Measuring Dissolved Oxygen. A little theory

The importance of measuring DO

Oxygen makes up approximately 1/5 of the earth's atmosphere. It is one of the most important elements. For energy to be transferred to live cells, oxygen needs to be combined with other substances. i.e. "life" is only possible if the oxygen content is above certain levels. That is why it is so important to measure oxygen content.

Oxygen is present in almost all liquids, to a greater or lesser extent. Oxygen concentration is fundamental, e.g. for:
- Fish and other micro-organisms to live in water.
- Certain degradation processes in water purifying.
- Avoiding corrosion in conductors.
- Preserving drinks.

All liquids absorb the amount of oxygen required to balance the partial pressure of the oxygen dissolved and that of the air or gaseous substances in contact with them. As a result, measuring the DO is equivalent to measuring the partial pressure of the oxygen dissolved in the sample.

How the DO is measured.

Historically, the determination of oxygen concentration involved labour-intensive methods. In 1959 Dr. Clark achieved a huge leap forward in measuring dissolved oxygen when he patented the membrane electrode, also known as the Clark electrode.

DO measurement units:

% of Saturation This measures the partial oxygen pressure, and is not dependent on the type of sample.
Concentration, ppm or mg/l. Depends on the type of sample. Based on Henry's Law:

$$Co_2 = Po_2 \times a$$

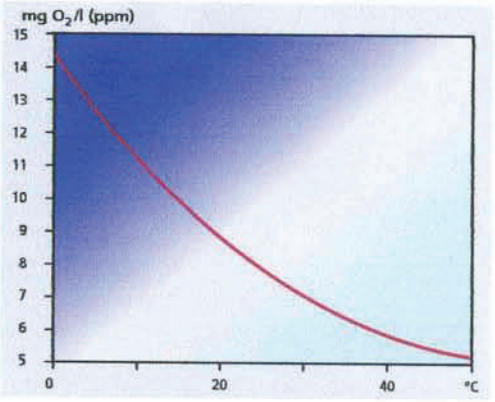
Where **a** is the solubility factor of oxygen in a solution. So the oxygen concentration depends on the composition of the solution.

Solution	Saturation (%)	Concentration (mg/l)
Pure water	100	9.2
KCl 4 M	100	2.0
Methanol-Water 50%	100	21.9

Effects to be taken into account when measuring DO

Temperature

Temperature affects both DO concentration and the permeability of the electrode membrane.
These days, the instruments can compensate for these two effects.



Pressure

Because the measurement of DO is a measurement of the partial pressure of the oxygen, it is affected by atmospheric pressure, a factor which modern instruments also compensate.

Salinity

This only affects measurement when working with concentration, ppm or mg/≠l units. The solubility factor of oxygen varies according to temperature. Most oxygen meters take this factor into account for water, and the information regarding salinity must be keyed in to correct this effect.

Calibration

One-point calibration is performed in air saturated with water vapour, with 100% relative humidity. This is easy to achieve with the OxiCal calibration vessel supplied with each electrode.

DO electrodes
A little theory

The invention of the membrane electrode for DO reading by Dr. Clark (patented in 1959) was a giant step forward because it did away with the slow, laborious methods used up until then for DO reading.
Dr. Clark's system comprised a double-electrode cell, with a cathode and an anode, joined by the electrolyte and separated from the sample by a permeable membrane.

There are two types of sensor:
- **Polarographic** sensor, to which voltage must be applied in order to conduct the measurement.
- **Galvanic** sensor. The sensor generates a potential, mV, related to the O_2 in contact with the membrane. The electrodes are usually made of lead (anode) and gold (cathode) and the electrolyte is a KOH solution.

Advantages of galvanic sensors over polarographic sensors.
The two sensors operate under the same electrochemical principle.
The advantage of the galvanic sensor is that it is always ready for use, and does not require prior polarisation.
This is a great advantage, particularly for portable instruments.

CRISON DO electrodes
CRISON portable oxygen meters use galvanic electrodes.

