



Oxygen Handbook

MEASUREMENT TECHNOLOGY THEORY AND TIPS FOR PRACTICAL APPLICATION



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Oxygen Handbook



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**Xylem Analytics Germany
Sales GmbH & Co. KG, WTW**

Dr.-Karl-Slevogt-Straße 1
D-82362 Weilheim
Germany

Tel: +49 881 183-0
Fax: +49 881 183-420
Email: Info.WTW@Xyleminc.com
Internet: www.WTW.com



More than 70 years of experience

Dissolved oxygen is determined via a partial pressure measurement, with the oxygen dissolved in the liquid depending on the pressure of the gas found above the surface. In 1965 we were ready for serial production of sensors for measuring dissolved oxygen to the market with our WTW brand. Since then the measurement technology for this parameter, which is decisive for the lives of flora and fauna in water among other things, has seen continuous development. Today we additionally offer optical dissolved oxygen sensors which facilitate precise measurements at lowest maintenance efforts and with highest precision.

This handbook wants to give some understanding of the measurement technology by practical tips, support users and allow interested people learning about the principles of measurement.

We are happy to be at your disposal at any time, just give us a call!

Dr. Robert Reining and Ulrich Schwab
(Directors of Xylem Analytics Germany GmbH)

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SECTION 1

Fundamentals

Oxygen is not just a component of the air; it also appears in fluids as a dissolved gas. An equilibrium state is then reached when the oxygen partial pressure, that is, the part of the overall pressure caused by the oxygen, is the same in both air and fluid (Fig. 1). The fluid is then oxygen-saturated. In relation to physical-chemical correctness, it should be added that the partial pressure in the fluid is actually fugacity. The equating of both values is, however, permissible in the relevant pressure range for the measurements, whereby we can limit ourselves to the par-

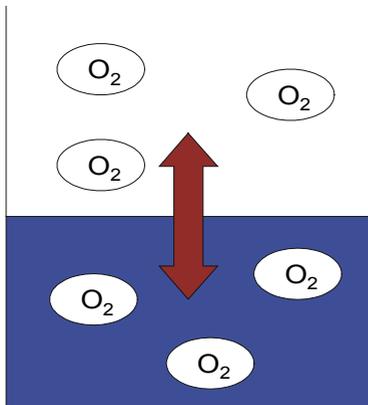


Fig. 1 Principle of partial pressure

tial pressure in the further discussion. In dry atmospheric air the oxygen partial pressure is 20.95% of the barometric pressure. This percentage is reduced over a water surface because water vapor also has a vapor pressure and thus a partial pressure (Fig. 2).

Under saturation conditions it follows from above:

$$p_{O_2}(T) = 0,2095 \cdot (p_{air} - p_W(T))$$

with $p_{O_2}(T)$ as the oxygen partial pressure, p_{air} as the barometric pressure and $p_W(T)$ as the water vapor pressure. (T) highlights temperature-dependent values.

In most cases however statements of oxygen concentration at $\beta_{O_2}(T)$

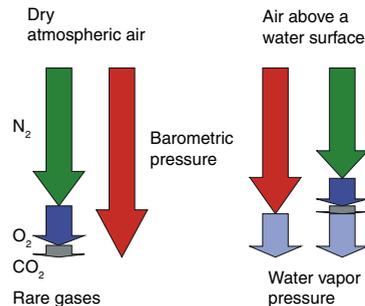


Fig. 2 Air composition

are desirable. This is proportionally linked to the oxygen partial pressure and of course to the type of fluid, reflected by the Bunsen coefficient $a_{O_2}(T)$.

$$\beta_{O_2}(T) = \frac{a_{O_2}(T) \cdot p_{O_2}(T) \cdot M_{O_2}}{V_M}$$

with M_{O_2} as the molar mass of the oxygen and V_M as the mole volume. For the measurement of the oxygen concentration the temperature must be known. If the result is desired in % saturation, the current barometric pressure is also required.

These comparisons demonstrate that water can dissolve more oxygen at a high rate of barometric pressure than under low barometric pressure conditions.

As the temperature rises the water vapor pressure rises, i.e. the oxygen partial pressure falls. To emphasize this impact here is a comparison between 20°C and 40°C at a barometric pressure of 1013 hPa. While at 20°C 9.09 mg/L of oxygen dissolves in water, at 40°C the amount is only 6.41 mg/l.

The volume change linked with the temperature change depends on the fluid under examination.

For water this effect plays a subordinate, negligible role.

The effect of dissolved materials is somewhat different. They can both reduce and increase the solubility of oxygen. A salt content (sodium chloride) of one percent in water leads to a saturation concentration of 8.54 mg/L instead of 9.09 mg/L at 20°C.

