Oxygen Theory Guide

A Guide to Oxygen Measurement

Theory and Practice of Oxygen Applications

METTLER TOLEDO

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Oxygen measurement and control plays an important role in many chemical, pharmaceutical, biotechnology, power, and food & beverage processes. In fermentation, oxygen control leads to increased yield and decreased production of unwanted byproducts. Oxygen management in the chemical industry helps to avoid the formation of explosive gas mixtures, and oxidation control in the brewing industry results in increased quality and shelf life of end products. The in-line measurement of oxygen in liquid and gaseous mixtures is vital in these and countless other processes for providing continuous, real-time data on oxygen levels.

Today, there are many electrochemical and optical technologies available for the measurement of oxygen in both aqueous and gas phase media. METTLER TOLEDO offers three such technologies; amperometric, optical and laser spectroscopy.

- Amperometric technology has been successfully used for decades in a variety of applications and is based on electrochemical reactions.
- Optical technology is relatively new but has gained wide acceptance in the biotech and beverage industries. Its measurement principle exploits the phenomenon of fluorescence quenching.
- The newest technology offered by METTLER TOLEDO for determination of gaseous oxygen and other gases, is tunable diode laser (TDL) spectroscopy. TDL is also an optical method and is based on light absorption.

This booklet provides an overview of oxygen measurement theories, an explanation of amperometric and optical sensor technologies, and an introduction to the benefits of the Intelligent Sensor Management (ISM®). For information on tunable diode laser spectroscopy, please refer to the TDL theory guide available at **www.mt.com/O2-gas**.

1 Theoretical background of oxygen measurements

1.1 Physicochemical background of oxygen measurement

Oxygen typically is encountered as a gas. Therefore, the in-line and on-line measurement of oxygen in processes is a measurement of the pressure which the oxygen applies either in the gas or in the liquid in which it is dissolved. Depending on the kind of application and also on the habits of a certain industry, the oxygen concentration is expressed either in relative numbers, such as percent saturation, volume percent, percent oxygen, ppm or in absolute numbers, e.g., mg/L or mmol/L.

1.1.1 Units of pressure measurement

The SI unit (International system of units) of pressure is the Pascal (Equation 1). There are also other units commonly used, especially in medicine and technological processes, such as mmHg (Torr), bar and atm. The following table (Table 1) gives the calculations from one unit to another.

$$1 \text{ Pa} = 1\frac{N}{m^2} = 1\frac{kg}{m \cdot s^2}$$

Equation 1   SI unit Pa of pressure

	Pascal	Bar	Technical Atmosphere	Physical Atmosphere	Torr
	N/m^2	$Mdyn/cm^2$	kp/cm^2	p_{STP}	mmHg
1 Pa	1	$1.0000 \cdot 10^{-5}$	$1.0197 \cdot 10^{-5}$	$9.8692 \cdot 10^{-6}$	$7.5006 \cdot 10^{-3}$
1 bar	$1.0000 \cdot 10^5$	1	1.0197	$9.8692 \cdot 10^{-1}$	$7.5006 \cdot 10^2$
1 at	$9.8067 \cdot 10^4$	$9.8067 \cdot 10^{-1}$	1	$9.6784 \cdot 10^{-1}$	$7.3556 \cdot 10^2$
1 atm	$1.0133 \cdot 10^5$	1.0133	1.0332	1	$7.6000 \cdot 10^2$
1 Torr	$1.3332 \cdot 10^2$	$1.3332 \cdot 10^{-3}$	$1.3595 \cdot 10^{-3}$	$1.3158 \cdot 10^{-3}$	1
1 psi	$6.8948 \cdot 10^3$	$6.8948 \cdot 10^{-2}$	$7.0307 \cdot 10^{-2}$	$6.8046 \cdot 10^{-2}$	$5.1715 \cdot 10^1$

Table 1   Units for pressure and calculation from Pascal (SI unit) to other units

Since the measurement is dependent on the pressure of the oxygen, there are two particular physicochemical laws concerning pressure that are central to oxygen measurement:

• Dalton's law on partial pressures for oxygen in gaseous and liquid phases and

• Henry's law on gas solubility in liquids for measurements of oxygen dissolved in liquids.

1.1.2   Dalton's law on partial pressures

Dalton's law states that, in ideal gases, the total pressure of a gas mixture is equal to the sum of the partial pressures of the individual gases. Air consists of nitrogen, oxygen, carbon dioxide and argon and other precious gases. According to Dalton's law, the pressure of air is the sum of the partial pressures of the individual gases:

$$P_{air} = p_{nitrogen} + p_{oxygen} + p_{carbon\ dioxide} + p_{precious\ gases}$$

Equation 2   Dalton's law for the composition of air

Figure 1 below shows the gaseous composition of dry air in volume percent. Oxygen contributes about 21 % to the total pressure of a given volume of air. If at an atmospheric pressure of 1013 mbar (hPa), 21 % of this pressure is contributed by oxygen, the so called partial pressure of oxygen (p_{O_2}).

In dry air it is 212 mbar (hPa) according to Dalton's law.

   ■ 78.09 vol % Nitrogen
   ■ 20.95 vol % Oxygen
   ■ 0.93 vol % Argon
   ■ 0.03 vol % Carbon dioxide
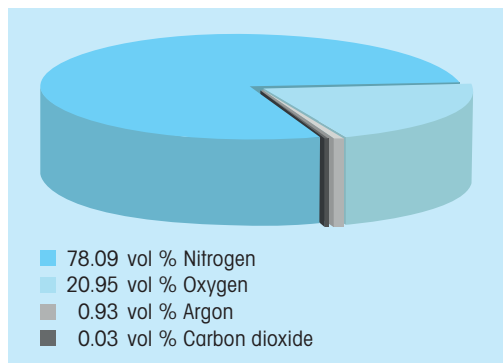
Figure 1   Gaseous composition of dry air

As shown in Figure 2 below, if total pressure on this system is doubled to 2026 mbar (hPa), the partial pressure also doubles to 424 mbar (hPa). The relative volume percent of oxygen remains 21 %. However, the transmitter would display a two-fold increase in the oxygen value in percent since the sensor is only responding to the partial pressure of oxygen. For this reason, it is extremely important that oxygen measurement equipment corrects for system pressure in order that accurate measurements can be made when measuring in relative units. Please note that this calculation is only valid for volume percent. If mass percentages are used as the output, the concentration has to be calculated via the partial pressure and the mole fractions.
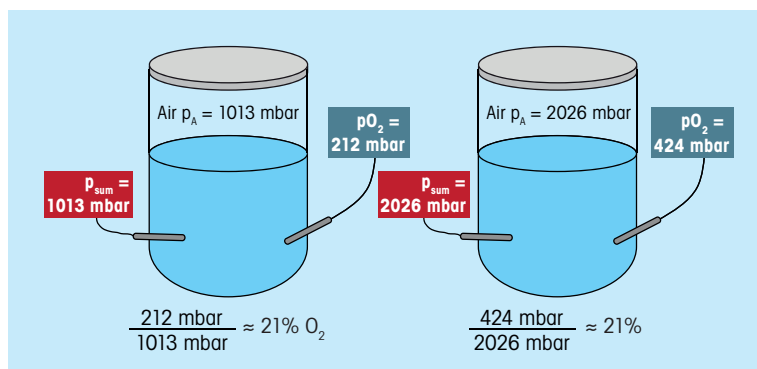
Figure 2   Influence of air pressure on partial pressures

Based on Henry's law, partial pressure influences relative oxygen measurements in systems that contain compressed gases in headspaces of monitored vessels. Closed systems completely filled with liquid do not require compensation for system pressures.

Note: The sensor measures partial pressures.

1.1.2.1   Influence of humidity

Relative humidity is the proportion of humidity relative to a water saturated gas mixture at a specific temperature. It can vary from 0 to 100 %.

The partial pressure of this humidity or the so called vapor pressure is – as all partial pressures – temperature dependent (Table 2, p. 13).

T [°C]	$p_{H_2O\,(sat)}$ [mbar]
0	6.1
10	12.3
20	23.4
25	31.7
30	42.4
40	73.8
50	123.3
60	199.2
70	311.6
80	473.4
90	702
100	1013

Table 2   Vapor pressure for 100 % relative humidity at different temperatures

For calculating the partial pressure of oxygen in percent saturation in a gas mixture, the vapor pressure of water and the ambient pressure (process pressure) need to be considered (see Equation 3 below, Figure 3/p. 14).

$$p_{O_2} = x_{O_2} \cdot (p_{air} - p_{H_2O})$$

p_{O_2} = Oxygen partial pressure
x_{O_2} = Mole fraction of oxygen
p_{air} = Atmospheric pressure
p_{H_2O} = Vapor pressure

Equation 3   Calculation of oxygen partial pressure in a humid environment
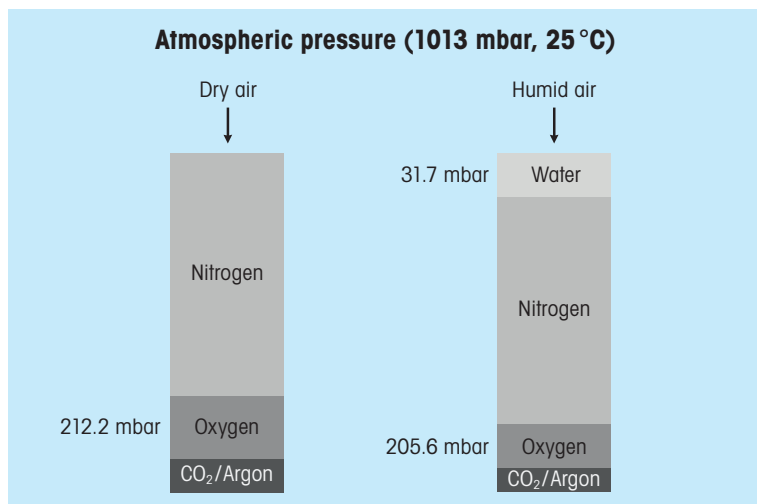
Figure 3   Partial pressures of oxygen in dry air and humid air with a vapor pressure (water) of 31.7 mbar (hPa) (p_{wsat})

Note: It is extremely important to correct for system pressure and humidity when calibrating the sensors on relative units like percent saturation or percent oxygen.

1.1.3   Henry's law for gases dissolved in liquids

When working with process liquids, the oxygen to be determined is normally dissolved in these liquids. This dissolved oxygen is in a steady-state or equilibrium with the oxygen in the ambient gas phase. The physical relationship is described by Henry's law. It states that the partial pressure of a gas above a liquid is directly proportional to the concentration of that gas dissolved in the liquid (see Figure 4, p. 15). This means that the concentration of dissolved oxygen can be measured by comparing the partial pressure of the dissolved oxygen to the partial pressure of the oxygen in the surrounding gas phase.

The concentration is determined by the Henry constant.
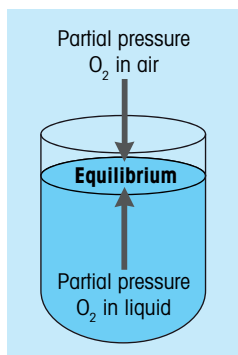
Figure 4   Henry's law – the concentration of oxygen in the liquid is proportional to the partial pressure of the oxygen in the gaseous phase surrounding the liquid

$$c_{O_2} = \alpha \cdot p_{O_2}$$

c_{O_2} = oxygen concentration in the solution

α = Henry constant

p_{O_2} = partial pressure of oxygen

Equation 4   Henry's law of gases dissolved in liquids

The Henry constant is dependent on the liquid, in which the gas is dissolved, as well as on the temperature, because these factors influence the solubility of oxygen (see Chapter 1.2).

1.2   Solubility – oxygen concentration

Gases are soluble in liquid to varying degrees.
Solubility of a gas in a liquid is a function of
– The temperature – the higher the temperature the lower the solubility (see Figure 5, p. 16)
– The salinity – increasing salinity leads to a reduced solubility of oxygen
– The solution itself (see Table 3, p. 16)
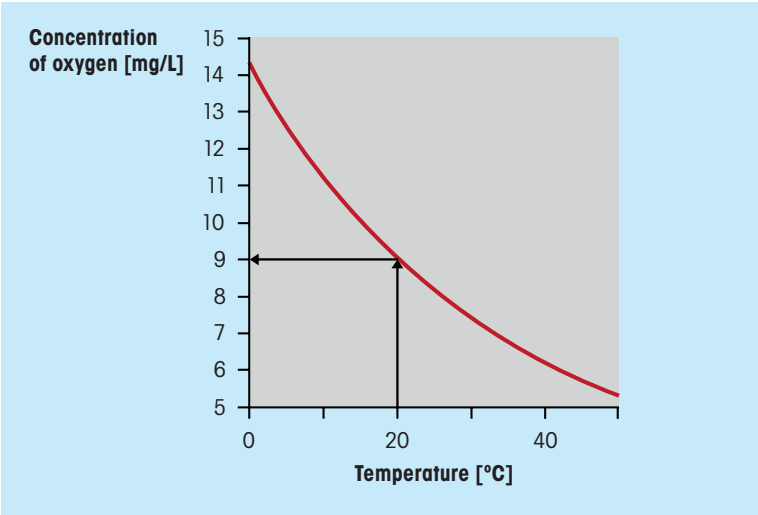
Figure 5   Oxygen solubility in pure water is dependent on temperature

This solubility, expressed as a mole fraction, is proportional to the partial pressure of the gas over the liquid (Henry's law).

