APPLICATION REPORT
PROCESS ANALYSIS
LDO

Optical measurement of oxygen concentration in water

The optimisation of oxygen transfer is a key element of control and regulation strategies in municipal and industrial sewage treatment plants.
In 2003, HACH LANGE became the first instrument manufacturer to launch the ➔ *LDO* (**L**uminescent **D**issolved **O**xygen) method for determining ➔ *dissolved oxygen* in water. The LDO technology is based on pulsed blue light, which brings benefits such as high precision, long service life and minimum maintenance costs. Since its introduction, the advantages of this method have enabled it to displace conventional electrochemical methods. This report describes the technical background and practical experience of thousands of satisfied users worldwide.

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Function of the LDO sensor

Oxygen is an important control parameter for sewage treatment plants.

Electrochemical sensors have to be regularly calibrated, serviced and cleaned in order to prevent drift from occurring.

The LDO optical measurement is a superior method without the weaknesses of electrochemical sensors.

The robust LDO sensor requires little maintenance and is extremely reliable.

Oxygen analysis in sewage treatment plants

Control and regulation of carbon degradation, nitrification and denitrification are dependent on knowing the oxygen concentration in the aeration tank. For sewage treatment plant operators, therefore, the question is not whether but simply how the oxygen concentration in the activated sludge can be continuously measured.

A characteristic aspect of electrochemical methods of oxygen measurement is the inexorable degradation of the anode and the consumption of the electrolyte during use. Both processes inevitably cause the measured values to drift so that low-bias results are obtained. These effects can only be kept within bounds by regular calibrations and changes of electrolyte.

A completely new type of oxygen sensor was developed and launched in 2003: the HACH LANGE LDO. It is based on the luminescence of a luminophore, and measures the oxygen concentration by carrying out a purely physical time measurement. As the time measurement is drift free, the user does not need to calibrate the sensor.

The main disadvantages of electrochemical measuring cells have therefore been overcome. The most important characteristic of the optical measurement method is that stable and precise measured values can be obtained over long periods of time. And the maintenance required to ensure precise oxygen measurements has also been drastically reduced.

Optical measurement method

The optical method of measuring dissolved oxygen avoids the disadvantages of traditional electrochemical measurement methods. The LDO principle is based on the physical phenomenon of luminescence. Some materials emit light when excited by a stimulus other than heat. In the case of the LDO principle, the stimulus is light. If a combination of a suitable luminophore and a suitable wavelength of excitation light is chosen, the intensity of the luminescence and the time it takes to fade are dependent on the oxygen concentration around the material.

The HACH LANGE LDO sensor consists of two components (Fig. 1):

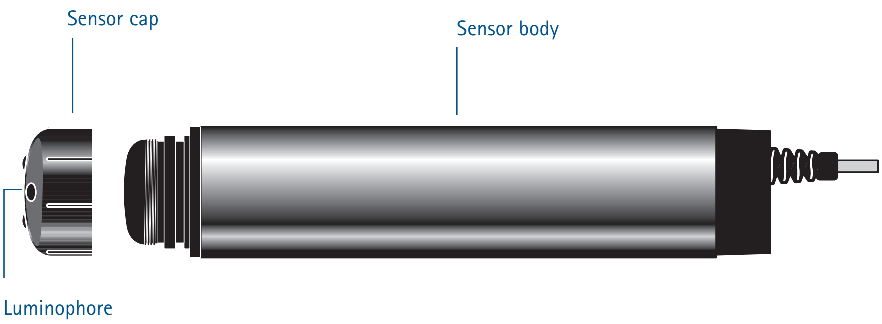

Fig. 1: LDO sensor with sensor cap

The sensor cap with the luminophore coating on a transparent carrier material, and the probe body with a blue LED which emits the light that triggers the luminescence. A red LED which serves as the reference element, a photodiode and an electronic evaluation unit.

In operation, the sensor cap is screwed onto the sensor body and immersed in the water. Oxygen molecules from the analysis sample are in direct contact with the luminophore.