Organic materials, on the other hand, normally increase the absorption of oxygen into water. The maximum saturation concentration increases with the proportion of the organic substance. Pure ethanol, for example, dissolves 40 mg/L of oxygen.

1.1 Dissolved oxygen sensors



Fig. 3 Cross-section through a galvanic dissolved oxygen sensor

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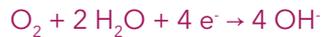
The bases for the electrochemical determination of oxygen concentration are membrane-covered electrochemical sensors. [1] The main components of the sensor are the oxygen-permeable membrane, the working electrode, the counter electrode, the electrolyte solution and potentially a reference electrode (Fig 3).

Between the gold cathode and anode, which is made from either lead or silver, there is a voltage that causes the oxygen to react electrochemically. The resulting current is higher, the higher the concentration of oxygen is. The measured parameter is the current in the sensor, which can be converted into the concentration of the dissolved oxygen following a calibration. If the anode is made from silver, the meter supplies the required voltage (amperometric sensor). If the anode is made from lead, it is a self-polarizing sensor i.e. the voltage is created by the two electrodes in the sensor itself in the same way as a battery (galvanic sensor). The measuring meter only evaluates the current.

In the case of the electrochemical determination of oxygen the

following electrode reactions take place (Fig. 4).

Oxygen is reduced at the cathode:



Here "the cathode supplies electrons" and the oxygen which has diffused through the membrane reacts with the water hydroxide ions.

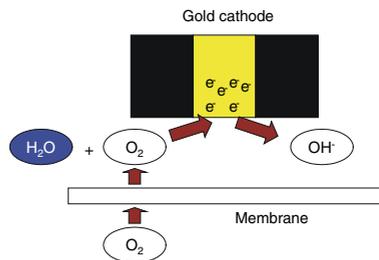


Fig. 4 Principle of electrode reactions

The electrode metal is oxidized at the anode, whereby the electrons required for the cathode reaction are set free. The reactions that take place are either

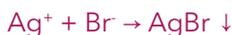


or

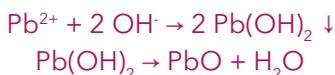


The equations of the anode reactions highlight the effect of the electrolyte solution. The components of the electrolyte solution bind the metal ions that result from the anode reactions.

The electrolyte solutions must be suitable for the type of electrode. The CelloX® 325 or StirrOx® G galvanic sensors require a ELY/G solution and amperometric sensors such as the TriOxmatic® require a ELY/N solution.



or



This is visually represented below for the silver electrode (Fig. 5):

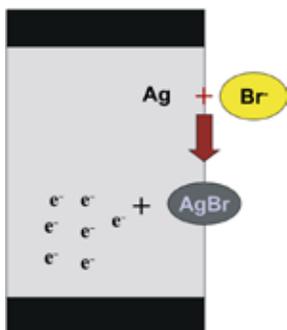


Fig. 5 Anode reaction with the silver electrode

The resulting, sparingly soluble substances also prevent the

lead or silver coating, fouling is a biological coating of the gold cathode which would take place if the ions were not captured.

Amperometric sensors can be operated as a three-electrode cell with an additional silver/silver bromide electrode. They no longer have any anode in the traditional sense. One of the silver/silver bromide electrodes takes on the task of the counter electrode (current dissipation), and the other the task of an independent reference electrode. This is currentless and shows a fundamentally better potential constance than a conventional electrode.

The potential of the reference electrode is determined by the concentration of the bromide ions and correspondingly represents an ion-selective electrode. As a result the concentration of the electrolyte solution can be monitored, this being a further feature of this sensor type. For WTW® sensors this is carried out in the so-called AutoReg Function in the TriOxmatic® sensors for online measurements.

The sensors' polarization times are also different and must be main-

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tained according to the operating instructions. The polarization time is the time which elapses between connecting the sensor and beginning of the measurement. It corresponds to the run-in period required to gain a stable measured value. Following a refill and change of the sensor head (see Regenerating Sensors) the new components contain an undefined percentage of oxygen which must first electrochemically react. In addition a current flows as result of the polarization of the electrodes. This current is comparable with the loading of a condenser.

The polarization time does not, however, just play a role following sensor regeneration.

As already explained the galvanic sensor is self-polarizing, i.e. polarization continues even after unplugging the sensor from the meter. As a result no waiting time is required when reconnecting. For amperometric sensors polarization must be carried out for a certain of time following every unplugging (see the operating instructions). This permanent standby is, however, linked to a slight disadvantage. As the polarization

is constantly taking place, the electrolyte solution is also being used up when the sensor is not connected to the measurement meter during rest times. It may thus be the case that regeneration is required even when no measurement has been carried out. The "battery is thereby consumed".