Type of liquid	Solubility of oxygen at 20°C and 1013 mbar
Pure water	9.1 mg/L
4 M KCl	2.0 mg/L
50 % Methanol/50 % water	21.9 mg/L

Table 3   Solubility of oxygen in different media at 20 °C and 1013 mbar; 100 % saturation

As mentioned, according to Henry's law the oxygen concentration is proportional to its partial pressure (p_{O_2}).

$$c_{O_2} = p_{O_2} \cdot \alpha$$
α = solubility factor, Henry constant

Equation 5   Conversion of partial pressure to concentration of dissolved oxygen

If "a" is constant, the oxygen concentration can be determined by means of a sensor.

This means that in media with constant temperature and constant solutions the oxygen concentration can be determined. If the nature of solution changes, a new calibration to this solution has to be done.

Although the solubility may vary widely (see Table 3, p. 16), the resulting relative dissolved oxygen measurement as partial pressure from a sensor will be the same in all solutions. Therefore, determination of the absolute oxygen concentration is only possible with constant and known solubility factors "a". Transmitters only show the solubility factor for water. Solubility tables and corrections for different pressures and salt contents can be found on the website of the USGS.
(http://water.usgs.gov/owq/FieldManual/Chapter6/6.2.4.pdf; accessed June 2015).

1.3 Units for measurement of oxygen concentration

Oxygen measurements are either done in absolute concentration units such as mmol/L ($mmol/dm^3$) or mg/L (mg/dm^3) or in relative units such as % saturation calculated on the basis of air or oxygen.

Unit as shown on transmitter	Absolute/relative	Segment	Application example
% air saturation	Relative	Biotech and Pharma	Fermentation
% O_2	Relative	Biotech and Pharma	Fermentation
ppm (parts per million)	Absolute, in case of $d = 1\,kg/dm^3$	Food & Beverage	Brewing in liquid phase; high concentrations
		Water	Waste water treatment
		Chemical	Hydrocarbons

Unit as shown on transmitter	Absolute/relative	Segment	Application example
ppb (parts per billion)	Absolute, in case of d=1 kg/dm^3	Food & Beverage Pharma Power Chemical	Brewing in liquid phase; low concentrations Water; Demin Water Water treatment Water
µg/L	Absolute	Power	Water; Demin Water
mg/L	Absolute	Chemical	Water
% O$_2$ G	Relative	Food & Beverage Chemical	Brewing in gas phase Blanketing, inerting
ppm O$_2$ G	Relative	Food & Beverage Chemical	Brewing in gas phase Blanketing, inerting

1.3.1   Concentration

For most dissolved oxygen applications the desired unit of oxygen concentration is either parts per million (ppm) or mg/L. The mole fraction is easily converted to these units. However, oxygen measurements depend upon the oxygen partial pressure and – in the case of amperometric sensors – the oxygen permeability of the membrane (see 3.2.2, p. 26 and 3.2.5, p. 28). The oxygen concentration in mg/L has to be calculated upon the values of the partial pressure, e. g., via intelligent sensors or via a transmitter, if the Henry constant of the medium is known.

1.3.2   Saturation

The saturation (as % air or % oxygen) is commonly used to express the relative amount of oxygen compared to the maximum amount of oxygen which dissolves in a given liquid at a given temperature.
To get a correct measurement the value needs to be pressure compensated (see Chapter 1.1.2, p. 11). If the total pressure changes during measurement without compensation, the measured value for saturation

would follow this pressure change. The higher the temperature, the lower the absolute concentration of oxygen which can be dissolved to reach 100 % air saturation (see Table 4).

Temperature [°C]	Saturation concentration of oxygen [mg/L]	Air saturation [%]
0	14.6	100
10	11.3	100
20	9.1	100

Table 4   Correlation of concentration and 100 % air saturation at different temperatures in water; pressure is normal pressure with 1013 mbar; T = 25 °C

2   Calibration of oxygen sensors

Each oxygen sensor has its own individual slope and individual zero point, expressed as current in nA for amperometric sensors and as phase shift Phi for optical sensors (see Chapter 3.1 / p. 23 and 4.1 / p. 38).

Both values are subject to change through, for example, electrolyte consumption, after exchange of electrolyte, membrane body or OptoCap™. To ensure high measurement accuracy of the sensor, calibration must be carried out after each exchange of a sensors' spare parts. Prior to calibration amperometric sensors have to be polarized for at least 6 hours (see Chapter 3.2.3, p. 28).

With digital ISM sensors the Adaptive Calibration Timer (ACT) tells when a new calibration is necessary according to the process conditions (see Chapter 6.4.2, p. 68).

Oxygen sensor calibrations can be performed as a 1-point or 2-point calibration. For the 1-point calibration normal calibration medium is air, for a 2-point-calibration additionally a gas with 0 % oxygen has to be used, which normally is pure nitrogen.

2.1   1-point calibration

By carrying out a 1-point calibration the factual slope of a sensor can be established. The calibration medium can be water with a known oxygen saturation index (e.g., air saturated water) or air with a known water vapor content (e.g., water vapor saturated air). After the sensor signal has stabilized the sensor can then be calibrated to the 100 % value of the desired measurable variable, e.g., 100 % air, or, in cases of water as the medium at normal conditions (at 25 °C and 1013 hPa), 20.95 % oxygen or in case of gas measurements to 8.26 ppm. One-point calibrations should be sufficient for almost all process applications in the ppm oxygen range. For process applications with lower oxygen values (in the ppb area) a 2-point calibration, especially when using optical sensors, has to be performed.

As an example: In fermentation processes in the pharmaceutical industry, the sensor will be calibrated at 100% air saturation of the medium without cells after sterilization at process temperature. Therefore, the sensor is working between 0% and 100% saturation. A calculation to absolute concentrations such as mg/L or mmol/L can only be done with known solubility of oxygen in the medium (Henry constant).

2.2   2-point calibration

Carrying out a 2-point calibration establishes both the slope and zero point of a sensor. When conducting a 2-point calibration, always start with the zero point calibration before calibrating the slope.
Due to the very low zero current of METTLER TOLEDO amperometric sensors, 2-point calibrations are normally not necessary for standard applications.
If an optical sensor is being used at ppb-measurements a 2-point calibration has to be performed.
A zero point calibration is advisable if very high accuracy is required at low oxygen concentrations. For correct calibration, nitrogen gas or other oxygen-free medium with a level of purity of at least 99.995% should be used.
After the sensor signal has stabilized, the sensor can be calibrated to the 0% value of the desired measurable variable, e.g., 0% air, 0.0% O_2, or 0.0 ppm.

2.3   General considerations for 2-point calibrations

- For calibration in air, the sensor membrane must be dry since adhering water drops can falsify the measured oxygen value.
- The pressure and the air humidity during calibration have to be considered and entered into the transmitter.
- Oxygen saturation index of the calibration medium has to remain constant during calibration.

- In the event of calibration in water or sample medium, the calibration medium must be in equilibrium with the air. Oxygen exchange between water and air is very slow; therefore, it takes a long time until water is saturated with atmospheric oxygen.
- For amperometric sensors a minimum flow rate of the calibration medium is necessary.
- Calibration in a fermenter should be performed after sterilization (as sterilization may alter the sensor slope) but prior to inoculation.
- All process parameters, such as temperature and pressure, should be constant during calibration and compensated for accordingly.

2.4   Process calibration

Process calibrations differ from 1-point calibrations in that the former are conducted with a sensor in situ in a reactor. For optical sensors, a process calibration establishes a new Phi 100 value against the stored calibration curve to create a new curve. Because calibration curves for optical sensors are not linear, 1-point process calibrations in vessels with head-space must accurately account for system pressures or risk jeopardizing the accuracy of the entire curve. Because of this we recommend using 1-point process scaling instead of process calibration for the vast majority of post-SIP applications.

2.5   Process scaling

Unlike 1-point calibrations or process calibrations, process scaling – a unique feature for METTLER TOLEDO sensors – sets the measurement value to a desired level without making any adjustments to the calibration curve. This procedure is recommended for most biotech applications after post sterilization (autoclaving) or SIP with systems set to an initial value. With process scaling the real process pressure and the solubility factor for oxygen can be ignored, resulting in improved accuracy.

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3   Electrochemical methodology

In 1953, Leland Clark described an amperometric procedure to determine in vitro oxygen in blood. He used an electrode composition which is still used today in different modifications to determine dissolved oxygen.

The Clark electrode generally consists of a platinum cathode and a silver anode which are conductively connected via an electrolyte (other metal combinations as electrodes are possible). These electrodes are separated by an oxygen permeable membrane from the measurement solution. This membrane distinguishes the Clark sensor from former polarographic sensors. As compared to the polarographic electrode without membrane, the Clark sensor possesses the following advantages:

• Oxygen measurement in gases as well as solutions
• No mutual contamination of electrode and solution
• No or little dependency on process medium flow

In the case of the platinum/silver electrode combination a polarization voltage of around -800 to -500 mV is applied at the platinum cathode against the silver anode.

3.1   Measurement technology

Oxygen diffuses according to its partial pressure through the membrane into the measuring chamber and is reduced at the cathode to hydroxide ions (OH^-). At the anode, silver will be oxidized and in presence of chloride the undissolvable AgCl will deposit at the electrode. These deposits have to be regularly removed so that there is a constant current in the sensor.

Cathode: $O_2 + 2\,e^- + 2\,H_2O \rightarrow H_2O_2 + 2\,OH^-$ and $H_2O_2 + 2\,e^-$
$\rightarrow 2\,OH^-$
Anode: $4\,Ag \rightarrow 4\,Ag^+ + 4e^-$ and $4\,Ag^+ + 4Cl^- \rightarrow 4\,AgCl$

The current is directly proportional to the partial pressure of oxygen $p(O_2)$ and this proportionality can be used to determine oxygen concentration. Figure 6 shows the design of a Clark-type sensor.
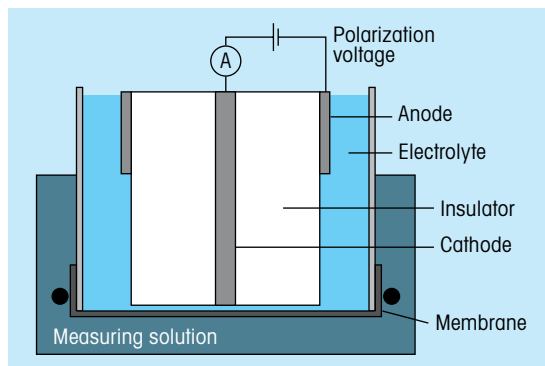
Figure 6   Cross section of a Clark-type oxygen sensor

3.2   Parameters determining current

The quantity of oxygen diffused through the membrane and the magnitude of the electrode current are influenced by the following parameters:
- O_2 partial pressure of the solution
- Membrane material and thickness
- Size of cathode
- Polarization voltage
- Temperature
- Flow conditions in the solution
  This dependency is expressed by a derivation of Fick's law which describes the correlation between current and the diffusion of the gas.

$$I = k \cdot D \cdot a \cdot A \cdot p_{O_2} \cdot 1/d$$

I   = electrode current
k   = constant
D   = coefficient of diffusion of O_2 in the membrane
a   = solubility of O_2 in the membrane material
A   = cathode surface
p_{O_2} = oxygen partial pressure in the solution
d   = thickness of gas-permeable membrane

Equation 6   Derivation of Fick's law shows that the current is mainly dependent on the nature of the membrane

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The amount of current is therefore highly dependent on the nature of the membrane and the size of the cathode. For this reason the electrode currents of different electrode types may differ by several powers of ten, and even between two different sensors of the same type different currents at 100 % air saturations may be measured. This is why calibration is essential after exchanging membrane bodies.

Parameter	Influence	Possible Correction
Oxygen partial pressure of solution	In systems that contain compressed gases in headspace (% saturation)	Correct for system pressure when measuring in relative units
Membrane material and thickness	The thicker the diffusion path, the lower the sensitivity	
Size of cathode	The larger the surface the greater the sensitivity	Larger cathodes for ppb measurements; longer polarization times and voltage at –500 mV to eliminate CO_2 influence
Polarization voltage	Selective for oxygen, should be as constant as possible	Between –675 mV to –500 mV, depending on sensors and application
Temperature	The higher the temperature the greater the diffusion	Temperature compensation
Flow conditions	Depending on velocity: Flow < 5 cm/s gives different signal	Minimum flow rate > 5 cm/s

Table 5   Parameters which influence the amount of current between anode and cathode

3.2.1   Oxygen partial pressure

According to Henry's law, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid (see Chapter 1.1.3, p. 14).

It is extremely important to correct for system pressure when measuring relative oxygen concentrations in percent. Closed systems completely filled with liquid do not require compensation for system pressures. Liquid column pressure has little impact on the oxygen partial pressure up to 100 m. This is based on the fact that air is compressible whereas liquid, under normal conditions, is not.

METTLER TOLEDO transmitters allow for manual entry of system pressure for compensation. Additionally, some transmitters may be configured with an external pressure sensors' analog signal (4 – 20 mA) for dynamic compensation of headspace gases and system pressures.

3.2.2 Sensor membranes

METTLER TOLEDO amperometric oxygen sensors feature a membrane with high permeability to oxygen molecules which also acts as an oxygen reservoir. There are two types of membrane which both consist of a silicone layer reinforced with steel mesh (see Figures 7 and 8, p. 27). The steel mesh gives enhanced stability and increases membrane life.

- S-type: The membrane is inside (at the measuring cell) coated with PTFE. The medium wetted part is the silicone layer (Fig. 7).
- T-type: The membrane is at the medium wetted part (outside) and the inside is coated with PTFE. The medium wetted part is a PTFE layer (Fig. 8).

