimensions:**

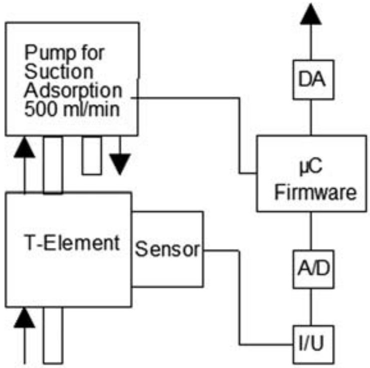


## 3.9.6 $O_3$ Probe for Gases

**Measuring Principle**

The ozone sensor FY 9600-O3 is based on an electrochemical three-electrode sensor. A membrane pump that is integrated in the sensor housing is used for taking air samples with a typical suction rate of 500 ml/min. For increasing the pump life the external air is sucked in using an interval operation and is measured during the second part of the suction phase.








**ALMEMO® Ozone Sensor**

The ozone sensor FY 9600-O3 can be used for many measuring tasks where ozone measurements have, so far, been too expensive. Each ozone sensor is supplied with a calibration certificate. As a result of the high long-term stability, only small maintenance costs are to be expected.

$$\text{Ozon}(\mu g/m^3) = \frac{0{,}57 * \text{Atm. Pressure}}{\text{Temperature}} * \text{Ozon (ppb)}$$

*Example:* *20°C and 1013 hPa = factor 2*
*Ozone (µg/m³) = 2 x Ozone (ppb)*
*This is the nominal value for conversion from ppb to µg/m³.*

**Measuring**

Unlike temperature, ozone expands in clouds, i.e. there is a strong local and time-based distribution. The measurement is performed in interval operation. As a result, ozone values can vary up to 50% in short intervals.

☞ We generally do not recommend connecting a filter in series, as it will usually 'contaminate' quite quickly (e.g. pollen in the air) and will lead to an invalidation of the measuring results.

**Applications**

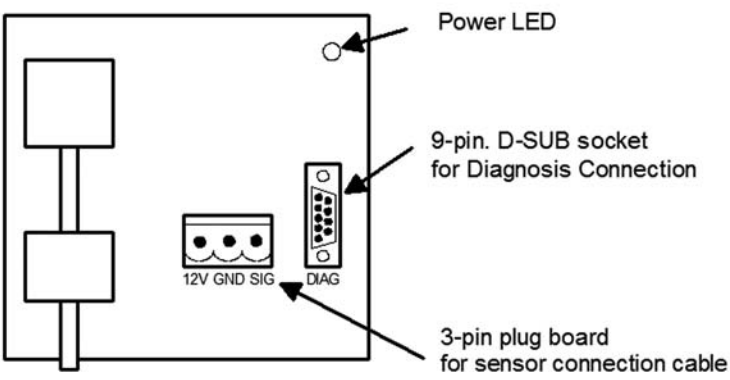
Ozone is a toxic trace gas that can cause major burns in human mucous membranes when breathed in high concentrations. Therefore, control measurements for the ozone content in air must be performed in many areas, for example:

- for leakage tests in industry
- for protection of health and safety standards at work
- for mobile air quality measurements
- for providing environmental data on advertising displays etc.

**Notes for Installation**

1. The maximum measuring accuracy can be achieved at a constant ambient temperature of approximately 20°C. We recommend the installation of the ozone sensor within a building, in a height of at least 3m, and with a suction hose (teflon hose) guided to the outdoor area.
2. The opening of the suction hose must be at a distance of at least 20cm from walls or other objects and must be directed downwards.
3. If an indoor installation is not possible, the ozone sensor must be mounted in a 24-hour shade position (North). However, in this case a lower measuring accuracy must be expected because of the larger temperature fluctuations. If mounted outdoors the ozone sensor should be protected from rainfall, e.g.  it should be mounted on a balcony, under a canopy or a cover.
4. Mount the ozone sensor so it remains easily accessible for regular maintenance.
5. Install the ozone sensor at a location that has good ventilation so the ozone cannot disintegrate, due to a missing convection.