The role of the sample temperature for oxygen measurement stems from the temperature-dependency of the different variables (e.g. Bunsen absorption coefficient) have been already mentioned in the equations at the beginning.

In addition, the oxygen permeability of the membrane is also temperature-dependent. For this reason, except the external temperature sensor (sample temperature!) a further one is required and this is found in the sensor head. With these two temperature values the meter is able to compensate temperature in-flow to the membrane's oxygen permeability (IMT Isothermic Membrane Temperature Compensation).

SECTION 2

Calibration and analytical quality assurance

2.1 Calibration

Analogous to the pH measurement, a calibration must also be carried out for the dissolved oxygen measurement at certain time intervals. The reason for this is the consumption of the electrolyte solution in the sensor head through the measurements, as it is clear from the previous electrode reactions. The ions of the electrolyte solution bond the resulting metal ions, whereby the composition of the solution changes. The recommended calibration interval depends on the dissolved oxygen sensor used. Two weeks is sufficient for portable meters and up to 2-3 months for stationary WTW® dissolved oxygen sensors.

Every linear calibration function is set through at least two points. In the case of a dissolved oxygen measurement with WTW® meters, one point is the straight line of the sensor's zero point. At the absence of oxygen, the sensor

signal at the sensor zero point is less than the sensor's resolution.

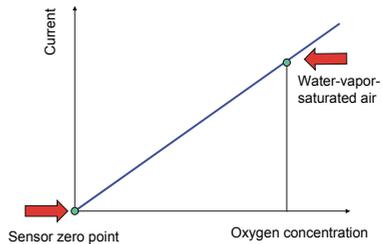


Fig. 6 Representation of linear calibration through two points

This is described as a zero-current free sensor. For the experimenter the calibration with WTW meters is then practically a one-point calibration.

The second point of the calibration curve can be determined in different manners (Fig. 6).

The reason for this is that in equilibrium state the oxygen partial pressure is the same in fluid and in air.

2.1.1 Calibration in water vapor saturated air

This condition is met over a large surface of water, such as a lake or

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even the aeration tank of a wastewater treatment plant.



Fig. 7 We provide specific air calibration vessels for laboratory measurements.

The air's oxygen partial pressure is calculated from the barometric pressure using the formula given above

$$p_{O_2}(T) = 0,2095 \cdot (p_{air} - p_w(T))$$

In line with this relationship the current barometric pressure P_{Luff} must be measured at the measurement location (not the one based on sea level, as is the practice with weather forecasts). This used to be carried out by users with a barometer or approximately resolved via the input of the height above sea level. Modern meters automatically determine the current pressure with an integrated pressure sensor.

The water vapor partial pressure $p_w(T)$ is merely a function of temperature if air humidity is at 100%. In order to determine this value, the sensor is additionally equipped with a temperature measurement probe.

It is important that the user ensures that there are no water droplets on the membrane. The calibration would then partly take place in water.

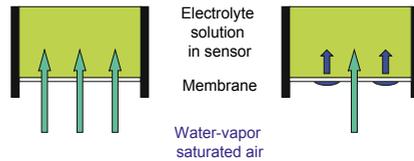


Fig. 8 Effect of water droplets on the sensor membrane

Caution is therefore particularly recommended if the sensor has been stored in the calibration vessel for a longer period of time and condensation droplets may have formed or fallen onto the membrane. The membrane must be checked before calibration in any case and, if necessary, dried with a soft paper cloth (Fig. 8).

It is sufficient if the sponge in the OxiCal® is moist (Fig. 7). It should, however, never be wet. The user should only moisten the sponge with distilled water and squeeze it. The dampness is fully sufficient.

2.1.2 Calibration in air-saturated water

The water is vented until the oxygen partial pressure in water and air is the same. However, this method conceals some risks:

- The barometric pressure in the ventilation hose is always a little greater than the normal barometric pressure and thus the water is always a little over-saturated following venting.
- The temperature in the water decreases as a result of the venting (cooling by evaporation).
- If a temperature equalization is waited for, the water will be a little over-saturated.
- The point of complete saturation is hard to estimate. There is the risk of under-saturation.
- Oxygen-consuming substances lead to under-saturation

The option of calibration in water vapor saturated air is supported by every WTW® meter and is, as indicated by the points given above, certainly to be preferred in comparison to a calibration in air-saturated water. It has also to be applied when working according to the Standard (ISO 5814).

The relative, not the absolute slope (as is the case for pH measuring meters) is displayed in % for the calibration result.

2.1.3 The calibration process in the measuring meter

The oxygen meter takes the electrode signal (current!) and compares it with the oxygen partial pressure, which is obtained using equation (1) for the current air conditions of barometric pressure p_{air} and temperature (T). The meter thus obtains a slope that allows measured currents to be converted into the oxygen partial value $p_{O_2}(T)$. At the same time a comparison is made between the actual measured value and the average saturation current of the electrode type following the refill (nominal current). The result represents the relative slope S .