The T-type is thicker but due to the repellent properties of the PTFE it is less sensitive to contamination by the medium (e.g., biological growth on the membrane). The membranes are designed for Clean in Place (CIP) and Sterilize in Place (SIP) tolerance. The diffusion of oxygen out of the sample solution into the silicone membrane is spread over a wide area. Since this results in less oxygen being extracted from the sample solution per unit area, the PTFE/silicone/PTFE membranes form an effective buffer against most disturbances due to hydrodynamic flow. This membrane design ensures, together with the other electrode components, excellent signal stability even when the hydrodynamic flow stops. Only a minimal flow of at least 5 cm/s is needed to maintain stable conditions.

Membrane

– Silicone layer reinforced with steel mesh to give enhanced mechanical stability
– **S-type:** Membrane inside coated with PTFE
– **T-type:** Membrane inside and outside coated with PTFE
→ enhanced coating-repellent and CIP/SIP capable
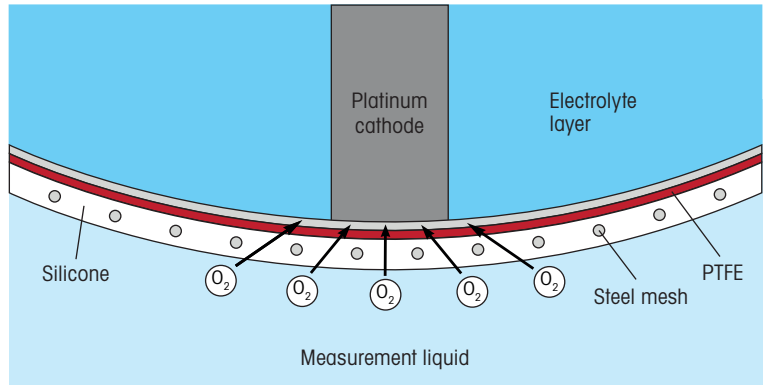
Figure 7   S-type membrane used in METTLER TOLEDO amperometric oxygen sensors
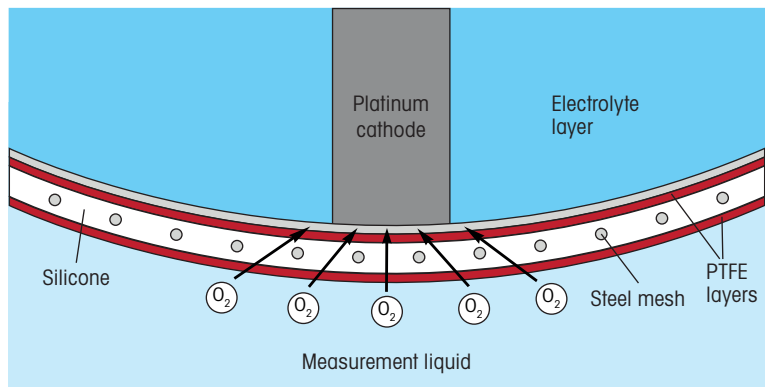
Figure 8   T-type membrane used in METTLER TOLEDO amperometric oxygen sensors

3.2.3 Polarization voltage

The voltage between the anode and the cathode is selected so that the oxygen is fully reduced but other gases are unaffected. The ideal voltage for the Pt/Ag/AgCl system is between and -675 mV and -500 mV. The polarization voltage should remain as constant as possible.

3.2.4 Temperature

The temperature dependence of the current passing through an oxygen electrode when referred to as constant O_2 partial pressure is determined mainly by the properties of the gas-permeable membrane.
Higher temperatures result in greater rates of diffusion and should be compensated for by the transmitter translating the raw current values.

3.2.5 Flow

With most oxygen electrodes the electrode current is smaller in stagnant solutions than in agitated ones. The reduction and consumption of oxygen by the electrode results in extraction of oxygen from the solution in the close vicinity of the cathode outside the membrane (the reduced and consumed oxygen is replaced via diffusion). If the electrode current is strong the diffusion rate of oxygen through the membrane can be lower since it takes time to establish the equilibrium. This results in an electrode current which is weaker than would correspond to the oxygen partial pressure in the solution. In agitated solutions the oxygen is conveyed to the surface of the membrane not only by diffusion but additionally by the flow (convection). In this case no oxygen impoverishment occurs at the membrane surface.

A high degree of flow dependence occurs mainly with large cathodes, and thin and highly permeable membranes, i.e. where electrode currents are large. The problem of flow dependence is often solved by prescribing a minimum flow rate.

3.3 Design of METTLER TOLEDO amperometric oxygen sensors

METTLER TOLEDO's amperometric oxygen sensors are all of a hygienic design (apart from InPro® 6050 i which was developed mainly for waste water applications). The aim is to offer sensors for different ranges of oxygen concentrations (ppm and ppb values) and therefore the most suitable sensor for every application can be selected (see Tables 6 / below and 7 / p. 30). The larger the cathode the more sensitive is the sensor. In some sensors additional guard rings, which consist of platinum, consume traces of oxygen which could disturb the measurement and therefore provide a more stable current signal.

Design	Oxygen concentration	METTLER TOLEDO sensor	Typical segment
2-electrodes	Medium to high oxygen concentrations	InPro 6800 InPro 6050	Biotech industry Waste water
3-electrodes	Medium to high oxygen concentrations; anode separated from reference	InPro 6850 i	Biotech industry
2-electrodes with guard ring, large cathode surface	Trace oxygen concentrations (1 ppb)	InPro 6900 (i) Thornton ISM DO sensor	Food & Beverage Power
3-electrodes with guard ring, large cathode surface	Trace oxygen concentrations (0.1 ppb)	InPro 6950 (i)	Food & Beverage

Table 6   Design of METTLER TOLEDO amperometric oxygen sensors for dissolved oxygen

Design	Oxygen concentration	METTLER TOLEDO sensor	Typical segment
2-electrodes	Medium to high oxygen concentrations	InPro 6800 G	Chemical industry − Inerting − Blanketing − Vapor recovery
3-electrodes	Medium to high oxygen concentrations; anode separated from reference	InPro 6850 i G	Chemical industry − Inerting − Blanketing − Vapor recovery
2-electrodes with guard ring, large cathode surface	Trace oxygen concentrations (1 ppb)	InPro 6900 i G	Chemical industry − Inerting − Blanketing
3-electrodes with guard ring, large cathode surface	Trace oxygen concentrations (0.1 ppb)	InPro 6950 i G	Food & Beverage

Table 7   Design of METTLER TOLEDO amperometric oxygen sensors for gas phase

In all sensors the function of the cathode is identical, whereas the design of the anode and reference systems are different.

Between cathode and reference a constant polarization voltage of −500 resp. −675 mV, which is specific for oxygen, is applied. Thereby, a reduction of oxygen into hydroxide ions takes place at the cathode.

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3.3.1 2-electrodes – for medium to high oxygen concentrations

These sensors are designed for medium to high oxygen concentrations. They consist of a platinum cathode and an anode with a combined reference system. Anode and reference are united in a silver/silver chloride electrode. Examples for this sensor design are the analog sensors InPro 6800 for hygienic applications in the biotechnology industry and the InPro 6050 in a rugged design for mainly wastewater applications.
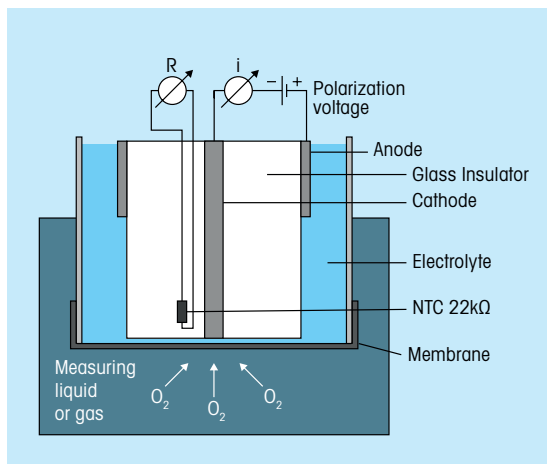
Figure 9   Schematic overview of a 2-electrode amperometric sensor

Figure 10   Examples of 2-electrode sensors InPro 6050 (above) and InPro 6800

3.3.2 3-electrodes – for medium to high oxygen concentrations

The anode is a platinum electrode and is separated from the reference electrode. The reference is a silver/silver chloride electrode with high resistance so that no polarization can take place at the reference. After polarization there is a stable equilibrium between the reference electrode surface and electrolyte. The advantage of separating the anode and reference is that no AgCl can precipitate at the anode surface and therefore the system is more stable.

In this design the InPro 6850 i, a digital sensor with full Intelligent Sensor Management (ISM) capabilities is available. These sensors are recommended for biotechnological applications such as fermentation monitoring.
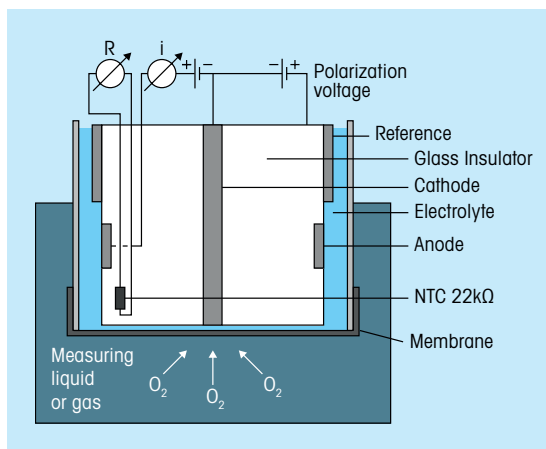
Figure 11   Schematic overview of a 3-electrode amperometric sensor

Figure 12   Example of a 3-electrode sensor (InPro 6850 i)

3.3.3 2-electrodes with guard ring – for traces of oxygen

These sensors are designed for oxygen measurement in the lower ppb range, which makes them ideal for the beverage industry. Here, the anode and reference are united in a silver/silver chloride electrode.

The sensors are equipped with an additional platinum guard ring around the cathode. This construction forms a closed electric circuit which prevents oxygen diffusing to the cathode and influencing the measurement. The cathode also has a large surface area which allows measurements in the lower ppb-range. In this design the analog InPro 6900 and the digital ISM sensor InPro 6900 i are available.
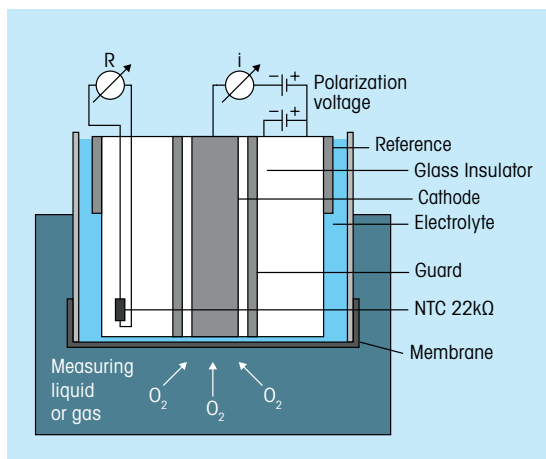
Figure 13   Schematic overview of a 2-electrode amperometric sensor with guard ring

Figure 14   Example of a 2-electrode amperometric sensor with guard ring
(Thornton ISM DO sensor)

3.3.4 3-electrodes with guard ring – for traces of oxygen

This design is intended for measuring trace oxygen down to 0.1 ppb, a level which is especially important in the beverage industry. It consists of three electrodes with an additional guard ring.

The anode (platinum) and reference (silver/silver chloride) are separated into two electrodes. A platinum guard ring is placed around the cathode. The cathode has a wide diameter and therefore a large surface which leads to a higher current during the measurement and higher sensitivity.