**Connectors and LEDs**



## Maintenance

For measurements in outdoor environments the maintenance must be performed once per year in spring time, so the maximum measuring accuracy is available during the 'ozone season'. In case of season-independent measurements, we recommend maintenance at 24 month intervals.
Maintenance set ZB9600O3S: new electrochemical meas. cell, pump replacement, re-adjustment including calibration certificate

Exceptional weather conditions such as a hot and dry summer and high pollen, or even foreign substances, e.g. varnishes, lead to a premature deterioration of the sensor properties. A shorter maintenance interval may be necessary.



## Technische Daten

| | |
|---|---|
| Gas : | ozone ($O_3$) |
| Measuring principle : | electrochemical three-electrode sensor |
| Measuring range : | 0 to 300 ppb |
| Detection limit: | 20ppd |
| Accuracy : | typically 5% of final value under nominal conditions (for intermittent operation) |
| Long-term accuracy : | after 12 months under nominal conditions typically 5% of final value (for intermittent operation) |
| Exposure period : | until specification is reached, at least 2 hours (at 200 ppb); for a prolonged period the device was in an ozone-free environment |
| Measuring interval : | pump on : 5 minutes / pump off : 10 minutes<br>Option : OY9600 O3 pump in continuous operation(factory setting) |
| Pump flow rate : | 500 ml / minute |
| Signal output : | 0 to 2 V Load resistance >100 kW |
| Voltage supply : | 6 to 14 V, stable |
| Current consumption : | pump on : 50 mA, typical<br>pump off : 25 mA, typical<br>pump blocked : 180 mA, typical |
| Overload capacity : | 1 ppm |
| Expected useful life : | Sensor, typically 24 months (at 20 °C)<br>pump, typically 6000 hours |
| Nominal conditions : | 20 °C, 30% RH, 1013 mbar,<br>no contamination of contact surfaces |
| Operating range : | -20 to +40 °C / 30 to 80 % rH |
| Storage temperature : | 0 to 20 °C at 30 to 80 % rH non-condensing |
| Dimensions | (LxWxH) 180 x 125 x 90 mm |
| Connecting cable : | 1.5 meters long, with ALMEMO® connector<br>programmed in ppb |

## 3.9.7 $O_2$ Probe for $O_2$ Measurement in Liquids

**Basic Principles of Oxygen Measurements in Water**

Oxygen is not only a component of the air but it is also contained dissolved in water. It is very important for animals and organisms living in water and for the biological treatment of municipal and industrial waste water. The dissolved part increases with increasing atmospheric pressures and with decreasing temperatures.

An oxygen balance develops between the air and the water. The saturation state (air-saturated water) is reached when the partial pressure of the physically oxygen dissolved in water **[$pO_2$(Water)]** equals the partial pressure of the oxygen in the air **[$pO_2$(Air)]**.

$$p\,O_2\,(\text{Water}) \quad = \quad p\,O_2\,(\text{Air})$$

As air does not only contain oxygen (20.9%) but also nitrogen (78.1%), rare gases (0.96%), carbon dioxide (0.03 %) and water vapour (humid air), the following equation is valid for the partial pressure of the oxygen in water-vapour-saturated air [p´O2 (air)]:

$$p'O_2\,(\text{Air}) \quad = \quad X\,O_2 \quad (p_L - p_W)$$

$X\,O_2$ = mole fraction of oxygen in air (0.2095)

$p_L$ = atmospheric pressure $p_W$ = water vapour pressure

The oxygen partial pressure in water-vapour-saturated air corresponds, at a balanced state, to the oxygen partial pressure in air-saturated water.

This is of a special practical importance when calibrating oxygen sensors.

For a valuation of the oxygen saturation state it is common to determine the oxygen saturation $O_2S$ in % or the direct concentration specification $O_2C$ in mg/l instead of the oxygen partial pressure. The value $O_2S$ in % indicates how large the dissolved oxygen concentration $O_2C$ is in water, in percent of the saturation value $O_2C_s$.