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With reference to the average saturation current, slopes greater than 1.00 are also possible. A slope of 0.81 following a calibration means that the slope is 81% of the nominal value. It does not indicate anything about the precision of the measurement, but rather is a reference for estimating the remaining operating time, i.e. the time until the next change of the electrolyte solution is recommended.

This also applies to the meaning of the sensor symbols in the display of the modern oxygen meters which evaluate the service life of the sensor in the same way.

The calculation of the oxygen concentration is correctly carried out with the internally stored absolute slope in nA/hPa.

2.2 Sensor function check

For pH measurements, calibration data offer a direct possibility to assess the quality of the measuring set-up of meter, electrode and standard buffer solution. This is not possible for oxygen measurement due to the relative slope. Nevertheless, in order to gain results from the sensor func-

tion, there is the visual check and three characteristic measurement points.

The gold cathode is examined for the visual check. If it is no longer gold in color, but instead covered with lead or silver, the sensor shows high values and is generally no longer free of a zero-current. A remedy to this can be found through regenerating the dissolved oxygen sensor according to the operating instructions. The gold cathode should be polished only using a special, moistened polishing strip with circular movements and little pressure. Only this strip has to be used in any circumstances as a scratched and unpolished electrode surface damages the sensor and negatively affects the measuring reliability.

Caution: The anodes, regardless of whether they are made from lead or silver, must not be polished in any case.

More comprehensive than the subjective, visual check is an evaluation at the three special measurement points:

1st in water vapor saturated air,
2nd in air saturated water and
3rd in oxygen free water.

2.2.1 Test in water vapor saturated air

In water vapor saturated air should provide a value between 100 and 104% oxygen saturation. If the values are below this benchmark, it is likely that the membrane has become wet during calibration, and there may be too much water in the calibration vessel. The target value of above 100% saturation results from the different viscosities of water and air as well as the tension of the water surface. Expressed in a simplified manner, it is easier for the oxygen molecules to permeate the membrane in air than in water. The normal measurement mode assumes a liquid sample, so on air the reading exceeds 100%.

2.2.2 Test in air saturated water

After calibration the value in air-saturated water should show between 97 and 102% saturation. The theoretical value is at 100% and is difficult to repeat. The cause of the relatively wide tolerance is not the sensor, but rather the saturation procedure.

This is also the initial reason for which we successfully looked for an alternative to the calibration in air-saturated water which was common beforehand. If no value is found in this tolerance interval, the sensor should be sent to the plant to be checked.

2.2.3 Test using zero solution

This test proves the absence of zero current in the sensors. At a oxygen content of 0 mg/L a sensor should only display a maximum of the resolution of the meter (1 digit). The check is carried out with a sodium sulfite solution. Sulfite reacts with dissolved oxygen to sulphate, whereby dissolved oxygen is removed from the water. The production is simple, as might be expected. A teaspoon of sodium sulfite is dissolved in 100 ml tap water. After 15 minutes of leaving the solution undisturbed it is free of oxygen. It must be kept undisturbed as otherwise oxygen from the surroundings will once more be stirred in.

One minute after the immersion of the sensors the measuring meter should display a value of maximum 2% and of a maximum 0.4% after 15 minutes. If not, the

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sensor is no longer free of zero current and must be cleaned again or sent to the service. After the test, thoroughly rinse the sensor with distilled water, in order to remove the rest of the sodium sulfite solution.

Galvanic sensors with lead counter electrodes (CellOx® 325 and StirrOx® G) may be immersed for a maximum of 3 minutes. Then also rinse them thoroughly with distilled water. The cleaning of the sensors is very important in order to avoid poisoning and thereby permanent damage.

SECTION 3

Measurement and analytical quality assurance

The measuring of the oxygen concentration is now easy. Immerse the sensor into the fluid to be examined and take the reading. That is basically correct, however a few important points should be considered nevertheless.

3.1 Cleaning the sensor

The part of the sensor that is sensitive to contamination is the membrane. Contamination makes itself evident in electrochemical sensors through lower readings for measurements or reduced slope during calibration, because the complete surface of the membrane is no longer available for the diffusion of the oxygen. Compensating these contaminations by adjustment is not compliant with AQA regulations. It is better to clean the membrane. For deposits of calcium carbonate or iron oxide 5 to 10 % (weight percentage!) concentrated acetic or citric acid is used for grease and oil warm (<50 °C) dish washing agent.

Any high mechanical stress of the membrane has to be avoided at all cleaning activities, as their thickness is in the μm range and it can easily be damaged. Ideally a soft paper cloth should be used. Cleaning in an ultrasound bath should be avoided as the coating of the anodes may spall.