To carry out a measurement, the excitation LED transmits pulsed blue light. The energy-rich blue light enables highly precise measurements to be made. The light pulse (50 msec) passes through the transparent carrier material onto the luminophore, to which it transfers part of its radiant energy. This causes some of the electrons in the luminophore to jump from their basic energy level to a higher one. Within microseconds they then fall back to their original level via a number of intermediate levels, emitting the energy they lose as they do so in the form of red light (Fig. 2).

When oxygen molecules are in contact with the luminophore, two effects occurs:

Firstly the oxygen molecules are able to absorb the energy of the higher level electrons and enable them to return to their basic energy level without emitting light. The higher the oxygen concentration, the greater the reduction in the intensity of the emitted red light.

The oxygen molecules also cause “shocks” in the luminophore, so that electrons fall back from the higher energy level more quickly. The lifetime of the emitted red light is therefore shortened.

Both phenomena are referred to as quenching. Figure 4 shows their effects: the light pulse transmitted by the blue LED at time t=0 strikes the luminophore, which responds immediately by emitting red light. The maximum intensity (I_{max}) and fade time of the red light depend on the surrounding oxygen concentration (the fade time t is defined here as the time that elapses after excitation before the intensity of the red light returns to 1/e of the maximum intensity).

To determine the oxygen concentration, the lifetime t of the red light is evaluated. The oxygen measurement is therefore based on a purely physical measurement of time.

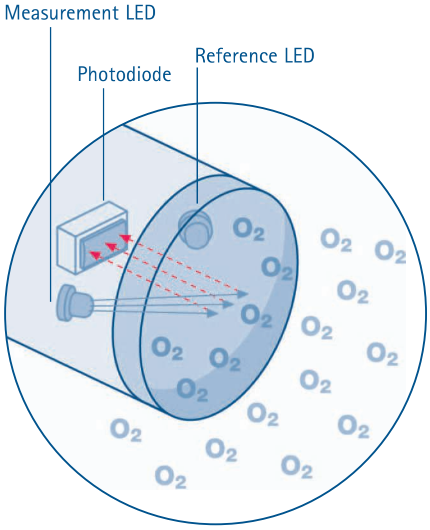

Fig. 2: Functional principle of the HACH LANGE LDO

Fig. 3: Blue and red LED in the sensor

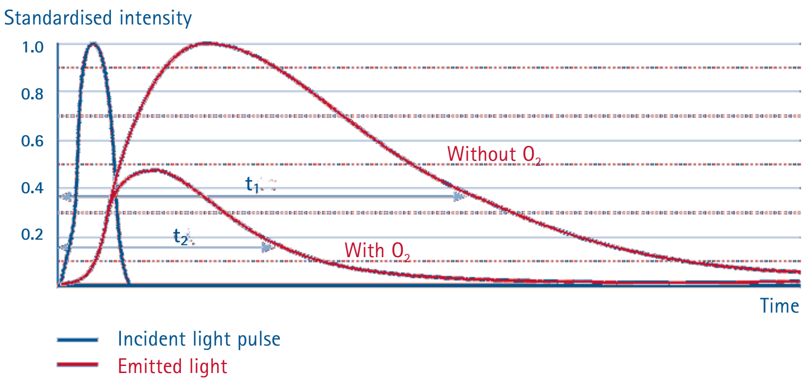

Fig. 4: Intensity of blue excitation light and red emitted light over time

Energy-rich blue light gives high resolution measurement signals. Blue light stands for high precision, which cannot be achieved with low-energy light, e.g. green light.

Advantages of the LDO sensor

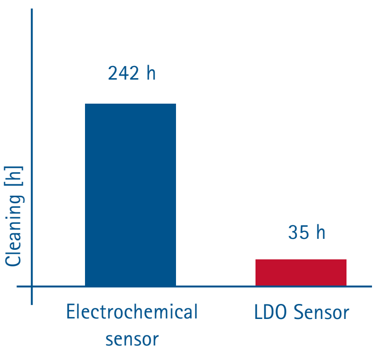

Fig. 5: Typical annual cleaning at a sewage treatment plant with 12 oxygen probes

The LDO measurement system is balanced before each measurement.