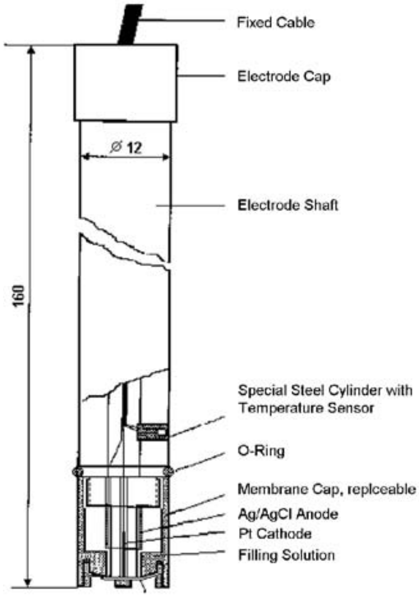
$$O_2S = \frac{O_2C}{O_2C_S} * 100\,\%$$

**Measuring Principle**

For determining the dissolved oxygen, membrane-covered sensors that are based on current measurements according to the Clark principle, have proven to be suitable in laboratory and in process control. These sensors operate based on the principle of polarography. Simplified, a constant polarisation voltage is applied to two electrodes and the resulting current is measured, which is proportional to the concentration of the corresponding measuring ions. The selectivity of the corresponding reaction is dependent on the half-stage potential of the present competing reaction partners. On connecting a defined voltage different substances can be selectively measured.

In the case of determining the dissolved oxygen by means of the membrane-covered Clark cell, the cathode electrode is platinum and the counter or reference electrode is silver/silver chloride. Both electrodes are immersed into a chloride-containing electrolyte solution, which is separated from the measuring solution by an $O_2$ permeable teflon membrane. The thin teflon membrane allows the oxygen gas to flow through, but not any dissolved ions or other foreign substances.






At this oxygen measuring method the oxygen that is dissolved in the water diffuses through the teflon membrane to the surface of a highly polished platinum electrode, which is acting as working electrode, and is electrochemically reduced to OH ions (base). An equivalent amount of electrons are absorbed by the silver counter electrode, which is the anode, and the resulting silver ions react with the chlorine ions of the filling electrolyte and form silver chloride that is separated on the silver electrode.

The individual reactions can be described with the following reaction equations:

Cathode: $O_2 + 2\ H_2O + 4$ elektrons $\rightarrow 4\ OH^-$
($U_{Ag/AgCl} = +611$ mV)

Anode: $4\ Ag + 4\ Cl^- \rightarrow 4\ AgCl \downarrow + 4$ elektrons

These reactions are not spontaneous but must be forced by applying a polarisation voltage of a minimum of +611 mV to the platinum cathode and the silver anode. The resulting current is measured and represents a measure for the concentration of the discharged oxygen.
To avoid any other reactions the polarisation voltage must be kept relatively constant. A polarisation voltage of +650 mV is applied to the oxygen electrode.
'Difficult to dissolve' silver chloride and a base (OH ions) within the inner electrolyte are reaction products forming at the operating oxygen electrode. After long operating periods (several months) of the oxygen electrodes the silver salt must be removed by means of sodium thiosulphate, ammonia solution or removed mechanically, and the used electrolyte must be renewed.

**ALMEMO® Oxygen Measurement**
For $O_2$ measurement in liquids the ALMEMO® $O_2$ probe FY A640-O2 contains a Clark cell with a measuring amplifier and a Ntc temperature sensor. Three measuring channels allow for recalling the measuring variables, temperature, $O_2$ saturation and $O_2$ concentration:

| Chan. | Meas. Variable | Meas. Range | Resol. | Dim | Range |
|---|---|---|---|---|---|
| 1. | Temperature | -5 ... 50 °C | 0.01 | °C | Ntc |
| 2. | $O_2$-saturation | 0 ... 260 % | 1 | % | O2-S |
| 3. | $O_2$-concentration | 0.0... 40.0 mg/l | 0.1 | mg | O2-C |

The oxygen saturation is influenced by the water temperature and the atmospheric pressure. Therefore, these two parameters must be considered when calculating the degree of saturation. The temperature sensor for temperature compensation has been integrated in the probe. Furthermore, an atmospheric pressure sensor can be connected. In case of constant conditions, the atmospheric pressure can also be entered. The reference value is 1013 mbar (normal pressure).
The oxygen concentration is calculated from the variables, saturation and temperature using the tables according to Wagner. The oxygen concentration is not dependent on the atmospheric pressure.