3.2 Regenerating the sensor

A regeneration of the sensor is required if the AutoReg Function is activated or the slope has strongly decreased after calibration ($S < 0.6$).

The AutoReg Function is only installed in the three-electrode sensors of WTW® (e.g. TriOxmatic®). It shows the user that regeneration is required.

Generally regeneration is required if the electrolyte solution is exhausted, if the gold cathode is lead- or silver-coated, if the reference electrode is poisoned, or

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if the membrane is damaged or contaminated.

It comprises the change of the electrolyte solution, the cleaning of the electrodes and a change of the membrane head.

It is important that the operating instructions are strictly adhered to in order to avoid faults. The following points should be emphasized:

- The sensor must be separated from the meter. In the case of a connected sensor, upon immersion in the cleaning solution, no chemical reaction takes place between the solution and the oxidized reference electrode surface, but an electrolytic decomposition of the cleaning solution may take place.
- In correspondence with the operating instructions, use suitable cleaning solution and electrolyte solution for the sensor! A solution for silver electrodes cannot regenerate any lead electrode.
- Only the gold cathode can be polished, the counter electrodes must only be cleaned

with a soft cloth in order to remove easily soluble salt crusts. A spotted coating following the regeneration of the lead or silver electrodes will not have an impact on the measurement.

- For the polishing of gold electrodes, only use a moistened WTW polishing strip, as it has a suitable granulation for polishing and causes no scratches.
- It is also recommended using a new membrane head, as the correct positioning of the membrane and the spacer grid on the gold cathode is no longer guaranteed when reusing the used and stressed head (Fig.9).

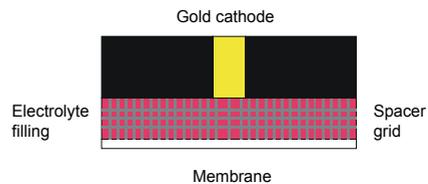


Fig. 9 Schematic diagram of the membrane head

- This spacer grid is clearly visible if the membrane head is held against the light.
- In the regeneration of three-electrode sensors (e.g. TriOx-matic®) the sensor may only be immersed to a depth that the already mentioned third electrode is not wetted by the cleaning solution (see operating instructions).
- The polarization time after regeneration has to be adhered to.

3.3 Unit and display of the measuring result

The result of an oxygen measurement can be documented in different ways:

3.3.1 Display as a concentration value

The meter requires the relevant data from the calibration curve to calculate, under consideration of the temperature dependence of the individual parameters, the concentration in mg/L (the display in ppm is for media with a density numerically equal to 1 g/mL; Fig. 11).

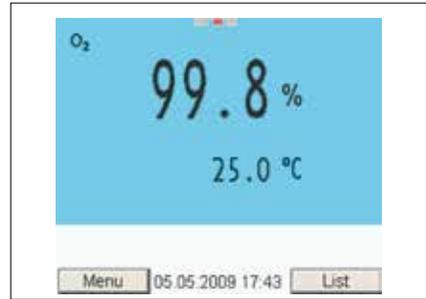


Fig. 10 Saturation

3.3.2 Display as oxygen saturation percentage

The meter measures the sensor current and calculates the oxygen partial pressure in accordance with the calibration. The current barometric pressure is measured for the calculation of the saturation partial pressure. The display corresponds to the quotient, converted into percent (Fig. 10).

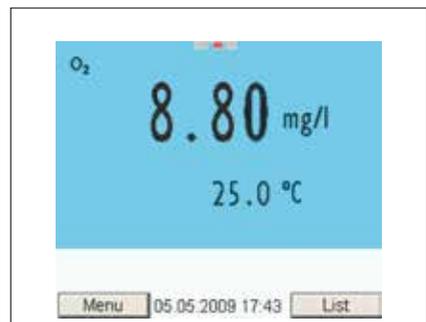


Fig. 11 Concentration

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For many meters the oxygen partial pressure can also be displayed in hPa.

3.4 Potential error sources

3.4.1 Polarization times (running-in time) before measurement

If the sensor has been separated from the meter, a corresponding polarization time is required for the start of the measurement upon reconnection of amperometric sensors (gold-silver electrode systems). Galvanic sensors (gold-lead electrode systems) are not affected by this, as these are self-polarizing and can be used immediately. Only after regeneration a certain waiting time has to be adhered before measuring.

3.4.2 Drift check (AUTOREAD)

Similar to the case of the pH measuring meters the drift check tests the stability of the sensor signal (Fig. 12). Here the temporal change of the measured values is examined and the response time of the sensor is evaluated. If the drift or the change is below a defined value, the signal is sufficiently stable and the currently

measured value is considered to be the actual measured value.