METTLER TOLEDO offers the analog InPro 6950 and the digital ISM sensor InPro 6950 i in this design.
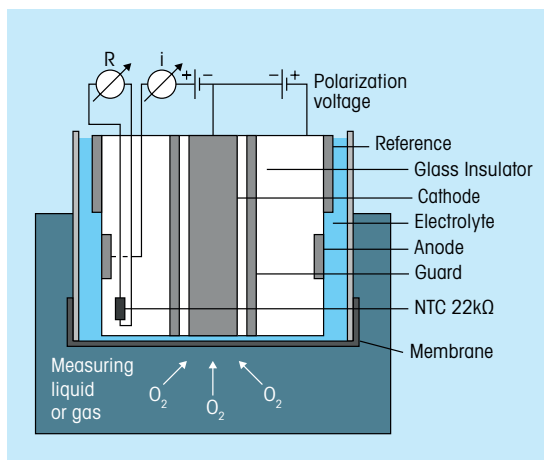
Figure 15   Schematic overview of a 3-electrode amperometric oxygen sensor with guard ring

Figure 16   Example of a 3-electrode amperometric oxygen sensor with guard ring (InPro 6950 i)

	2-electrodes	3-electrodes	2-electrodes with guard ring	3-electrodes with guard ring
Design	• Cathode • Combined reference/anode	• Cathode • Reference • Anode	• Cathode • Combined Reference/anode • Guard Ring	• Cathode • Reference • Anode • Guard Ring
Reaction at Pt cathode	$O_2 + 4\,e^- + 2\,H_2O \rightarrow 4\,OH^-$	$O_2 + 4\,e^- + 2\,H_2O \rightarrow 4\,OH^-$	$O_2 + 4\,e^- + 2\,H_2O \rightarrow 4\,OH^-$	$O_2 + 4\,e^- + 2\,H_2O \rightarrow 4\,OH^-$
Reaction at Ag anode	$4\,Ag^+ + 4\,Cl^- \rightarrow 4\,AgCl$		$4\,Ag^+ + 4\,Cl^- \rightarrow 4\,AgCl$	
Reaction at Pt anode		$4\,OH^- \rightarrow O_2 + 4\,e^- + H_2O$		$4\,OH^- \rightarrow O_2 + 4\,e^- + H_2O$
Reference		Ag/AgCl no current		Ag/AgCl no current
Guard ring (Pt)			$O_2 + 4\,e^- + 2\,H_2O \rightarrow 4\,OH^-$	$O_2 + 4\,e^- + 2\,H_2O \rightarrow 4\,OH^-$

Table 8 Chemical reactions in different METTLER TOLEDO amperometric sensor designs

3.4   Initial start-up and polarization

When operating the system for the first time or if the sensor has been disconnected from the voltage source (transmitter or oxygen sensor master) for longer than 5 minutes, the sensor has to be polarized. The purpose of polarization is to consume any residual oxygen molecules found in the electrolyte layer between the cathode and membrane (Figure 17, next page).
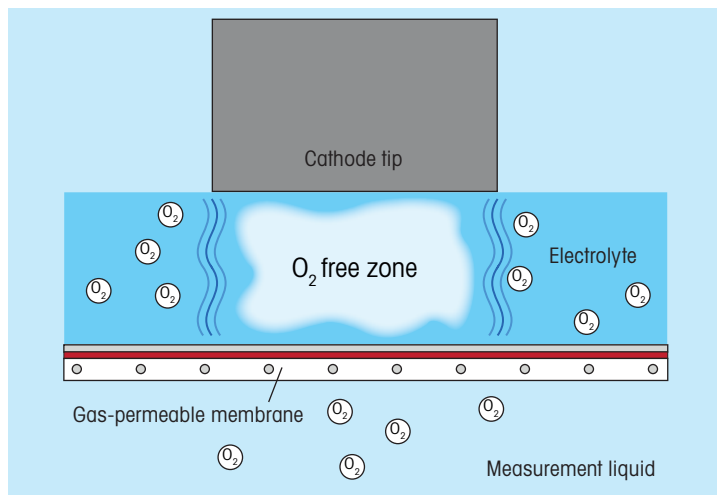
Figure 17   Polarized oxygen-free zone

Trace, non-consumed oxygen molecules will result in readings higher than actually present in the measured media. The reduction of residual oxygen during polarization occurs logarithmically, with $92-95\%$ consumed within the first 30 minutes. Functionality and performance verification is possible at this time. Additionally, applications monitoring oxygen at saturation levels are possible.

However, 6 hours are required for full polarization or even over night for more sensitive sensors. Full polarization is recommended for applications requiring the highest level of accuracy and for monitoring low to trace levels of oxygen. A shorter polarization period is sufficient for full polarization if the sensor has been disconnected for only a few minutes. The following table (Table 9, p. 37) shows the full polarization time in relation to the depolarization time.

After exchange of the electrolyte or the membrane body, a full polarization is always required.

Depolarization time t_{depol} [min]			Ideal polarization time [min]
	t_{depol}	> 30	360
30 >	t_{depol}	> 15	6* t_{pol}
15 >	t_{depol}	> 5	4* t_{pol}
	t_{depol}	< 5	2* t_{pol}

Table 9   Ideal polarization time according to depolarization time

Polarization time defines the time span during which the sensor is under a polarization voltage.

Depolarization time means the time span in which polarization voltage is cut off from the sensor. This is the case when the cable is disconnected or no transmitter or sensor master is connected to the cable. The ideal polarization time can be taken from Table 9.

4 Optical oxygen measurement

Optical measurement technologies use light to determine physical
values either directly or indirectly.
The method for oxygen determination with optical sensors is based
on fluorescence and the time the fluorescence lasts. The higher the
concentration of oxygen, the shorter the lifetime of the fluorescence.
This effect is called fluorescence quenching.
It is the result of an energy transfer between an excited fluorescing
chromophore (fluorophore) and oxygen molecules.

4.1 Measurement technology

The measurement of dissolved or gaseous oxygen with optical sensors
is as illustrated in Figure 18.

• A dye or fluorophore is illuminated with modulated green-blue light
  from an excitation LED. The modulation or pulsing, which is a high
  frequency sinus modulation of the intensity of the LED (1 – 6 KHz
  corresponding to 1 – 6 times modulation per µsec) is important for
  the later measurement.
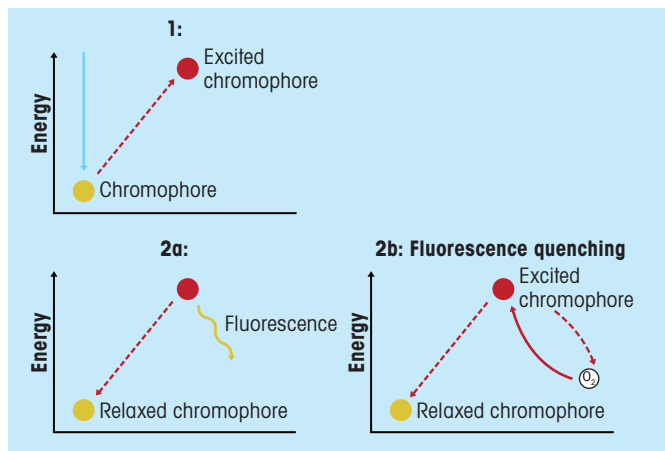
Figure 18   Steps of fluorescence and fluorescence quenching

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- The fluorophore absorbs the energy of the green-blue light and the molecules in the dye go to an energy-rich or "excited" state.
- These energy-rich molecules emit some of that energy as red fluorescence. The lifetime of the fluorescence is measured. This is done by comparing the modulated phases of the reference LED with the modulated phases of the measuring LED after excitation.
- A detector in the sensor reads the phase shift of the emitted fluorescence light in comparison to the phase of the reference LED and the transmitter displays the values in phase shift (Phi) values.
- Oxygen migrates through the gas-permeable membrane of the OptoCap and absorbs energy from the excited fluorophore. This leads to a reduction of lifetime of the excited state (quenching). The fluorescence lifetime is reduced with higher concentrations of oxygen, and the phase shift Phi is smaller compared to lower oxygen concentration.
- Phi is dependent on the oxygen level or oxygen partial pressure. The phase shifts by various oxygen concentrations are calculated using a Stern-Volmer equation (see Equation 7, p. 40). They are not linear, especially at higher oxygen concentrations, and are corrected for linearity using a specific algorithm in the transmitter or by the intelligent sensor.
- Sensors are thus able to calculate oxygen concentration from measured Phi of the modulated light. Higher oxygen concentrations absorb more energy resulting in less energy to excite the fluorophore. This causes a smaller phase shift compared to the reference LED than samples with lower oxygen concentrations.

Figure 19 (see below) compares Phi measurement values at high and low oxygen concentrations.

$$I_0/I = 1 + k_q t_0 * p_{O2}$$

Stern-Volmer relation with:

I_0 = intensity or lifetime of fluorescence without the quenching molecule (O_2) at the time point 0

I = intensity or lifetime of fluorescence with the quenching molecule (O_2)

k_q = quencher rate coefficient

t_q = fluorescence lifetime of the dye to be quenched

pO_q = partial pressure of oxygen

Equation 7   Stern-Volmer relation
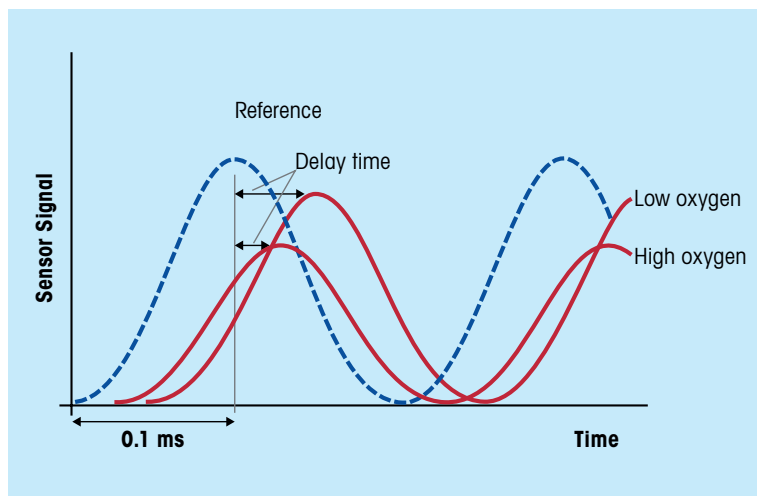
Figure 19   Phi measurements at high and low oxygen concentrations

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4.2   Design of METTLER TOLEDO optical oxygen sensors

METTLER TOLEDO optical oxygen sensors consist of a sensor head containing the electronics and LED sources, a sensor shaft with fiber optic cable, and the OptoCap containing the optical fluorophore layer (see Figure 20). Sensors are powered from a transmitter or external 24 V DC power source.

OptoCaps utilize a wetted PTFE membrane over a relatively thick silicone membrane. Both are highly permeable to oxygen molecules. The fluorophore layer embedded in an organic matrix sits behind the silicone. The PTFE and silicone layers protect the fluorophore layer from being directly wetted by the media and also from the diffusion of other chemicals from the sample solution into the fluorophore layer.
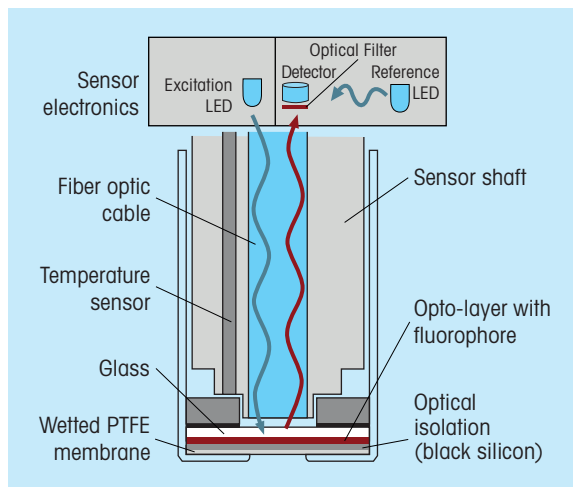
Figure 20   Optical sensor cross-section example

4.3   Optical sensor calibration

As mentioned in Section 2, the calculation of the Phi values at various oxygen concentrations, most often 100 % air (Phi 100) and 0 % air (Phi 0), is the basis of sensor calibration. Optical sensor calibrations

establish Phi values for known concentrations and calculate remaining points with a Stern-Volmer correlation. This results in a calibration curve (e.g., Figure 21, below) which allows accurate calculations of oxygen concentration.
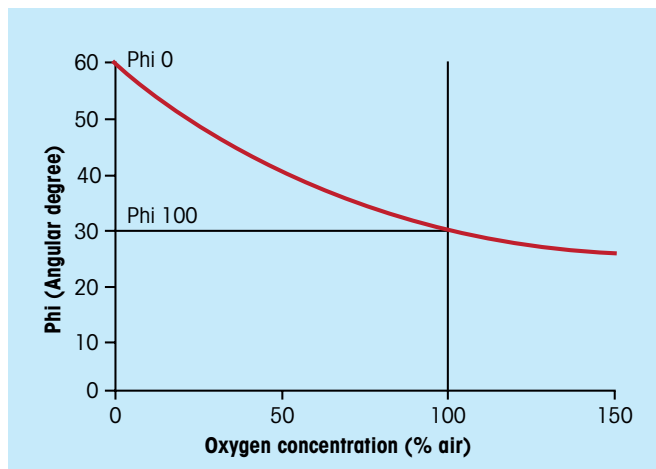
Figure 21   Example of an oxygen calibration curve with optical oxygen sensors

4.3.1   Calibration requirements

Each OptoCap has specific values for Phi 100 and Phi 0 due to differences in the thickness of the dye layer and membrane (see Table 10, p. 44). Therefore, an initial calibration at those two points is necessary. New METTLER TOLEDO sensors are 2-point calibrated at the factory and do not need an additional 2-point calibration prior to operation.

Important considerations for calibration:
• For calibration in gas (air), the OptoCap must be dry as adhering water drops can falsify the measured oxygen value.
• Temperature and pressure have to be constant.
• Calibration always needs accurate pressure, relative air humidity and temperature measurements. Only process scaling is independent of pressure and air humidity.
• Make sure that the correct calibration pressure, humidity and salinity values are set in the transmitter before the calibration is started.

- If calibrating in water or sample medium, the calibration medium must be in equilibrium with the air.

Oxygen exchange between liquid and air is slow. Therefore, for dissolved oxygen measurements it takes some time until the equilibrium between the dissolved oxygen in the liquid and the oxygen in the atmosphere is reached.

- Sensor adjustments in a fermenter post-sterilization should only be performed as process scaling and not as a process calibration unless process pressures are accurately accounted for.