Fig. 6: The surface of the probe is easy to clean.

The choice of the pulsed blue excitation light results in the emission of intensive, readily measurable red luminescence, thus ensuring a large measuring range and a low detection limit.

The sensor is continuously balanced with the help of the red reference LED in the probe. Before each measurement it transmits a beam of light with known radiation characteristics, which is reflected at the luminophore and passes through the total optical system in the same way as the luminescence light.

Advantages of LDO technology

The established electrochemical methods of measuring dissolved oxygen require the user to carry out regular maintenance. Cleaning, calibration, changing the membrane and electrolyte, polishing the anode and the documentation of these activities are viewed as necessary and unavoidable, as this is the only way that the tendency of the sensors to give low-bias results can be kept within bounds. In view of the absence of any alternative methods and the importance of the oxygen parameter in biological sewage treatment plants, users were largely resigned to accepting this additional work.

The new, optical measurement method provides an alternative. In comparison with the electrochemical methods, optical methods offer users considerable advantages in terms of the quality of the measured values and the amount of necessary maintenance (Fig.5).

No calibration

The optical LDO method measures the oxygen concentration on the basis of a drift-free time measurement.

Any wear or photobleaching of the luminophore on the sensor cap influence the intensity but not the lifetime of the emitted red light, which is solely dependent on the oxygen concentration of the sample.

All optical components are adjusted before each measurement by reference to a light pulse from the red LED, which is transmitted over exactly the same path as the emitted luminescence.

Faulty calibration by the user is therefore excluded.

No change of membrane or electrolyte

In the LDO method, the electrolyte, electrodes and membrane are replaced by the oxygen-sensitive coating on the sensor cap. All that the user has to do is change this cap every two years.

High measurement accuracy

The energy-rich blue excitation light ensures the constant high measurement accuracy of the LDO sensor.

No need for sample to be kept in motion

Electrochemical measurement methods determine the current or voltage resulting from the reduction of oxygen to hydroxide ions at the cathode. To compensate for this “oxygen consumption”, oxygen molecules must diffuse continuously in the electrolytes. Depletion of the oxygen molecules in the direct vicinity of the sensor can only be prevented by keeping the sample in motion around the sensor.

The LDO method involves no oxygen consumption. The oxygen molecules simple have to stay in contact with the oxygen-sensitive layer. The sample does not have to be kept in motion around the sensor.

Unaffected by contamination

If the conversion of oxygen in an electrochemical measuring cell is restricted because fouling of the membrane impedes diffusion, low-bias measurement results will be obtained. The LDO measurement principle does not involve any consumption of oxygen. Fouling by non-oxygen consuming material therefore simply increases the response time but does not cause low-bias measurement results to be obtained.

No contamination of the sensor by H_2S

Gaseous H_2S causes an almost insoluble silver sulphite layer to form on the anode of electrochemical measuring cells. This renders the cells useless. The LDO luminophore is resistant to H_2S and numerous other chemicals. The sensor can therefore be used for difficult applications without any problems.

Fast response times

The optical method only requires the oxygen molecules to be in contact with the luminophore. The response times of the optical measuring method are therefore expressed in seconds. If a smoother signal pattern is desired, the transformer can be adjusted to attenuate the signal.

Excellent sensitivity at low oxygen concentrations

The sensitivity of the measurement effect (change of lifetime of luminescence/ change of oxygen concentration ($\Delta\tau / \Delta c_{O2}$)) increases as the oxygen concentration decreases. The measurement principle therefore gives especially good resolution in the low measurement range.

Rugged sensor

The LDO sensor cap is especially resistant to mechanical stresses. Membrane ruptures during operation or while the user is carrying out cleaning work are reduced.

Long service life of sensor

The pulsed blue excitation light is a guarantee of intensive luminescence, but also of an extremely long service life of the sensor cap. On the basis of its outstanding long-term experience, HACH LANGE provides a 2 year warranty for the sensor cap!

