



Oxygen Measurement: OPTICALLY OR ELECTROCHEMICALLY?

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WATER
Waste Water

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Comparison of Theory and Practical Experience in OnLine Measurements.

For some time now, optical processes for measuring dissolved oxygen, which are based on the luminescence of dyes, have been subject to extensive promotion. In their advertisements, the manufacturers of these products claim characteristics which are far superior to those of conventional electrochemical sensors. The functional principle of optical measurement also proves this superiority in theory. However, in practice, certain application constraints become obvious.

An overview of these constraint are presented here.

Development

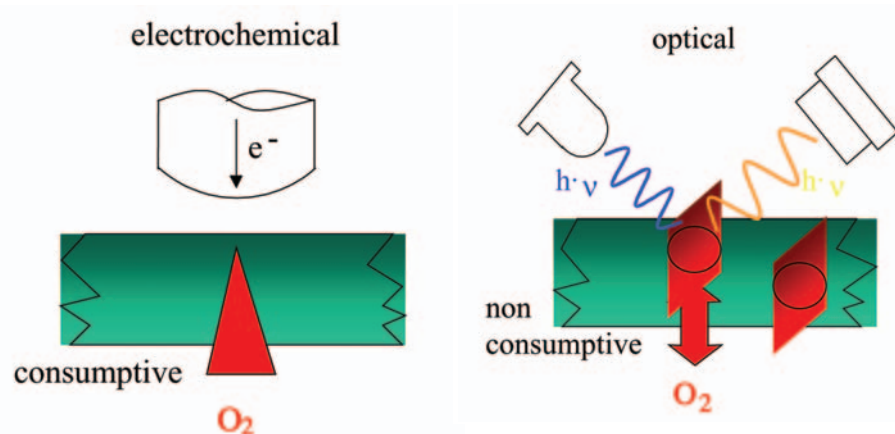
Originally developed 50 years ago by Dr. Clark for medical purposes, soon after the probe was developed for water analysis.

European companies continued to develop this measuring principle, and achieved a high level of technical development. While in the USA, the home of the invention, development has lagged far behind [1].

Nor is the optical measuring process new. The first optodes were developed 30 years ago, again for medical applications [2]. In this case, history was reversed. Initially developed in Germany, development other than for medical purposes took place in the USA.

As a result of this historic development, it is hardly surprising that arguments in favour of optode technology and against the electrochemical sensor in water analysis are based on a technical status which exists in the USA but does not correlate to the reality in the rest of the world.

Measuring Principles



Electrochemical

Oxygen diffuses through the membrane and is chemically converted within the sensor. Oxygen and the electrolyte are "consumed" in this case.

- The consumed oxygen has to be replaced by sample flow across the membrane
- The chemically converted electrolyte has to be replaced when exhausted; during the operating time, the sensor signal drifts to a greater or lesser extent depending on the design of the probe
- Deposits on the membrane reduce oxygen diffusion

Optical

A dye is embedded in a carrier material. The dye is excited by means of short-wave length light source. On transition to its ground state, a longer-wave length light is emitted and measured by a photodiode. If oxygen diffuses into the carrier material, the intensity of the red light is reduced proportionally to the oxygen concentration; the dye's transition time to ground state is simultaneously reduced.

In addition to the length intensity, this transition time may also be evaluated as a measuring signal

- The oxygen is not consumed; it is in equilibrium with the oxygen in the measuring medium
- No oxygen reaction takes place in the carrier material
- Organic deposits on the membrane consume oxygen and reduce the measuring signal

Theory and Practice

From this comparison of principles, it initially appears permissible to promote characteristics such as the following for the optical sensor:

- No calibration required
- No membrane replacement
- No electrolyte replacement
- No incoming flow required
- No H₂S influence
- Short response time

However, these primary advantages over and above the market's leading, conventional sensors on closer observation by precise theoretical analysis, practical execution and, in particular, on application have relative validity.

The optical sensor also has a "wearing part", the dye. Due to light excitation, the dye fades, necessitating periodic replacement of the sensor cap.

Zero Point

The residual product of the "consumed" dye may reveal inherent fluorescence, changing the characteristic curve and therefore generating measuring errors.

Slope

The dissipation of energy of the excited dye is significantly dependent on the state of the membrane. For certain products, it can be demonstrated that a membrane which has been soaked in water for a long time (3 to 4 weeks) shows a slope up to 10% higher compared to the dry status. When questioned by customers about such higher measurements versus conventional instruments, one manufacturer simply states that the previous measuring principles are defective [3].

The optical components, e.g. the LED or age, necessitate re-calibration "several times" per year [4].

Selectivity

Like oxygen, other gases such as ClO₂ and SO₂ also "quench" the excited dye, leading to false results.

On the other hand, appropriate design and selection of materials for an electrochemical sensor reduce the negative effects of "consumption" drastically, making it negligible in almost all applications.