**Calculation Formulae:**
The following formulae are used by the measuring instrument to calculate the degree of saturation and the absolute amount of oxygen in mg/l by using the $O_2$ measured value and the temperature.

| | | | |
|---|---|---|---|
| $O_2$ saturation, corrected: | $O_2S$[%] | = | $O_2$m SK Tk(Tm) Pn/Pm |
| | | | |
| Measuring signal: | $O_2$m | = | $O_2$ saturation measured |
| Slope correction: | SK | = | 100 / ($O_2$c Tk(Tc) Pn/Pc) |
| | $O_2$c | = | $O_2$ saturation during calibration |
| | Tc | = | temperature during calibration |
| | Pc | = | atm. pressure during calibration |
| | | | |
| Temp. compensation: | Tk(T) | = | exp(k1/(Tm+T0))/k0 (range 5 to 50°C) k0=4840, k1=2530, T0=273.15 |
| | Tm | = | temperature measured |
| | | | |
| Atm. press. compensation: | Pn | = | normal atm. pressure 1013 mbar |
| | Pm | = | atm. pressure during measurement |
| | | | |
| $O_2$ concentration: | $O_2C$[mg/l] | = | $O_2$m SK/100 Tk(Tm) $O_2CS$(Tm) |
| | $O_2CS$ | = | $O_2$ saturation concentr. acc. to Wagner |

**Atmospheric Pressure Compensation:**
Three different methods can be used for atmospheric pressure compensation:
1. Manual entry in function 'mb'
2. Entry via interface using command: g 0xxxx [mbar] (see 6.2.6)
3. Measuring with additional atm. press. sensor FDA612SA (see 6.7.2)

**Calibration**
The oxygen probe can be calibrated with regard to zero point and slope to achieve accurate measured values. The electrodes must be sufficiently polarised before starting the calibration. For this purpose, the electrode is connected to the measuring instrument that is being switched on. The polarisation time can take up to 30 minutes, especially when the electrode has not been in operation for a longer period. A sufficiently polarised electrode, which is in proper working order, provides a stable, non-drifting measured value.
Oxygen electrodes are calibrated at 0% oxygen saturation (calibration point 1) and 101% oxygen saturation (calibration point 2).

**Preparation of Null Solution for Calibration Point 1:**
Sodium sulphite salt solution ('null solution') is used as oxygen-free liquid (0% saturation). This solution can be prepared by dissolving sodium sulphite (Na2SO3) in water (accessory ZB 9640-NS). Either distilled (de-ionised) or tap water can be used. The required amount of sodium sulphite depends on the water that is used. Distilled or stale water usually contains less dissolved oxygen than fresh tap water. The required amount of sodium sulphite is therefore smaller. As a standard value, 1g sodium sulphite can be assumed for 100ml water.

☞ When stored for a long period, the null solution absorbs oxygen from the air.
Therefore, the null solution should always be checked before the calibration is started.

Add, at first, a small amount of sodium sulphite to the null solution if your measuring instrument measures saturation values >0% in the null solution. The dissolved oxygen is chemically combined and the measured value for the oxygen saturation is reduced. A true 'null solution' is only achieved and allows for the calibration to be started when further salt additions do not lead to a further reduction of the saturation value (stable measured value).

**Adjustment for Calibration Point 1:**
1. Immerse the oxygen sensor deep enough in the null solution so that the integrated temperature sensor (special steel insert in shaft) is also immersed in the solution.
2. Allow for a settling time of approximately 2 to 3 min (display <50).
3. Select the function LOCKING MODE.
4. Unlock connectors (wherever possible only briefly and temporarily; see device instructions).
5. Select the function MEASURED VALUE.
6. Perform a zero point adjustment (see device instructions).
7. Thoroughly rinse the sensor afterwards with water to remove all residues of sodium sulphite.
8. Dab the membrane cap thoroughly to dry (e.g. with a cellulose cloth) before the calibration is started in water-vapour saturated air.

☞ Water droplets on the membrane can lead to an invalidation of the calibration.

**Preparation for Calibration Point 2:**
Water-vapour saturated air is used instead of air-saturated water. For this purpose, a moistened sponge is placed in a calibration vessel (accessory ZB 9640-AS). After 5 to 10 minutes the air contained in the vessel will be water-vapour saturated. Due to the properties of the membrane the calibration with water-vapour saturated air involves, even in the case of sufficient water-vapour saturation, minor differences (approximately 2%) compared to the sensors in air-saturated water. Despite the flow, an unaffected diffusion layer remains in the water, which leads to a reduction of the measured value. ALMEMO® measuring instruments are, therefore, set at calibration point 2 to the saturation value 101%, to obtain a correct measurement of the saturation value in water.