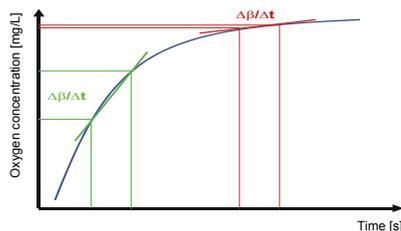


Fig. 12 Oxygen concentration dependent on time

A subjective assessment of the measured value stability is omitted and the repeatability of the measurement is improved.

Particularly recommended for the determination of the biochemical oxygen requirement is the use of the AUTOREAD function as precision measurements with significantly higher reliability can be carried out.

3.4.3 Importance of flow

For a correct oxygen measurement the sensor's membrane must have a constant flow on it. The diffusion of the oxygen molecules into the sensor head of electrochemical sensors causes an oxygen impoverished area which results in an apparently low oxygen concentration. The concentration in front of the mem-

brane must be the same as in the rest of the sample.

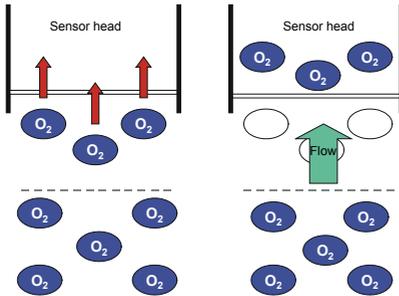


Fig. 13 Diffusion behavior with and without incident flow

This condition can be fulfilled either by stirring the sample or moving the sensor in the sample.



Fig. 14 Stirring attachment for laboratory dissolved oxygen sensors

We offer specific stirring attachments (Fig. 14) which rotate like small turbine blades and constantly provide fresh samples to

the membrane. This is driven by an electromagnetic alternating field from a laboratory stirrer.

The great advantage of this equipment is the dimension of the stirring attachment. It has the same diameter as the sensor and is mounted on the sensor head. This facilitates a simple measurement in sample flasks, such as the Karlsruhe bottles for the BOD measurement.

The WTW sensor StirrOx® G has been specifically designed for the BOD measurement. A propeller is installed in the sensor shaft and provides flow to the membrane. The stirring effect is hereby so strong that the homogenization of the sample is also assured.

If agitators or magnetic stirrers are used, the possible formation of eddies must be taken into account. The dissolved oxygen sensor must not be positioned in the eddy because air at the membrane would falsificate the measuring result. This can be prevented by reducing the stirring frequency or positioning of the sensor outside of the eddy formation.

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In the case of the installation in pipes the sample bypasses the sensor head and provides sufficient flow. WTW provides stationary measurement systems with specific mounting fixtures for pipes.

Alternatively the sensor can be moved in the measured medium. For example, stirring the sensor in a beaker glass or by slewing it in a lake. For measurements at great depths, armatures for measurements up to 100 m are available.

It must be ensured that the stirring causes no falsification of the measured values. This may particularly be the case if the sample examined is over- or under-saturated with oxygen and oxygen can be expelled or stirred in. Oxygen over-saturation is, for example, to be found in still waters in summer if the photosynthesis of rampant algae produces oxygen. An example of oxygen under-saturation is the BOD determination where bacteria lower the oxygen concentration by respiration in the Karlsruhe Bottles.

Correspondingly the sample volume is also of importance. A measurement in a lake or aera-

tion tank is non-critical due to the high sample volume. In an open beaker glass, on the other hand, the oxygen concentration can be easily changed through stirring.

In the case of optical sensors, which, as a matter of principle, do not require any flow to function, the stirring does still help to reach the end value faster.

3.4.4 Salt content correction

The temperature-dependent Bunsen coefficient (see Equation 2) changes if substances are dissolved in the water. This effect is taken into account by the input of salinity. The salinity can be determined with a conductivity meter and, to some extent, the salt content of seawater in g/kg. This function can also be used for other waters, as the deviations are often small.

3.4.5 Impact of interfering gases

The membrane of the dissolved oxygen sensor can also be permeated by other gases alongside oxygen (Fig. 15).

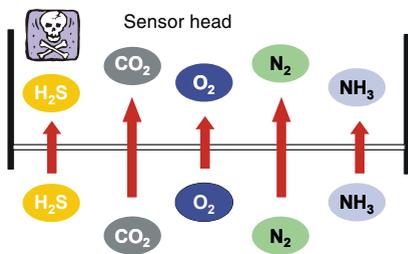


Fig. 15 Permeability of the membrane for different gases

Nitrogen is not very reactive and does not play any role here.

The interference by ammonia is negligible due to the high pH of the electrolyte.

