TECHNICAL NOTE

Electrochemistry **July 2014**

Dissolved Oxygen Measurement – understanding O_2 measurement results

Oxygen measurement technique

Oxygen molecules (O_2) are essential for life on earth and in water. The normal atmospheric O_2 concentration in air at sea level altitude is 20.942 % by vol.

Air bubbles (O_2 molecules) are held dissolved in water by physical forces and are bound or released depending on temperature, pressure and salinity.

Example: the solubility of O_2 in water (salinity=0, temperature 20°C, ambient pressure 1013 hPa) is 9.09 mg/L O_2 (see e.g. ISO 5814 "Determination of dissolved oxygen - Electrochemical probe method").

The measurement of dissolved oxygen is usually based on O_2-sensors for practical reasons. There are two main sensor techniques available, which are defined in norms and regulations: electrochemical (DO) and optical (LDO).

The electrochemical DO electrode has an oxygen permeable membrane, a cathode (e.g. gold), an anode (e.g. silver or lead) and an electrolyte solution. By applying a voltage between the gold cathode and anode oxygen molecules at the surface react electrochemically. Oxygen, crosses the membrane into the inner DO chamber and is reduced at the gold cathode.

$$O_2 + 2H_2O + 4\,e^- \rightarrow 4\,OH^-$$

In parallel the metal anode (Ag = polarographic or Pb = galvanic sensor) is oxidized and releases electrons (= current flow).

$$Ag \rightarrow Ag^+ + e^- \quad \text{or} \quad Pb \rightarrow Pb^{2+} + 2\,e^-$$

The higher the O_2 concentration, the higher the resulting current flow. The meter software converts (with calibration at 0% and 100% DO) the measured current into a concentration of dissolved oxygen.

The optical DO method (LDO = luminescent dissolved oxygen) is more and more replacing the electrochemical method. A flashing blue light LED excites the chemical in the sensor cap to return red light depending on O_2 concentration in the sample.

$$Chemical + O_2 + blue\ light \rightarrow red\ light$$

From calibration at 0% and 100% DO the intensity of the red light is converted into a concentration of dissolved oxygen. With optical DO sensors, the relationship is inversely proportional: the lower the O_2 concentration, the higher the emitted red light intensity. This is an advantage, because usually low O_2 concentrations have to be determined.

A second red light LED imposes a reference beam to "zero" the system. Based on the optical technique this is a unique advantage of LDO (luminescent dissolved oxygen) electrodes. If the outer sensor cap is scratched, the active surface area is reduced but because of the inner red reference beam, up to ¼ damage of the chemical surface can be compensated and still gives correct DO readings.

DO calibration

The standard 100% DO calibration is performed in a BOD bottle*) with water saturated air (bottom is covered with approx. 5 ml tap water).

For 0% DO calibration a BOD bottle filled with tap water can be purged with N2 gas until no more oxygen is present, or a mixture of ascorbic acid in 5N sodium hydroxide solution can be used. The alkaline ascorbic acid solution needs a few minutes to remove all present O_2.

The formerly described 0% standard using sodium sulfite and cobalt salt (catalyst) is hazardous and is no longer recommended.

**) The DO/LDO probe could be calibrated just in air, but the BOD bottle with water saturated air defines a stable environment for reproducible calibrations (no local temperature or pressure fluctuation).*

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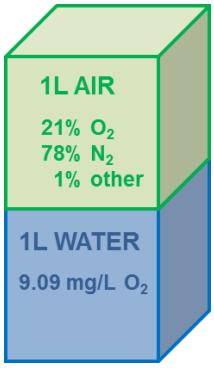
Understanding the 100% DO calibration

Why does the DO probe show 100% O_2 in air (21% O_2, 78% N_2), but when measuring in water, it shows around 9 mg/L and also ~100%O_2 ?

Let's assume, the ambient pressure is 1013 hPa and the temperature is 20°C. The experiment should be 1 Liter of air and 1 Liter of water:

1 mol O_2 = 22400 ml = 32 g/mol



In AIR (100% O_2):
21% of 1000 ml = 210 ml
210 ml = 0.009375 mol
= 300 mg/L O_2 = 100% O_2 in **air**

In WATER (100% O_2):
9.09 mg/L[**)] = 0.0002841 mol/L
= 6.363 ml O_2 = 100% O_2 in **water**

300 mg/L O_2 ≠ 9.09 mg/L O_2 !

100% O_2 ≠ 100% O_2 ?

When selecting the DO probe calibration procedure, the user has to select the type of calibration. This is mainly the "100% DO" calibration: BOD bottle with water saturated air. The probe is in air and **measures** 100% O_2 (=21% by volume of air).

When measuring in water, the meter **calculates** the theoretical value of dissolved O_2 in water (for that specific °C, hPa and Salinity). The measured result is calculated relative to the theoretical value. Assuming 9.09 mg/L is the theoretical maximum, a sample reading 8.9 mg/L O_2 would equate to 97.9% O_2.

The reference is always the ambient air with 21% O_2, but in water the maximum solubility is the reference and the measurement is expressed as %O_2 from the theoretical dissolved oxygen.

How often should the DO/LDO electrode be calibrated?

Because the LDO system is less sensitive to changes (no metal electrodes, no electrolyte, etc.), the LDO probe should be checked in 100% O_2 standard every month, or if measuring low DO concentrations, every week additionally with 0% DO standard.

The electrochemical DO sensor is much more sensitive to changes and needs almost daily calibration with 100% DO. Where low O_2 concentrations are common a 0% DO combined with 100% DO calibration is recommended.

Trouble shooting

Takes long (too long) for calibration

Most of the time the long stabilization time is caused by different temperatures of LDO probe and sample. Place the probe into the sample (or 100% DO standard) and wait for 5-10 minutes for temperature adjustment. Then the following calibration should be quick, accurate and reproducible.

Negative readings at low DO concentrations

O_2 measurement in samples with less than 0.5 mg/L O_2 can show negative readings, if the DO/LDO probe has not been calibrated additionally with a 0% DO standard. After 0% DO calibration the 0 mg/L origin is recalculated by the meter and then the readings are positive and correct.

Can a salinity correction be done after DO/LDO measurement?

The stored O_2 readings cannot be recalculated in the DO meter for a salinity correction. The salinity must be measured or manually entered before the DO measurement is done.

However, there is a "recalculation tool" available on the internet: see www.hach-lange.com.

**) *ISO 5814 Water quality - Determination of dissolved oxygen*
Electrochemical probe method, Table A.5 — Solubility of oxygen in water vs. temperature and barometric Pressure:
O_2 solubility (1013 hPa, 20°C) = 9.09 mg/L

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