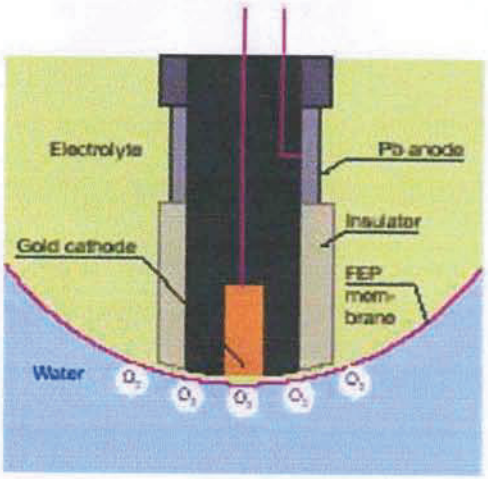
The electrode potential develops as a result of the oxygen reduction on a surface which acts as a cathode and also as a reaction catalyst.

Gold cathode
$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$ (reduction)

Lead anode
$2Pb + 4OH^- \leftrightarrow 2Pb(OH)_2 + 4\ e^-$ (oxidation)

The current produced is proportional to the amount of oxygen reduced.

Diagram of the interior of a DO electrode



DO electrode
Essential parts and practical considerations

Cable and connector
DO electrodes are fixed-cable and have a DIN connector, IP 67 water- and dust-proof.

Body material
POM plastic material, which ensures a strong electrode.

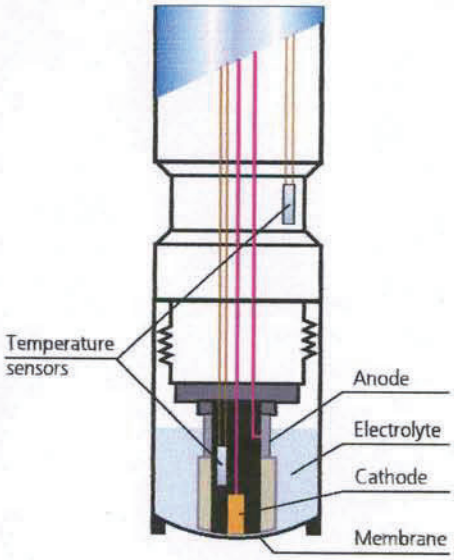
NTC Temperature sensor

Measurement electrodes
- Ring-shaped lead anode
- Gold cathode, as a central terminal.

Electrolyte
KOH solution

Membrane
This is an O_2 selective membrane. The material it is made of, FEP, is a variation on PTFE.

Membrane protector
Only for the DurOx model. *See page 92.*
Very useful for certain applications where the membrane is open to attack such as could reduce its life span.



Immersion depth
Minimum, 4 cm. To perform measurement correctly it must be submerged at least to the level at which the temperature sensor is located.
Maximum 6 m. Because the cable and the head of the electrode are watertight, they can be fully submerged.

Stirring the sample. Flow speed
A DO electrode consumes oxygen from the solution being measured, which it is why it is important to ensure that the sample is stirred appropriately. If not, the reading will decline progressively.
However, if the solution is stirred to excess, the sample will absorb oxygen from the atmosphere, giving rise to higher values.

Life of an electrode
If the electrode is correctly maintained, it can last for a very long time.
Correct maintenance of a DO electrode requires:
- Cleaning the cathode and the anode and replacing the electrolyte.
  Due to the reaction occurring inside the electrode, gold and lead electrodes must be cleaned and the electrolyte replaced periodically.
- Replacing the membrane
  The membrane may be exposed to attack from outside, particularly if not protected.

Most frequent problems, possible causes and action
- The instrument cannot be calibrated. Clean the electrodes, replace the electrolyte and if the problem persists replace the membrane, following the instructions given in the manual.
- Readings which differ from those expected
  Calibrate the instrument and the electrode, using the calibration vessel.
- Alteration (breakage) of the electrode, caused by measuring temperatures exceeding 50°C.
- Alteration of the surface of the electrodes, cathode-anode, caused by inappropriate or aggressive cleaning.

Guarantee
CRISON DO electrodes are guaranteed for 6 months.
The guarantee only covers manufacturing defects.
The guarantee does not cover defects that may arise from incorrect use, handling, application or maintenance, or as a result of premature wear inherent to certain samples.