Carbon dioxide, on the other hand, is problematic. The buffer capacity of the electrolyte solution is sufficient for short-term exposure, but under longer-lasting exposure carbon dioxide shifts the pH value into the aciduous range and leads to too high readings. Here galvanic sensors can regenerate the buffer capacity better than amperometric sensors, as they form excess hydroxide ions through the electrode reactions.

In the case of high carbon dioxide content (e.g. in beer, champagne, lemonade), the buffer capacity of the electrolyte solution in the sensor is insufficient. The pH shifts

into acidic, the measuring meter displays too high readings.

The greatest danger for dissolved oxygen sensors comes from hydrogen sulfide because this poisons the counter electrodes through the sulfide ion created by neutralization reaction.

The sensors can cope with a small amount but a longer exposure will noticeably shorten the sensor operation time. Hydrogen sulfide is easily detected due to its smell, which is similar to rotten eggs and can be noted even in the smallest concentrations without the need for measurement technology.

3.4.6 Solubility function

If the aim is to determine the concentration of the dissolved oxygen in non-water-based fluids, the corresponding solubility function must be known. In this case, the oxygen measurements are to be carried out analogous to the measurement in water.

SECTION 4

Optical oxygen measurement

In the past few years a further technology has been established for dissolved oxygen measurement. Oxygen is no longer solely electrochemically measured but also optically. [2] Of course the basics of oxygen determination also remain applicable here. Corresponding to the measurement technology there are new aspects which are explained below.

4.1 The principle of optical measurement

A sensor for optical measurement is also described as an optode. Optodes equipped with special dyes show optical measurable reactions when they come in contact with the specific molecules. A mass and energy conversion does not take place as for example with the Clark cells. It is only an energy conversion because a incident light beam of a certain wavelength is changed into light of longer wavelength and other properties than the original light. This type of reaction is known as

fluorescence (Fig. 16). As part of this, dye molecules are excited by light. Upon return to the ground state the absorbed energy is emitted in the form of light with changed (larger) wavelengths.

There are substances which measurably affect this mechanism depending on their concentration. These are the so-called quenchers. This means that these materials absorb the energy of the excited state so that the dye can no longer emit fluorescent light and is thereby "extinguished". The intensity of the fluorescent light becomes smaller the higher the concentration of the quencher molecule is. This context is basically described in the Stern-Volmer Equation:

$$\frac{I_0}{I} = 1 + k_{sv} \cdot C_Q$$

Here I_0 is the light intensity without the quencher, I the intensity with the quencher in a corresponding concentration, k_{sv} the

Stern-Volmer constant and c_Q the concentration of the quencher. In this context is also interesting that not only the intensity but also the temporal decay of the fluorescent light after excitation continues to behave correspondingly with the Stern-Volmer Equation.

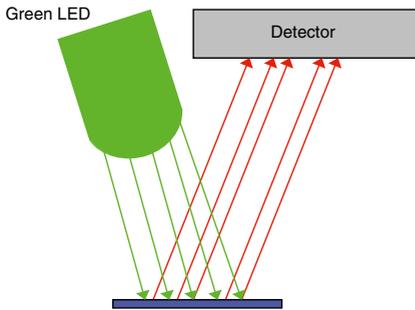


Fig. 16 Luminescence excitation using light of a short wavelength (green here), emission of a red and so low-energy fluorescent beam.

What does this mean for the dissolved oxygen measurement? There are dyes which are excited by visible light and react on oxygen with a high selectivity. The oxygen molecules serve as the quenchers described above. They extinguish or change the light resulting from the dye depending on the oxygen partial pressure. By

means of this dye suitable membranes can be produced for the measurement of oxygen in fluids or gases.

LEDs serve as the light source. The exciting of the fluorescence takes place in a modulated manner (Fig. 17). The light emitted from the dye in the membrane is detected, converted into an electrical signal and converted into an oxygen signal.

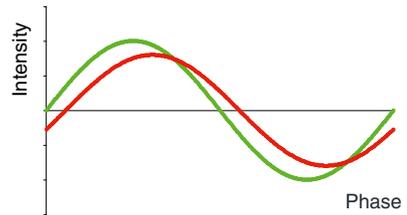


Fig. 17 Simplified representation of modulated stimulus and emitted fluorescence beam

Green graph: light periodically beamed in, red graph: light emitted from the dye at a shifted phase resulting from the changed decay ratio.

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4.2 Characteristics of the optical dissolved oxygen sensors

The significant difference from the classical dissolved oxygen sensors is that optical sensors consume no oxygen. There are no electrochemical reactions. In addition, there is a further characteristic: The optical sensor does not require any flow to replace "consumed" oxygen. Stirring systems are then superfluous. In addition, there is no necessity for the electrolyte change or cleaning the electrode system. The life span of the optical sensor caps with the dye-containing membrane usually is at least one year.