**Adjustment for Calibration Point 2:**
1. Place the thoroughly cleaned and dried sensor in the calibration vessel with water-vapour saturated air (101% $O_2$).
2. Add approximately 2ml water into the vessel and check the correct positioning of the receiving tube in the vessel (check the marking). The electrode must not rest on the water-soaked aerated plastics. A spacing of >1cm must be ensured.
3. Wait a few minutes until the balance is reached (stable reading). Select the function MEASURED VALUE.
4. Perform slope correction and zero point correction
5. Restore locking mode; (not necessary if unlocking was only brief and temporary).

**Maintenance and Service**
**Storage:**
The oxygen electrode should always be stored with the protective cap mounted to avoid evaporation of the electrolyte and to protect the membrane.

**Cleaning the electrode:**
For cleaning in daily use, simply rinse the electrode and dab it dry thoroughly, but avoid any damages to the membrane.

**Renew the electrolyte filling:**
If large air bubbles have been forming in the electrolyte area due to evaporation, or if this area is only filled to approximately 80%, the electrolyte filling must be renewed:
1. Position the electrode vertically.
2. Unscrew the membrane cap downwards.
3. Empty the membrane cap and fill it to the brim with electrolyte.
4. Re-screw the membrane cap to the vertically positioned electrode so that no air bubbles will be sealed in.

**Replace the membrane cap:**
The entire membrane cap must be replaced if the teflon membrane is damaged. Leakages of the membrane can be identified by formation of small water

droplets on the membrane surface and by the measured values 'overflowing'. The cap replacement is handled in the same way as the electrolyte renewal.

**Cleaning the electrode surfaces:**
If the silver anode is coloured black after several months of measuring operation, the electrode surfaces should be cleaned.

1. Unscrew the cap with the gas-permeable membrane.
2. Immerse the sensor head approximately 2cm deep in sodium thiosulphate cleaning solution for approximately 30 minutes.
3. Rinse the sensor head thoroughly using distilled water.
4. Wipe the silver anode intensively with cellulose material or polishing linen.
5. Provide the electrode cap with a new solution filling and re-screw it on the oxygen electrode.
6. The electrode is operational again approximately 30 minutes after switching on (polarisation time).

## Technical Data

| | |
|---|---|
| Measuring ranges: | |
| Temperature range: | -5.0 to 50°C |
| $O_2$ saturation: | 0 to 260% saturation |
| $O_2$ concentration: | 0.0 to 40mg/l (5 to 40°C) |
| Measuring principle: | Clark |
| Working electrode (cathode): | Pt |
| Reference electrode (counter electrode): | Ag/AgCl |
| Membrane: | teflon |
| Settling time (t90%): | approx. 10 to 15s |
| Zero current at 0% saturation: | < 5nA |
| Measuring current at 100% saturation: | approx. 700nA |
| Accuracy oxygen measurement: | < ±1% of measured value |
| Flow velocity (incoming): | approx. 10cm/s |
| Storage temperature: | -10 to 50°C |
| Depth of immersion: | 40mm |
| Filling volume (electrolyte): | 0.6ml |
| Temperature sensor: | NTC type N (10k at 25°C) |
| Accuracy of temperature measurement | -20 to 0°C: ±0.4°C, 0 to 70°C: ±0.1°C (at nominal conditions): |
| Nominal conditions: | 25°C ±3°C/1013 mbar |
| Shaft material: | PVC, black |
| Membrane cap: | replaceable (spare part) |
| Dimensions: | diameter 12mm, length 145mm |
| Connecting cable: | 1.5m long with ALMEMO® connector |
| Polarisation voltage: | 650mV |
| Service life (with one electrolyte filling): | several months |
| Overall service life (life): | several years |

## Accessories

| | |
|---|---|
| Adjustment Set:<br>25g sodium sulphite in 20 ml PE bottle for preparation of the null solution; vessel for adjustment of the saturation level | Order No. ZB 9640 AS |
| 25g sodium sulphite in 20 ml PE bottle | Order No. ZB 9640 NS |
| 20ml filling solution in PE bottle for $O_2$ probe | Order No. ZB 9640 NL |
| Spare membrane cap with protection (2 pieces) | Order No. ZB 9640 EM |