Fig. 7: The LDO sensor functions normally in even the most required environments. The amount of maintenance remains minimal.

To carry out a measurement, the excitation LED transmits a pulse of blue light. This short, energy-rich pulse exerts minimal stress on the luminophore and ensures reliable readings are obtained with a 2 year warranty!

Measuring results

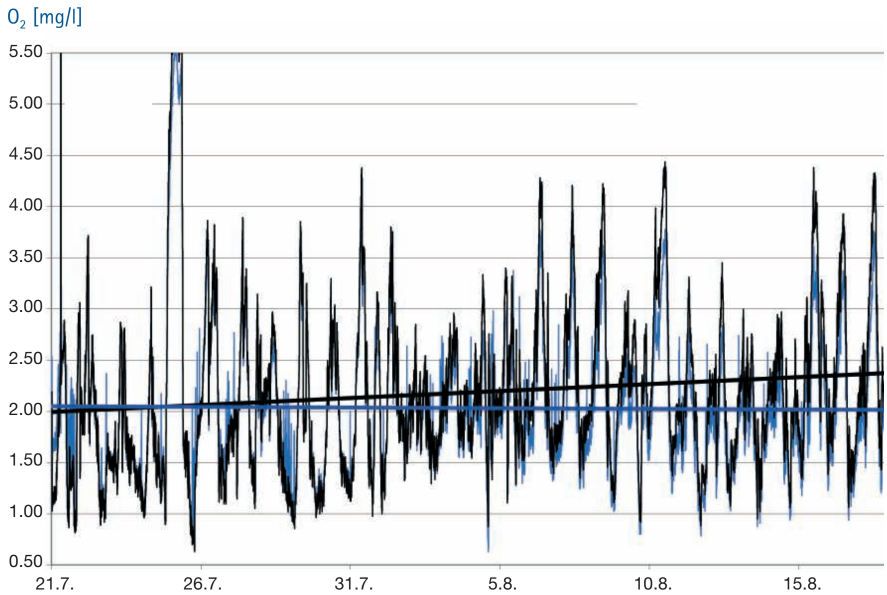

Fig. 8: Comparison between electrochemical (blue) and optical sensor (black)

The LDO sensor measures more reliably than conventional sensors and saves energy costs.

Measurement results

Figure 8 shows measurement results of the optical oxygen sensor together with the measurements of a conventional electrochemical sensor over a period of four weeks. The measurement location was the aeration tank of a municipal sewage treatment plant.

The oxygen is regulated on the basis of the measured values of the electrochemical sensor. The controller sets the aerator so that the average measured value supplied by the electrochemical oxygen sensor corresponds to the desired target value. If the sensor gives a reading that is lower than the real concentration, this results in an undesirably high oxygen concentration in the aeration tank, which cannot be immediately recognised in the closed control loop.

In the example here, the low bias of the sensor readings result in the average value of the oxygen concentration in the aeration tank (represented by the black straight line) being 0.4 mg/l above the desired average of 2 mg/l after the given period of four weeks. Such a difference has technical disadvantages for the process, such as carryover of oxygen into the denitrification zone. The real oxygen concentration in the aeration tank is shown by the new optical sensor.

Unnecessarily high oxygen concentrations in the aeration tank should be avoided, as they reduce the cost-effectiveness of the process. According to ATV work sheet A 131 [1, 2]:

$$N \sim C_s/(C_s - C_x)$$

where

C_s: is the assumed oxygen saturation concentration and

C_x: is the oxygen concentration

It follows that the energy demand N and the energy costs for the oxygen transfer in the aeration tank increase as the oxygen concentration C_x increases.