Electrochemical sensors form in water a 10 μm thick layer of water molecules that can not be stirred. As consequence this layer serves as an additional diffusion barrier. On air these sensors show a saturation signal of about 102%. The optical sensor measures 100% air saturation as this barrier does not exist here.

However it may be reasonable to apply flow to an optical sensor. As with all systems with interfaces, even when using the

optical dissolved oxygen sensor, there is diffusion of the dissolved oxygen in the water depending on the concentration into or out of the membrane. This process naturally runs faster the better the exchange takes place at the interface. A stirring supports this exchange.

There is no polarization time for optical sensors as it has no electrodes which have to reach an operating condition.

Optical dissolved oxygen sensors are sensors which have active components (LEDs, detector, processor). In contrast to the electrochemical sensors, they are more power consuming which leads to a markedly reduced operating time in the case of portable systems. Additionally optical sensors need different meters.

The measurement range is noticeably restricted in comparison to the electrochemical sensors above. The reason for this is the quenching. Simplified, no oxygen leads to a strong signal, a large amount of oxygen leads to a weak signal. In general the measurement range does not exceed ap-

prox. 200% air-saturation respectively 20 mg/l.

4.3 Calibration of optical dissolved oxygen sensors

An advantage of the optical dissolved oxygen sensors is that very stable drift behaviour. The changes in the membrane are mainly caused through the irradiated light. A decrease in sensitivity results, triggered by the so-called bleaching to a decrease in intensity and a change of the phase shift.

These changes are generally much smaller than 5% of the initial value over the course of a year. If this tolerance can be accepted, the sensor does not need to be calibrated.

We apply the dye to changing caps that the user simply puts onto the sensor. These exchange caps contain a chip with the specifications of the individual membrane determined in the production process ("factory calibration"). These data are automatically transferred to the sensor and used for the correct calculation of the oxygen concentration.

Of course a calibration carried out by the user is also possible. It is implemented analogously to the electrochemical sensors in water-vapor-saturated air in the calibration vessel. As already mentioned above, the resulting saturation display is at 100%.

4.4 Cleaning of optical dissolved oxygen sensors

The sensitive surface of an optical oxygen sensor is protected by a light proof top layer. This top layer is very thin and must therefore not be scratched or damaged as otherwise this could lead to malfunctions. In relation to the cleaning the same measures apply as to the conventional oxygen membranes. In the case of easily adhesive contamination careful cleaning with a soft cloth is recommended, further notes can be found in the operating instructions.

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4.5 Impact of interfering gases

In contrast to the amperometric sensors, carbon dioxide and hydrogen sulfide play no role in relation to the operation life of or damage to the sensors. It must solely be noted that, for example, hydrogen sulfide also functions as a quencher due to its molecular mass. An example from practice would be the decreasing oxygen content in limnological depth measurements at increasing depths, which seem to undergo an increase if the sensor is immersed into soft sediment. However the reason for this is the

hydrogen sulfide, which results from the putrefaction processes in many waters, that here dissembles an oxygen signal. This signal is reversible, the sensor does not undergo any damage.



Bibliography

[1] DIN EN ISO 5814, Water quality - Determination of dissolved oxygen - Electrochemical probe method, 2013

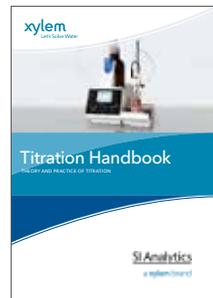
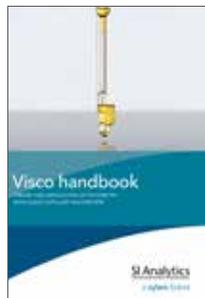
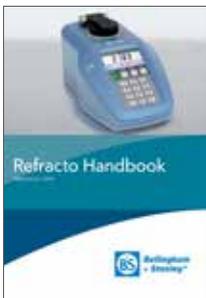
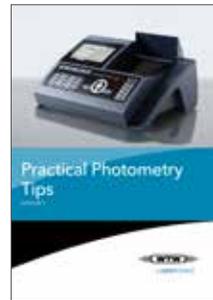
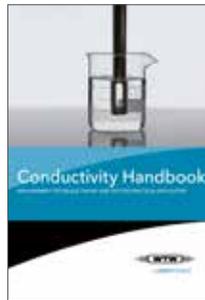
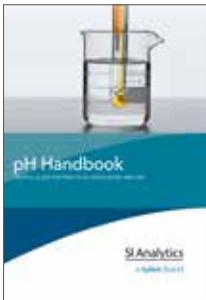
[2] DIN ISO 17289 : 2014-12
Water quality - Determination of dissolved oxygen - Electrochemical probe method

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