4.3.1.1 Simulated amperometric standardization and direct integration

METTLER TOLEDO sensors InPro 6860 i for biocontroller or retrofit installations use a simulated current for oxygen measurements. The current is linearly proportional to the calibrated Phi 100 and Phi 0 with ~65 nA set for 100 % at 25 °C and 0 nA set for 0 %. Standardization of biocontrollers and non-ISM-enabled transmitters simply follow the calibration/standardization recommendations for amperometric sensors. The sensor also can integrated directly into any 4 – 20 mA installation using the HART™ protocol to monitor and control the sensor with commercially available HART tools.
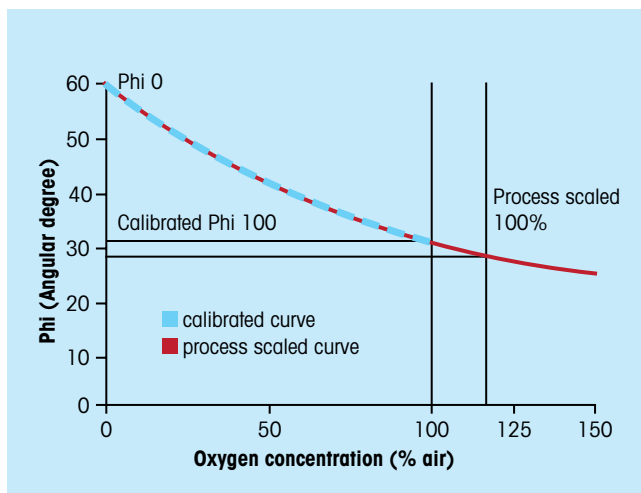
Figure 22   Example of process scaling

Model	Criteria	Alarm	Good	Alarm
InPro 6860 i				
	Zero Point (Phi 0)	< 50°	50 ... 65°	> 65°
	Slope (Phi 100)	< 20°	20 ... 38°	> 38°
	Phi 0 – Phi 100	< 20°	> 20°	
	KSV	< 0.01	0.01 ... 0.05	> 0.05
InPro 6870 i				
	Zero Point	< 50°	50 ... 65°	> 65°
	Slope (Phi 100)	< 15°	15 ... 35°	> 35°
	Phi 0 – Phi 100	< 20°	> 20°	
	KSV	< 0.01	0.01 ... 0.1	> 0.1
InPro 6960 i				
	Zero Point	< 53°	53 ... 68°	> 68°
	Slope (Phi 100)	< 18°	18 ... 38°	> 38°
	Phi 0 – Phi 100	< 20°	> 20°	
	KSV	< 0.01	0.01 ... 0.1	> 0.1
InPro 6970 i				
	Zero Point	< 74°	74 ... 82°	> 82°
	Slope (Phi 100)	< 10°	10 ... 18°	> 18°
	Phi 0 – Phi 100	< 55°	> 55°	
	KSV	< 0.015	0.015 ... 1.5	> 1.5

Table 10   Sensor status of different METTLER TOLEDO optical oxygen sensors as shown in iSense (KSV: Stern-Volmer constant)

4.4 Optical aging, stability control and calibration recommendations

Actual Phi 100 and Phi 0 change unequally with time and operation (shown in Figure 23, p. 46). This change is caused by normal and expected degradation of the fluorophore. Phi values change as part of the degradation process with a bigger change of Phi 0 than of Phi 100. During the measurement the LED sample rate, the oxygen concentration, and process temperature directly influence the rate of degradation. High sample rates in high oxygen media with high temperatures degrade the optical dye causing the greatest shift in the Phi values. An active LED is the primary contributor of degradation. High oxygen levels and high temperatures do not significantly contribute to degradation without the LED being active. Therefore, as long as the sensor is switched off, e.g., during sterilization, the degradation is extremely small. Figure 23 (p. 46) shows an expected calibration shift due to normal degradation of the fluorophore.

4.4.1 Automatic Stability Control (ASC)

The degradation of the fluorophore is quite linear over the lifetime of an OptoCap. The purpose of periodic calibrations is to correct for the normal sensor ageing. As shown in Figure 23 (p. 46), calibrations adjust the values to provide accurate readings. METTLER TOLEDO is able to offer dynamic compensation of sensor ageing to limit its impact on the precision of measurement.

The sensors utilize a proprietary algorithm that monitors the sample rate, oxygen level and process temperature to accurately calculate shifts in Phi values caused by degradation. METTLER TOLEDO terms this compensation, Automatic Stability Control or ASC. As implied by the name, Automatic Stability Control stabilizes the oxygen reading and significantly reduces the need for calibrations.

This stability control is able to learn process specific sensor ageing. By performing a 1-point calibration in air after some batches, the sensor compares calculated Phi shift values with calibration Phi shifts to most accurately compensate for future fluorophore degradation. As a result, there is nearly no drift of the sensor in the process, as shown in Figure 24 (p. 47).
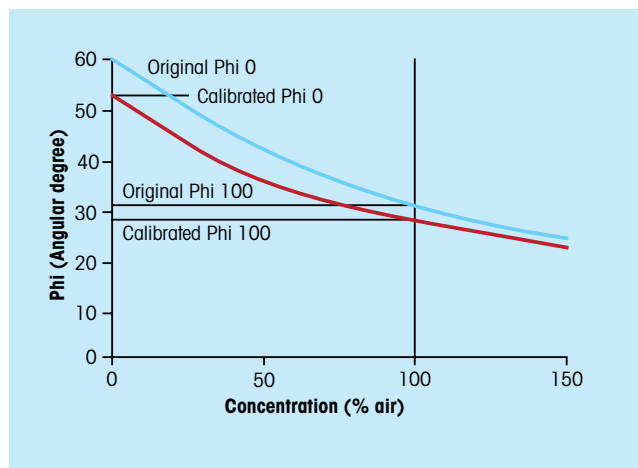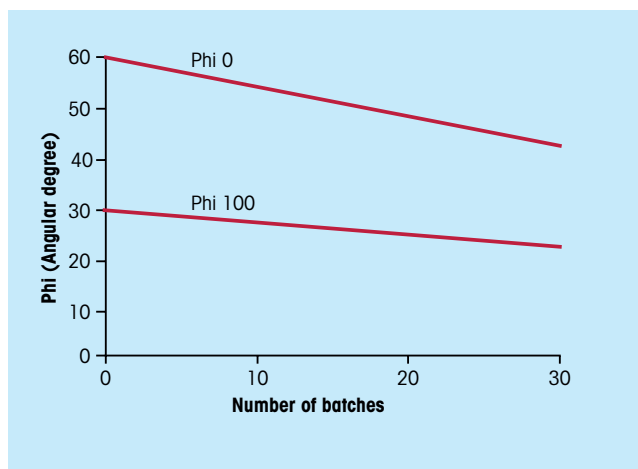
Figure 23   Phi 0 and Phi 100 shifts and the effect of calibration

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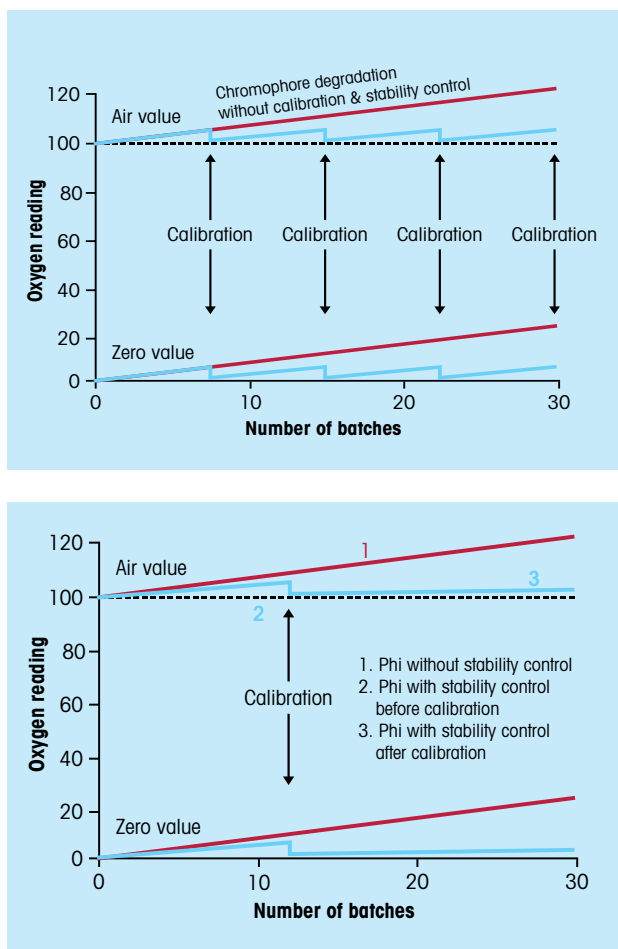
Figure 24   Calibration adjustments without and with Automatic Stability Control

4.4.2   Recommended calibration frequency

Optical oxygen sensors should have an initial 2-point calibration upon exchange of OptoCaps. The 2-point calibration process establishes the initial Phi 100 and Phi 0. Subsequently, only periodic 1-point calibra-

tions with infrequent 2-point calibrations are required on systems with Automatic Stability Control. The Automatic Stability Control algorithm provides accurate compensation for OptoCap aging. In general:

A 2-point calibration is required:
• For each new OptoCap
• If high accuracy is needed below an oxygen partial pressure of 60 mbar

A 1-point calibration is sufficient:
• As long as the oxygen level is above 60 mbar partial pressure

Recommended calibration procedures are listed in Table 11.

Application	Oxygen concentration	Sensor	Recommended calibration
Biotech	High	InPro 6860 i	1-point calibration
Biotech	High	InPro 6870 i	1-point calibration
Food & Beverage (high)	High	InPro 6960 i	1-point calibration
Food & Beverage (low)	Low	InPro 6970 i	2-point calibration
Food & Beverage	Low	InPro 6980 i	2-point calibration
Power	Low	Thornton Pure Water Optical DO sensor	2-point calibration

Table 11   Recommended calibration procedures for METTLER TOLEDO optical oxygen sensors; "high" means in ppm range, "low" means in ppb range

Frequency of calibration is best determined by duration of process batches and frequency of sterilization cycles.

For normal three to five day pharmaceutical batch processes it is advisable to wait for at least five batches before performing a 1-point calibration in order to provide the Automatic Stability Control algorithm with sufficient process condition data. After this it is unlikely that an additional 1-point calibration will be required for another five to ten batches.

One-point or 2-point calibrations in applications measuring below 60 mbar prior to commencement are recommended in processes of longer duration such as fed-batch and perfusion methods.

4.5   Communication installation options

Some METTLER TOLEDO optical oxygen sensors provide both digital communications (RS 485) and simulated amperometric oxygen sensor operation. Digital communication is possible with selected transmitters from METTLER TOLEDO and is ideal for new installations. Simulated amperometric operation, on the other hand, enables optical oxygen sensors to be retrofitted into existing installations or connected to a wide variety of biocontrollers.

4.5.1   Digital communication

The digital communication interface RS485 provides optimal performance and maximum functionality with selected METTLER TOLEDO transmitters. The 2-way communication between sensor and transmitter takes full advantage of the advanced performance of systems with Intelligent Sensor Management (ISM) (see Chapter 6, p. 64). Additionally, selected METTLER TOLEDO transmitters, with the exception of those powered from digital bus networks, provide power to the sensors which simplifies installation. Bus-powered METTLER TOLEDO transmitters require an additional power source for optical sensors (24 V DC, 800 mW) independent of the bus protocol.

4.5.2   Simulated amperometric communication

Some METTLER TOLEDO sensors simultaneously generate a current signal in nanoAmpere for corresponding to the oxygen partial pressure besides the resistance signal in Kilo-Ohm for temperature measurements (NTC 22 KOhm) and compensation.

Simulated signals are used to retrofit sensors into existing installations or provide functionality with the majority of biocontrollers found throughout process development facilities. The vast majority of biocontroller or retrofit installations require the oxygen sensors to be powered independently. METTLER TOLEDO offers a variety of cable and adapter options to facilitate powering of sensors.

5 Common challenges with oxygen measurements

As with any sensing technologies, accurate measurements may be influenced by a variety of elements, which generally may be divided into three categories: sensor related, media related, or external factors.

5.1 Sensor related factors

	Amperometric	Optical
Calibration	Correct for system pressure	Correct for system pressure
	Homogenity of oxygen concentration in vessel	Homogenity of oxygen partial pressure in vessel
Physical damage of measuring system	Cracks in anode/cathode assembly	OptoCap wear and damage
	Delamination of cathode	Cracks in optical fiber
Membrane	Tears in membrane	
	Deformation of membrane	

Table 12   Sensor related factors, which influence oxygen measurements

Sensor related issues may be caused by improper calibration or sensor setting. Improper calibration and bad zero offset will impact the ability of the sensor to provide reliable measurements.
Errors resulting from process calibrations conducted in vessels with headspace pressures are common occurrences. Many operational challenges to accurate and reliable dissolved oxygen measurements stem from not accounting for headspace pressures during process calibrations. METTLER TOLEDO recommends the use of process scaling in place of process calibrations for the majority of applications.
If process calibration is required, ensure system pressures are correctly input for on-line measurements to most accurately match any grab samples. Physical damage of sensors is another common cause of sensor related issues.

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5.1.1 Amperometric sensors

The anode/cathode assembly is relatively rugged but is made of glass and will crack if improperly handled. Delamination of the cathode from the assembly glass surface is also known to happen. Sensor applications in which regular steam cleaning occurs will accelerate this tendency (Figure 25).

Symptoms of cracking and delamination appear as high zero or air values during system response testing. Sensors will not respond to zero per specifications. More severely damaged sensors will not reach zero and may "hang" at the low end of measurement. Sensors may also display higher than normal or specified current values in 100 % air samples.

During maintenance the anode/cathode assembly should be inspected for any visible signs of damage. Assemblies with cracks or delamination should be replaced.

Delamination Zone

Figure 25   Cracked and delaminated anode/cathode

Membrane damage is the most common issue that affects measurements. Membranes are expendable components and should be periodically replaced as part of standard operating procedures/maintenance. Membrane damage may occur due to:

– Splitting and pin holes caused by improper membrane handling.
– Defect in membrane
– Dirty or contaminated membrane from improper membrane handling

– Stretched membrane from sterilization or fluctuating process pressure or aggressive cleaning agents from CIP processes.