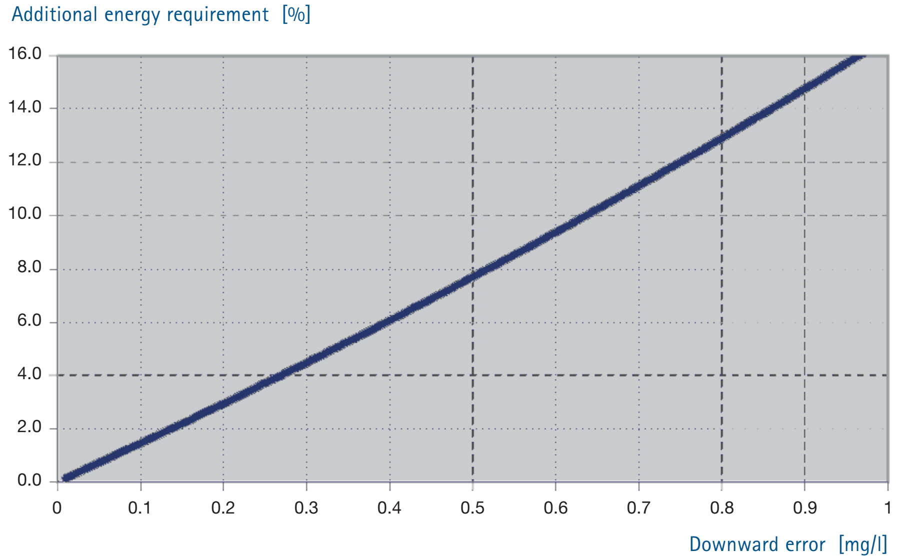

Fig. 9: Additional energy requirement due to downward error in oxygen measurements (based on an oxygen concentration of 2 mg/l and a saturation concentration of 9.0 mg/l)

Figure 8 shows the additional energy input due to the low-bias oxygen measurements, assuming an oxygen saturation concentration C_s of 9.0 mg/l and a target oxygen concentration of 2.0 mg/l. In the example, the fact that the measurements indicated that the oxygen concentration was 0.4 mg/l lower than it really was resulted in a 6% increase in energy input.

Given that 60-70% of the energy consumption of sewage treatment plants is used to aerate the activated sludge, it is clear that such low-bias results should be avoided under all circumstances.

Summary

The key characteristics of the optical LDO oxygen sensor from HACH LANGE are the pulsed excitation by energy-rich blue light and the continuous balancing of the measurement system by a red reference beam. They make LDO the ideal oxygen sensor, with maximum accuracy even at low concentrations, stable drift-free measured values and minimal maintenance. All the user has to do is change the sensor cap every two years and occasionally clean the sensor. Conclusion: LDO overcomes the weaknesses of conventional electrochemical sensors and is superior to other optical systems.

Fig. 10: The LDO sensor is also available as a portable model for use in the field and the laboratory.

Literature & technical data

Literature

[1] Merkblatt ATV-DVWK -A 131: Bemessung von einstufigen Belebungsanlagen, Mai 2000
[2] ATV Handbuch Betriebstechnik, Kosten und Rechtsgrundlagen der Abwasserreinigung, Ernst & Sohn Verlag, 4. Aufl. 1995, S. 208-225
[3] EPA Letter Recommendation of LDO Method 10360

Technical data

Article number	LXV416.99.00001
Description	Dissolved oxygen probe with sensor cap
Measurement method	Luminescence, optical
Excitation	Pulsed blue light
Calibration	Not necessary
Measuring ranges	0.1 – 20 mg/l (ppm) O_2; 1 – 200% O_2 saturation; 0.1 – 50 °C
Accuracy	± 0.1 mg/l O_2 < 1 mg/l; ± 0.2 mg/l O_2 > 1 mg/l
Reproducibility	± 0.5% of end value of measuring range
Response time	T90 < 40 sec (20 °C), T95 < 60 sec (20 °C)
Temperature range	0 – 50 °C
Temperature sensor	NTC integrated, automatic temperature compensation
Sensor cable	10 m strong cable with an easy to disconnect plug
Minimum flow	No flow required
Material	NORYL, stainless steel 316
Dimensions L x D	292 x 60 mm (11.5 x 2.4 inches)
Warranty	2 years for probe and sensor cap
Mounting kits	In tank, either pole, floating ball or chain mounted; rail-mounted; in-line on request; in bypass

Subject to change.

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