Tears in the membrane (see Figure 26) result in extremely erratic signals. Deformation or stretched membranes cause higher than expected readings. Catastrophic membrane failures result in close to zero or very high readings (e.g., 999 %) depending upon the electroconductive nature of the process media.

Figure 26   Membrane tear

5.1.2   Optical sensors – OptoCap wear and damage

Normal OptoCap wear is the most common sensor related measurement issue for optical sensors. Depending upon operating process conditions and LED sample rates, OptoCaps can have an operational lifetime of up to one year. Figure 27 (p. 53) provides examples of how new, worn and bleached OptoCap fluorophores appear.
The sensor continuously monitors if OptoCap performance (Phi values and intensity) is within acceptable levels. Systems found to be out of tolerance return error messages during transmitter operation or system calibrations with iSense™ software (see Chapter 6.5, p. 70). An OptoCap should be replaced if this occurs.
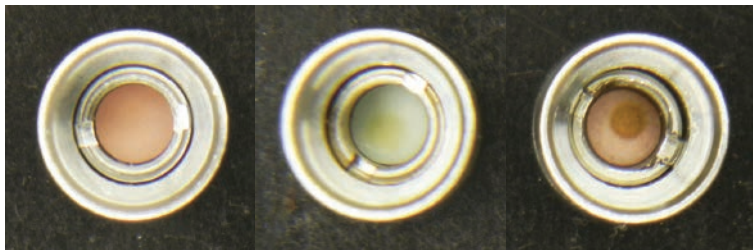
Figure 27   OptoCaps with original fluorophore (left), bleached fluorophore (middle) and worn fluorophore (right)

Symptoms of worn OptoCaps or damaged sensors can be observed during system response testing. For example, symptoms could include sensors not responding to zero within the specified time or not reaching zero at the low end of measurement (see Chapter 5.6.1, p. 62).

Physical damage to the sensor can also be a cause of sensor related issues. METTLER TOLEDO optical sensors are rugged and capable of withstanding SIP and autoclave cycles. However, they contain a fiber optic cable in the sensor shaft that, although extremely uncommon, can crack if the sensor is improperly handled or dropped. The primary symptom of a cracked fiber optic is highly erratic and unstable readings resulting from an inconsistent transmission of light energy to and from the fluorophore layer. Sensors with suspected cracked fiber optics cannot be repaired and will require replacement. Suspect sensors should be sent to METTLER TOLEDO for evaluation.

5.2   Media related factors

5.2.1   Amperometric sensors
Erroneous dissolved oxygen measurements may be caused by the following substances:
– Hydrogen sulfide (H_2S)
– Sulfur dioxide (SO_2)
– Chlorine
– Carbon monoxide (CO)
– Nitrous oxide and nitric oxide

– Halogens
– Hydrogen
– Ozone
– Strong solvents, acids and alkalines may damage probe materials such as stainless steel and silicone

In the event of media contamination in the sensor, signals will spike past 100 % scale or crash to zero. The surge or crash of signal generally occurs at a steady, linear pace once contamination infects the sensor. Removal of the contamination from the media and replacement of membrane and electrolyte will likely correct the issue.

Level of Interference

Hydrocarbons			**Solvents**			**Alkaline/Acid**			**Critical**		
Propane	C_3H_8	●	**Alcanes**			Ammonia	NH_3	●	Hydrogen sulfide	H_2S	●
Ethane	C_2H_6	●	Hexane	C_6H_{14}	●	Carbon dioxide	CO_2	●	Hydrogen	H_2	●
Methane	CH_4	●	Heptane	C_7H_{16}	●	Hydrogen fluoride	HF	●	Chlorine	Cl_2	●
Butadiene	C_4H_6	●	**Aliphatic HC**								
Acetylene	C_2H_2	●	Benzene	C_6H_6	●	Sulfur dioxide	SO_2	●			
			Toluene	C_7H_8	●	Sulfur trioxide	SO_3	●			
			Ketones								
			Methyl ethyl ketone (MEK)	C_4H_8O	●	Hydrogen chloride	HCl	●			
			Acetone	C_3H_6O	●						
			Alcohols								
			Isopropanol (IPA)	C_3H_8O	●						
			Ethanol	C_2H_6O	●						
			Methanol	CH_4O	●						

Explanations

Higher chemical reactivity will lead to higher probability of interference	Stronger electrochemical activity will cause higher interference	Substances with lower acid dissociation constant (pKa) cause higher interferences	Substances with lower acid dissociation constant (pKa) cause higher interferences

Applications

Petrochemical Refining	ChemPharma Petrochemical	Bulk chemicals Fine chemicals	Petrochemical Bulk and fine chemicals

● = high concentration acceptable*;
   * under standard conditions

● = medium concentration (<10-5%) acceptable*;
   * 78

● = low concentration (<1.0-0.1%) acceptable*;
   * internal usage only

Table 13   Interference of different chemical substances with amperometric sensors

5.2.2 Optical sensors

The dyes of the sensors have been optimized for their specific area of application, such as biotech processes or processes in the food & beverages industry. Chemical substances not common to those processes may chemically react with the fluorophore, accelerating its degradation (e.g., H_2S, Cl_2, other strong oxidizing chemicals). This is especially true if the sensor LED is sampling during exposure to chemicals. OptoCaps are compatible with most Clean in Place chemicals as long as the LED is shut off during these operations.

Media attack on OptoCaps will generally result in the depletion or "bleaching" of the fluorophore. Sensor signals will spike past expected values and rise above 100 % scale or completely over range if the dye is bleached.

Removal of the contamination from the media, ensuring the LED is turned off during periods of chemical exposure, and/or replacement of the OptoCap will likely correct the issue.

5.3. External related factors

5.3.1 Trapped air

Gas bubbles adhering to the membrane which have a higher oxygen partial pressure than the liquid, may cause increased rates of oxygen penetration through the membrane than is present in the media (see Figure 28 and 29, p. 56). This occurrence is common if sensors are installed in vessels with sparger systems. Care should be taken to ensure the sparger is not too close to the sensor and to ensure a 15 degree entry of the sensor into the vessel as this will help prevent air bubbles adhering to the membrane.

5.3.2 Biological growth

Biological growth on sensor membranes may occur in some installations. The biological growth will coat the membrane and consume oxygen molecules, preventing them from entering the sensor (see Figure 28 and Figure 29, p. 56). Biological growth on amperometric sensors can be prevented by the use of sensors with a T-type membrane as the PTFE layer acts as a repellent to micro-organisms.

Sensors should be mounted at an angle in applications in which biological growth is expected to coat membranes to help prevent cells becoming attached. In extreme cases operators may consider mounting sensors in the headspace and rely on Henry's law for the calculation of dissolved oxygen content.
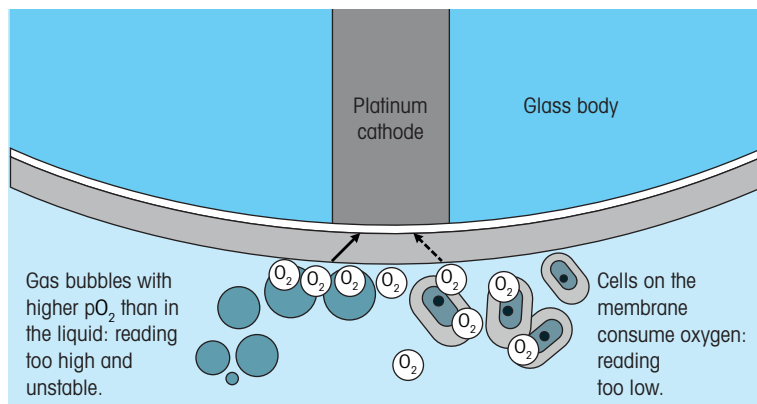
Figure 28   Impact of air bubbles and biological growth on an amperometric DO sensor
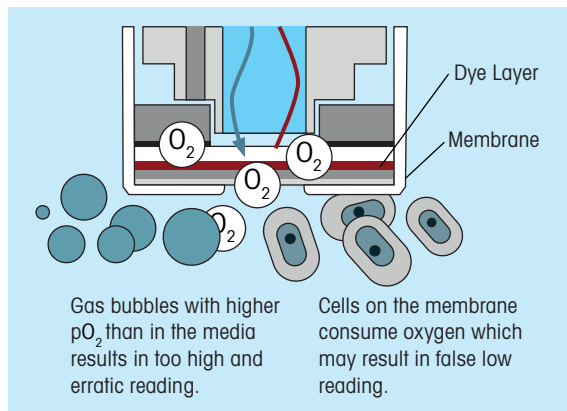
Figure 29   Impact of air bubbles and biological growth on an optical DO sensor

5.3.3   Varying system pressure

As oxygen sensors measure the partial pressure of oxygen, vessels with fluctuating headspace pressures will result in fluctuating partial pressure measurements. METTLER TOLEDO transmitters have the ability to dynamically compensate for fluctuating system pressures.

5.3.4 Amperometric sensors: fluctuating flow

Because sensors measure the partial pressure of oxygen, systems with fluctuating flows will necessarily have changing oxygen partial pressures. System fluctuations will result in erratic measurements often corresponding directly to a shift in pressure.

An exception to this may result from a sudden loss of system pressure. The sensor membrane may "relax" during depressurization. Oxygen rich electrolyte will be drawn into the previously oxygen-free layer directly below the cathode. Sudden measurement spikes immediately following system depressurizations may be experienced, since the diffusion resistance rises.

5.4. Other factors

Fast temperature changes, e.g., after CIP processes in food & beverage applications, leads to an inaccurate temperature measurement and compensation by the transmitter. Therefore, the correct oxygen value is measured after stabilization of the temperature.

5.5 Sensor maintenance: amperometric sensors

METTLER TOLEDO amperometric oxygen sensors are extremely reliable when properly calibrated and operated. It is important to note that the sensors contain consumable items such as the membrane and anode/cathode assembly. These components will require periodic replacement as standard operating procedure.

There are three parameters to check in order to tell if an amperometric oxygen sensor needs maintenance or replacement or still can be confidently used:

- Nominal Sensor Current in Airflow (NSCiA) – at 100 % oxygen saturation
- Nominal Zero Point Current in Nitrogen (NZPCiN) – at 0 % oxygen
- Response time testing

5.5.1 Nominal sensor current in airflow

Amperometric oxygen sensors can be quickly function checked in atmospheric air against acceptable current values. As previously stated, InPro oxygen sensors experience a current change (nA) proportionate to the amount of oxygen in the media. InPro oxygen sensors will have, in atmospheric air, an nA value as shown in Table 14 at 25 °C and 1013 mbar (hPa), depending on the size of the cathode and polarization voltage applied. Acceptable current values will correspondingly change as the ambient temperature decreases or increases. Sensors with values out-of-specification should be troubleshooted. With ISM sensors the TTM and DLI will change and warnings will be displayed (see Chapter 6, p. 64).

Please note that the polarization voltage (Upol) is different for different sensors. Table 14 lists some typical values.

Temp [°C]	InPro 6050 Upol −675 mV		InPro 6800/ 6850 i (G) Upol −675 mV		InPro 6900 Upol −675 mV		InPro 6900/ 6900 i Upol −500 mV		InPro 6950/ 6950 i (G) Upol −500 mV	
	min.	max.	min.	max.	min.	max.	min.	max.	min.	max.
25	−50	−110	−50	−110	−250	−500	−250	−500	−2500	−5000

Table 14   Nominal Sensor Current in Airflow [NSCiA] in nA at 1013 mbar (hPa) and 25 °C

5.5.2 Nominal zero point current in nitrogen

This value is measured in nitrogen with a purity of at least 99.995 % nitrogen (4.5 quality). For trace oxygen sensors such as the InPro 6950 (i) the N_2 quality has to be 5.0. The sensor should be tested directly in a flushing chamber into which nitrogen is fed (ballvalve set to N_2; flow rate approx. 0.2 L/min.). At room temperature, the value on the display should change as listed in Table 15 (p. 59).

Temp [min]	Current InPro 6050	Current InPro 6000/ 6800/ 6800 i (G)	Current InPro 6900/ 6900 i (G)	Current InPro 6950/ 6950 i (G)
5	< NSCiA/100	< NSCiA/100	< NSCiA/100	< NSCiA/500
30	< NSCiA/250	< NSCiA/1000		
60			< NSCiA/5000	
120				< NSCiA/8000

Table 15   Zero current in different METTLER TOLEDO sensors at different time intervals

5.5.3   Response testing

Response testing is the best means available to ascertain the proper functionality of amperometric oxygen sensors. Response testing involves cycling a fully polarized sensor from an oxygen rich environment to an oxygen-free environment.

Response time (in N_2) should be < 2 % of initial air value after 90 s. Figure 30 (p. 60) provides response test examples. "A" charts an example of a fully functioning sensor. Response from an oxygen-rich to an oxygen-free environment is quick with 90 % of the final zero value achieved within 30 seconds.

Sensor B remains in specification by achieving the final value of ≥ 2 % of initial air value after 90 seconds. However, it is sluggish in its approach to its final zero value. While in specification, sensor B is likely approaching the end of service life for its membrane and/or anode/cathode assembly.

Anode/cathode assemblies with visual signs of cracking or delamination should be replaced.

Sensors C and D fail the response test as both sensors fail to reach final zero. The anode/cathode assemblies have most likely reached their end of service life or the membrane is damaged.

With digital ISM sensors and their predictive diagnostics, amperometric sensors tell the user when maintenance will be required (see Chapter 6, p. 64).
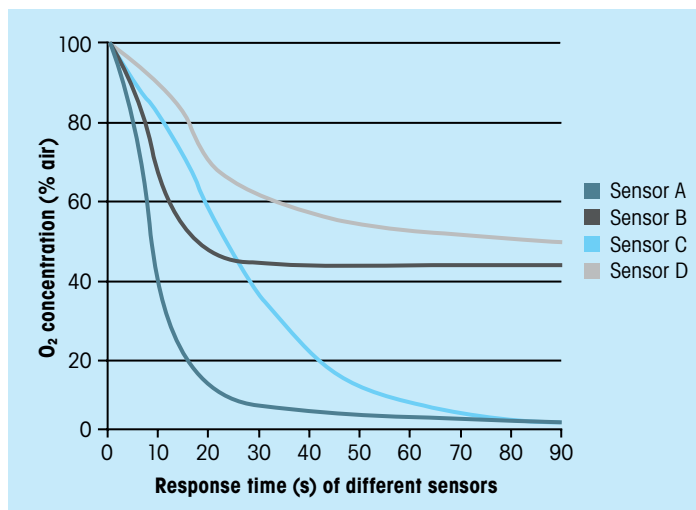
Figure 30   Response testing examples

5.5.4   Maintenance: Changing the electrolyte and membrane body

If a sensor is to be stored for several months the electrolyte should be replaced before use. If the membrane exhibits signs of failure (long response time, increased current in an oxygen-free medium, mechanical damage, etc.) the membrane body has to be replaced.

5.5.5   In situ troubleshooting

Accurate in situ troubleshooting can be challenging. Response testing is always the preferred method to determine functionality of analog amperometric oxygen sensors. Application experience can also be used as a cross check against sensor performance.
Figure 31 (see next page) provides some typical examples for signals indicating maintenance and possible errors.

Figure 31   Typical sensor signal examples for troubleshooting amperometric oxygen
              sensors

5.6   Sensor maintenance: optical sensors

METTLER TOLEDO optical sensors are extremely reliable when properly calibrated and operated. Beyond periodic replacement of OptoCaps little to no maintenance is required. To replace the OptoCap you first have to unscrew the cap sleeve.

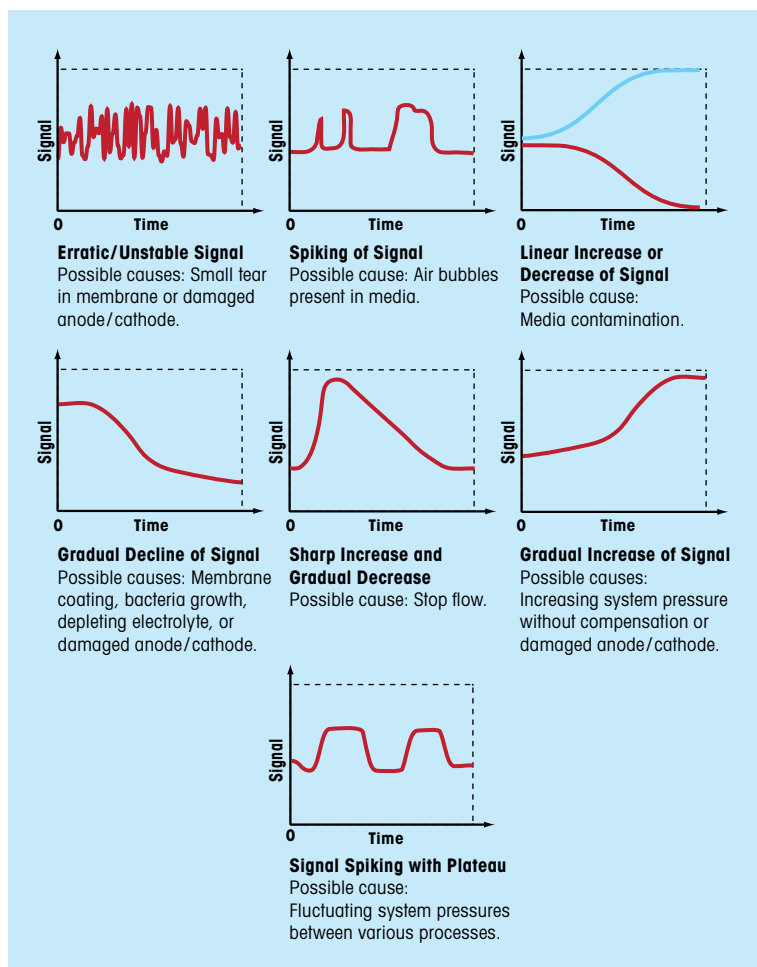If the cap sleeve is detached be aware of the fiber optic cable in the center of the sensor shaft. Damage and soiling of the fiber optic cable may influence the signal or destroy the sensor. Small soiling can be removed with a lint-free cloth.

OptoCap replacement is quick and easy:

• Unscrew the OptoCap from the sensor shaft and carefully pull it off the sensor.
• Place the new OptoCap over the sensor shaft and screw it into place.
• After each exchange of the OptoCap, reset the DLI manually using either a transmitter or iSense.
• Perform a 2-point calibration after each exchange of the OptoCap

5.6.1 Response testing

Response testing is the best means available to ascertain the proper functionality of optical oxygen sensors. Response testing involves cycling an optical oxygen sensor from an O_2-rich environment to an O_2-free environment.

Good sensor specifications are:
Response time from air to zero in N_2: $< 2\%$ SAT after 70 s
Response time from zero to air: $> 98\%$ SAT after 70 s

Erratic/Unstable Signal
Possible causes: Small tear in membrane or damaged anode/cathode.

Spiking of Signal
Possible cause: Air bubbles present in media.

Gradual Decline of Signal
Possible causes: Membrane coating, bacteria growth, depleting electrolyte, or damaged anode/cathode.

Gradual Increase of Signal
Possible causes: Increasing system pressure without compensation or damaged anode/cathode.

Signal Spiking with Plateau
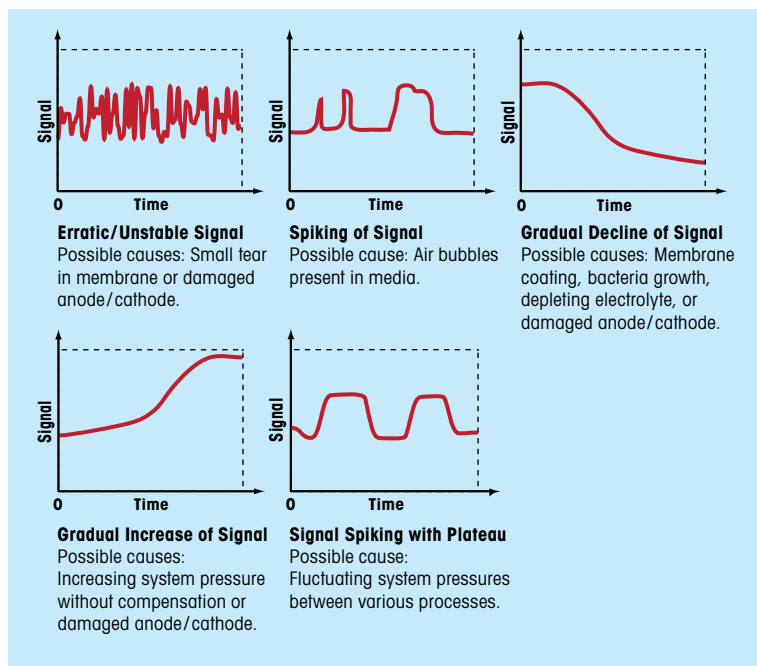Possible cause: Fluctuating system pressures between various processes.

Figure 32   Typical sensor signal examples for troubleshooting optical oxygen sensors

6 Intelligent Sensor Management (ISM)

The most significant development in recent years in in-line process analytical measurements has been the introduction of digital measurement systems. These allow a number of sensor installation, measurement, calibration, and maintenance advantages that analog systems cannot provide. METTLER TOLEDO's Intelligent Sensor Management (ISM) platform is one such technology. ISM simplifies sensor handling, enhances process reliability, and reduces sensor lifecycle costs. Central to ISM is the inclusion of a microprocessor in the sensor head. It is this feature that permits ISM's many benefits.
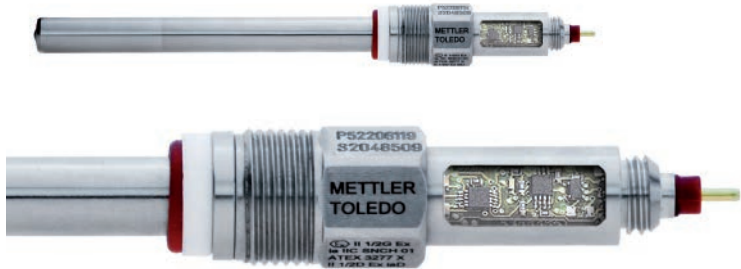

Figure 33 Sensor with ISM chip in sensor head

6.1 Signal integrity

As mentioned earlier in this guide, oxygen sensors transmit an electrical signal to a transmitter which converts the signal to a displayed level of oxygen. With analog sensors, environmental influences such as humidity and electromagnetic interference from surrounding equipment, plus the length of cable from sensor to transmitter, can negatively impact the integrity of the signal.

In ISM sensors the oxygen level is calculated in the sensor's microprocessor. The digitized signal is then transmitted over coaxial cable to the transmitter for display and/or forwarding to a PLC system. Being digital, the signal is unaffected by environmental or cable effects; therefore, the signal integrity of ISM systems is extremely high. This makes ISM sys-

tems particularly suitable for processes where the sensor and transmitter are physically far apart, and processes where there is a lot of moisture present in the environment.

6.2 Pre-calibration

A further advantage of ISM is the storing of sensor calibration data on the sensor's microprocessor. This means that sensors can be calibrated, using computer software (see Chapter 6.5, p. 70) or an ISM-equipped transmitter, in a convenient location and then stored, until they are required. This feature is particularly useful, for example, in the biophar-maceutical industry where taking calibration fluids into a cleanroom presents a contamination risk, or in chemical processes where there exists a potential health risk to employees.
Further, when connected to the transmitter, due to the calibration and other configuration data held on the sensor, the new probe is instantly recognized and the system is ready to measure in under a minute. This Plug and Measure feature not only significantly reduces the time for which a measurement system cannot be used, it eliminates the risk of incorrect calibration data being entered into transmitters, thereby increasing process reliability.

6.3 Predictive diagnostics

During batch and continuous processes, the failure of a measuring sensor can be hugely detrimental. Ideally, operators want to know that a sensor will operate correctly until the batch is complete. ISM technol-ogy is able to provide expert diagnostic information that is particular to each measurement point. This information is available to operators via the display on ISM-equipped transmitters, or can be sent to the PLC.

The diagnostic tools allow a measurement point to be optimized on an ongoing basis and all critical situations to be predicted so that operators can respond before production is affected.

Dynamic Lifetime Indicator

The DLI estimates in real time the remaining lifetime of the sensor. A unique algorithm uses current and historic measurement and calibration values to calculate the remaining lifetime of an oxygen sensor.

Adaptive Calibration Timer

Based on the DLI, the ACT calculates when the next sensor calibration will be required.

Time to Maintenance

The sensor also indicates when the next maintenance should be performed.

CIP/SIP Counter

CIP and SIP cycles are interpreted with a proprietary, patented algorithm.
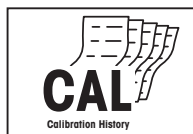
Calibration History

Calibration history is stored in the electrode and can be used for diagnostics.
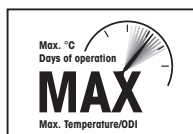
Maximum Temperature

Maximum Temperature/Operating Days Indicator. Information about the maximum temperature the sensor has ever been exposed to and the number of operating days.

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6.4 ISM algorithms in more detail

6.4.1 Dynamic Lifetime Indicator

The Dynamic Lifetime Indicator (DLI) is a diagnostic parameter providing information about the remaining reliable lifetime of the inner body of an amperometric sensor or of the OptoCap of an optical sensor. The DLI is expressed in units of days and counts down the remaining days of reliable operation.

As long as the DLI is above zero days the system is within the specified accuracy after a calibration. If the DLI is zero after a calibration the inner body of an amperometric sensor or the OptoCap of an optical sensor has to be replaced.

The DLI may be monitored dynamically through a transmitter's analog output and relay or through an analog input of a bus-enabled transmitter. The DLI can also be associated with a transmitter alarm for indication when it falls below a set level.

Contributing factors for the counting down of the DLI include:

• number of measurements
• temperature during measurement
• oxygen concentration during measurement
• number of CIP cycles
• number of SIP cycles
• number of autoclavings

The DLI is calculated in two different ways:

1. Continuously: Using the above parameters actual sensor stress is calculated. With each measurement the sensor load is increased. The accumulated load divided by the elapsed time is the basis of the calculation of the remaining lifetime. Changes in process conditions such as temperature and oxygen value are automatically taken into consideration.

2. During calibration: Calibrated values are compared to the values of the first calibration of the actual sensor.

Using the previously calculated sensor load and the elapsed measurement time since the first calibration, the remaining lifetime of the inner body or OptoCap is calculated. The calculation after a calibration gives a higher accuracy of the DLI compared to the continuous calculation. Thus the DLI value can be significantly different after a calibration. The longer an oxygen sensor is in use, the more accurate is the DLI information. Short term process changes with a new sensor influence the DLI much more than after a longer time in use.

Notes: For an accurate DLI calculation an accurate calibration is essential. Also, the date and time must be set correctly in the transmitter before connecting a sensor.

For optical sensors, depending on the age of the OptoCap, the phase values typically decrease over time compared with a new OptoCap. The DLI continuously monitors the OptoCap Phi 100 and Phi 0 values to ensure they remain in specification.

6.4.2 Adaptive Calibration Timer

The Adaptive Calibration Timer (ACT) provides information as to when the next calibration is required to ensure measurements will remain within the specified accuracy. The initial calibration interval in days is user programmed.

Systems with higher stress, such as high temperatures and, in the case of optical sensors, high LED sample rates will countdown the remaining days to calibration more quickly than systems with lower temperatures. The ACT may be monitored dynamically through a transmitter's analog output or through an analog input of a bus-enabled transmitter. The ACT can also be associated with a transmitter alarm for indication when it falls below a set level.

6.4.3 Time to Maintenance – for amperometric sensors

Time to Maintenance (TTM) gives an indication as to when the membrane body of an amperometric sensor should be exchanged.

6.4.4 Total Operation of OptoCap (tooCap) – for optical sensors

Bus-enabled transmitters provide a continuous count in days of total time of operation of an OptoCap. The tooCap counts up in increments of days and provides operators with a snapshot of how long a particular OptoCap has been in operation, providing useful trending information when compared with the DLI. The tooCap is an excellent parameter to ensure that OptoCaps have been exchanged and calibrated before starting with a product change or entering a long-term batch process. The tooCap parameter may be monitored through a transmitter's analog output or through an analog input of a bus-enabled transmitter. The tooCap can also be associated with a transmitter alarm for indication when it rises above a set level.

6.4.5 Calibration history

The last three calibrations and the factory calibration data are stored in the sensor memory. This data can be read out with a transmitter or with iSense software. The calibration history gives valuable information regarding the quality of the calibration and the wear of the membrane body or OptoCap.

6.4.6 Control – for optical sensors

The primary contributing factor to the aging of an OptoCap is the measurement itself. To prolong OptoCap lifetime, the measurement can be switched off if the system is not needed. Active measurement during CIP cycles or when the sensor is exposed to higher oxygen levels during standby of the plant should be avoided. With the LED shut off, the sensor sends a constant measurement value of −1 % air to the transmitter and the transmitter is set to the "Hold mode". To configure the "Hold mode" please refer to the transmitter's manual.

6.4.6.1 Automatic switch off at high temperature for optical sensors

If the LED mode is set to "Auto" (default setting) the sensor LED will be switched off as soon as a specified process temperature is reached. The specified temperature could be, for example, 60°C / 140°F for an InPro 6860 i but this limit can be set to an individual value below 60°C with a METTLER TOLEDO transmitter or with iSense. Above 60°C

the sensor will always be switched off. These settings are also active if the sensor is connected to the process as a simulated amperometric sensor. The switch off temperature should be set at least 5 °C higher than the highest process temperature. For example, if the highest process temperature is 37 °C, 43 °C should be the minimum set-point. In this situation, as soon as the temperature exceeds 43 °C the sensor will stop measuring and the LED will be switched off. For the switch on, a hysteresis of 5 °C is implemented, meaning that the sensor (and LED) will be switched on as soon as the temperature drops to 37 °C.

6.4.6.2 Switch off of the sensor for optical sensors

The sensor LED can be switched off manually through the transmitter menu by setting the LED mode to "off" or by a remote signal (digital input). To restart the measurement, the LED mode needs to be set manually to "on" via the transmitter menu, or via a remote signal (digital input). Selected METTLER TOLEDO transmitters with FOUNDATION fieldbus and PROFIBUS PA also have the ability to switch the LED off and on through commands sent over the bus network.

6.4.6.3 Remote switch off through hold function for optical sensors

METTLER TOLEDO transmitters can be set to "Hold" by applying an external digital signal (see transmitter manual). In this situation the sensor and the sensor LED are switched off. As soon as the "Hold Mode" is off, the optical sensor will continue to measure using the previous settings.

6.5 Asset management software

iSense is computer software for use with ISM sensors. iSense provides a number of functions including sensor calibration, electronic documentation, and management of all the ISM sensors at a facility. iSense runs on PCs and laptops and is designed to be used in a location where sensor maintenance is most convenient. In chemical industry applications this could be in a workshop or maintenance room which is close to the production environment. In the pharmaceutical industry a laboratory would be suitable.

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6.5.1   Calibration

Calibrating ISM oxygen sensors using iSense is a straightforward and quick process. Once completed, the calibration data is automatically recorded in a database for that particular sensor.

6.5.2   Electronic documentation

For the pharmaceutical and biopharmaceutical industries, meeting stringent regulations includes being able to supply accurate records on the calibration history of process analytical sensors used at a facility. The time taken for technicians to transfer written notes to a PC can be considerable, and there is always the possibility of human error in the data transfer.

With iSense, a record of a sensor's calibration and maintenance history is automatically stored in the internal database. Additionally, data on maximum temperature exposure, operating time, number of CIP/SIP cycles, etc. are also uploaded from the sensor to iSense. All this data can be documented electronically or printed from a PDF. A user management and electronic logbook allows control and tracking of all activities ensuring a complete record of oxygen sensor assets over their lifetime.

Figure 34   Calibration protocol of an optical sensor with iSense

6.5.3   Sensor management

Every time an ISM oxygen sensor is connected to iSense, the software's Key Performance Table tells you if the sensor is "healthy". The data shown is appropriate for the sensor type and provides the most essential information, including sensor condition and history (e.g., exposure to CIP/SIP cycles).

The key to effective sensor management with iSense is the Dynamic Lifetime Indicator (DLI) mentioned above. The unique algorithm behind the DLI distills METTLER TOLEDO's many years of experience regarding the influence of process environment and maintenance (e.g., temperature, pH level, calibrations) on sensor lifetime and compares this historical data with the current process conditions. From this information the DLI produces a real-time display of remaining electrode life. By monitoring the condition of ISM assets you are able to ensure you always have sufficient stock of healthy sensors.

When the DLI indicates that a sensor can no longer be used, for process security iSense can disable the sensor and issue a deactivation report. If a deactivated sensor is accidently connected at a measurement point, the transmitter will recognize that the probe has been disabled and it will not be accepted.

A complete view of all sensor data is provided by an SQL database allowing you to access all previously stored data of all ISM sensors used at a facility. Unlimited data export opens new possibilities for optimizing measurement systems and processes, as well as maintenance management of the installed sensor base.

7 Comparison of optical and amperometric technologies

The following table shows some features of amperometric and optical oxygen sensors. These are illustrated and pointed out in the practical cases below.

Optical	Amperometric
Innovative	Proven, reliable
Electrolyte free – no polarization	With electrolyte – polarization required
Not flow dependent	Flow dependent
Extended maintenance intervals and easy maintenance	Regular maintenance
Dye reduces fluorescence during lifetime – OptoCap needs replacement	Membrane body and electrolyte need replacement
High signal reliability	Wide measurement range
Can be installed in any direction	Installation in a 15 degree angle

7.1 Application in breweries: Highest sensor performance in low oxygen applications

In the filler line of breweries, very low dissolved oxygen levels have to be measured and the detection of changing oxygen levels has to be very fast to prevent filling from "out of spec" beer.

It was the requirement from breweries for beers with increasingly longer shelf life that led METTLER TOLEDO to develop an optical sensor with outstanding measuring performance. Excellent signal stability, low drift and low noise reduce the need for recalibration. The fast response time enables the user to start the filling process much more quickly after a switch from rinsing water to beer, and consequently possible beer losses are reduced.

Most of the in-line dissolved oxygen sensors available today suffer from a "stop of flow" effect. When the filling line is stopped the resulting increasing oxygen reading of the sensor is often the cause of false alarms in the process control system. With an optical oxygen measurement system a stop of flow effect is negligible.

In addition to the shorter response time, reliability and process safety are also improved. The risk of errors caused by the sensing element is much less likely. The quality of the OptoCap changes very slowly and failure such as membrane cracks or electrolyte leakage into the beer caused by extreme process conditions (e.g., pressure shocks) is not possible.

One component, the OptoCap, has to be replaced periodically as a consumable. Due to easy and hassle-free replacement and speed of calibration, the system is available in less than a minute. Alternatively, pre-calibrated sensors can be mounted to the process and a correct oxygen reading is available immediately.

After calibration, the operational availability of the system is displayed on an M400 series transmitter. The longer lifetime of the OptoCap, together with the fast and easy replacement, reduces maintenance costs and risk of operating errors.

Plug and Measure for highest availability – Intelligence starts in the head …
All sensor data, including calibration data, is stored on a microchip in the sensor head itself. This allows maintenance and calibration to be conducted in the controlled and clean conditions of a laboratory. This is especially important for a zero point calibration with oxygen-free gas. Having a gas supply and a gas-tight calibration station in a laboratory is more convenient than taking these items into the plant.

Installation of the calibrated sensor into the process becomes very simple: after connecting the sensor to the transmitter all relevant data is automatically transferred to the transmitter and an oxygen reading is

available in less than a minute. No pre-polarization is necessary. METTLER TOLEDO optical sensors help you to focus on the most important thing – the process itself.

7.2 Application in the pharmaceutical industry: High fermentation yields in the quickest possible time

Running a fermentation process is a bit like walking a tight rope. It is a balancing act involving monitoring and control of physical and analytical parameters, and in the case of fed-batch mode operations, also regulating substrate feeding. If you maintain your poise throughout the run, the results are high fermentation yield in the quickest possible time. Wobble, and yield reduces and run time increases. Stumble, and the batch can be lost. For some APIs loss of a 15,000 liter batch can amount to $ 1,000,000.

APIs produced via biofermentation are extremely sensitive to the manufacturing process. Lot to lot variability in product quality is commonly observed even when fermentation has been performed using exactly the same process; and variability has also been known to affect final product quality. In order to minimize batch inconsistency, analytical parameters are measured and controlled. The goal is to keep these parameters at a constant setpoint or on a predefined trajectory. However, as a run progresses, cell metabolism and accumulation of metabolic side products may alter the fermentation medium in an unpredictable way, necessitating corrective action.

Cell cultures require dissolved oxygen for the production of energy from organic carbon sources, e.g., glucose. Given oxygen's poor solubility in water, the control of air flow is carefully regulated to ensure it does not become a rate-limiting factor in the process. Overdosing dissolved oxygen is not harmful to the microorganisms, but is a waste of energy used to run air compressors. The signal from an oxygen sensor can be used to build-up closed-loop control for the air supply.

7.3 Application in the power industry: Minimize power plant corrosion with improved optical DO technology

In power plant cycle chemistry, control of dissolved oxygen (DO) is essential to minimize corrosion and the subsequent deposition of metal oxide corrosion products in critical components. Therefore, measuring DO in power plants is a fundamental process management parameter. However, many plants still use membrane-based polarographic sensors for DO determination, and although this technology is reliable under ideal conditions, in practice it can be problematic. Issues with DO measurement using polarographic probes have been eliminated by sensors that utilize optical measurement. The high performance and reliability of optical sensors is the reason for their increasing use in power plants.

Membrane-based DO sensors typically have a slow downscale response. This is because any oxygen which accumulates in the electrolyte during air calibration, startup, or high DO excursions takes a long time to diffuse back out of the membrane, or be consumed at the cathode or at a guard electrode. Therefore, high DO readings will persist after the probe is returned to a low DO sample. This issue is particularly frustrating after an air calibration cycle when the operator has to control DO in some applications while waiting for the sensor to recover to normal measurement levels. It can also be costly during plant startups when feedwater must be deaerated to acceptable levels before proceeding to full pressure. If slow DO sensor response delays a plant startup, massive amounts of fuel are wasted and power sales opportunities are forfeited until the DO measurement response finally meets the startup requirement.

Dissolved hydrogen interferes with most membrane-based, polarographic DO sensors. Hydrogen is often present in power plant stator cooling and nuclear power plant water samples, and it can suppress the measurement of DO or even result in negative readings. However, the most frequently voiced problem with polarographic technology centers around the frequency and costs of maintaining and calibrating the sensors. Power plant operators have reported that such sensors can

require membrane replacements and calibration as frequently as monthly. This is driven by performance degradation, causing a loss in measurement confidence. Depending on the sensor type, maintenance can require disassembly involving specialized tools, cleaning with hazardous chemicals, polishing electrode surfaces, and careful reassembly where membrane placement is critical. Even quarterly maintenance cycles mean unnecessary measurement downtime, additional costs, and a heavy labor investment at a time when most power plants are looking to reduce maintenance workload.

METTLER TOLEDO's Pure Water Optical DO Sensor incorporates the latest developments in this technology, including the use of an easily replaceable unit, the OptoCap, which houses the chromophore. Response time is in the order of four to five times faster than that of polarographic sensors. Maintenance is simplified and its frequency greatly reduced. Rather than the complicated and time-consuming maintenance several times per year for polarographic sensors, the Pure Water Optical DO sensor only requires annual replacement of the OptoCap. The significantly faster response of the Pure Water Optical DO Sensor means air calibration is simple and far less time consuming. Additionally, process calibrations allow performance optimization of the sensor without interfering with plant operation.

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Notes

Alliance Technical Sales, Inc.
312 Park Avenue Unit 145
Clarendon Hills, IL 60514-0145
Phone: 630-321-9646
Fax: 630-321-9647
Email: sales@alliancets.com
Web: www.alliancets.com

www.mt.com/pro