For example, flow dependence, H₂S resistance and a short response time are not relevant for the typical application in the aeration tank of a waste treatment plant.

Turbulence across the membrane is desired for sensor self-cleaning alone; a short response time would generate noisy measuring signals and has to be electronically compensated; H₂S is unable to occur.

Those characteristics which are genuinely important for use in an aeration tank are compared in the following Table:

Measuring accuracy	Electrochemical Better than 1% of the measured value after calibration, i.e. 0.02 mg/L deviation in the case of a measured value of 2 mg/L	Optical Better than 2% of full range of 20 mg/L, i.e. 0.4 mg/L Accuracy is improved by calibration
Drift	Drift approx. 0.02 to 0.1 mg/L in 6 months, no zero point drift Reproducibility better than 0.5%	Theoretically, no drift. In practice, drift occurs when outside influences are observed and following sensor cap replacement. Reproducibility better than 0.5%
Calibration	Required approximately every 3-6 months	Theoretically, not necessary. However, it is necessary when outside influences are observed and following sensor cap replacement in order to achieve sufficient accuracy
Maintenance interval / ageing	In conventionally available sensors, the theoretical life time of an electrolyte filling is > 10 years in the case of 2 mg/L; in practical terms, 2 to 7 years depending on the application A defective membrane or exhausted electrolyte automatically trigger a warning signal	Recommendation: Annual replacement of the sensor cap, cleaning and damage check every 90 days No long-term experience is available. Membrane defects or other interferences are NOT indicated
Check	Both sensor types are equally affected by deposits which consume oxygen. This risk is present in all oxygen measurement applications; inorganic deposits are extremely rare. To avoid "biological growth" the efficiency of the self cleaning system is the key for proper function. Automatic detection is not possible. In extreme applications, a cleaning additive has to be used to keep the sensor clean. For well designed electrochemical sensors, this is necessary only in less than 1% of all probes.	

Conclusion:

Checking sensors at regular intervals is basically good operating practice. All operators have plans for ensuring reliable function in the case of critical measuring systems. Both types of sensor therefore require a certain level of maintenance and evolution which typically occurs after 3 to 6 months and is comparable.

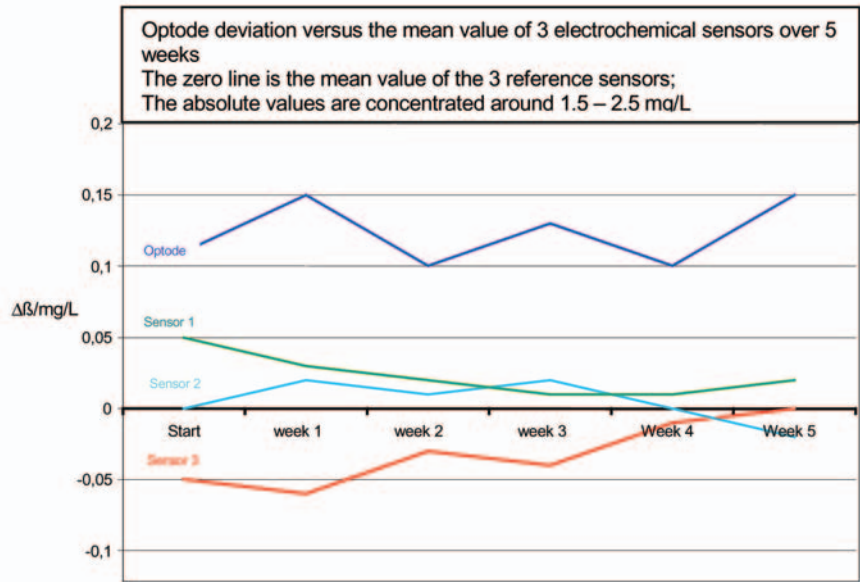
In the case of the electrochemical sensor, however, this is also simultaneously a convenient calibration, and can be carried out automatically at the push of a button in air without any auxiliary equipment.

Although the optical sensor can also be calibrated in air, it has to be placed into a light-proof vessel – due to the optical system’s sensitivity to light, which is more laborious than conventional air calibration, error can be as high as 5, 8 or even 10%.

System self-cleaning is vitally important, as this is the major source of operating errors! The primary factors in this case are the selection of a suitable material, the geometry of the sensor and suspension during measurement.

The above statements were proven by means of comparative tests conducted over a period of 5 weeks at a major waste treatment plant. In comparative tests carried out without a reference process, no statement regarding the "true" value can be made, and deviations amongst the test specimens can therefore only be interpreted in relative terms. In order to counter this difficulty to a certain degree, a mean value, which serves as the reference curve, was formed from 3 leading, state-of-the-art electrochemical sensor types which, together, control significant market share.

This mean value may therefore be applied as a meaningful reference. The individual sensors' response behaviour differs. As measurement was carried out in a dynamic process, a mean value was formed, in each case, over 1 hour at the start of the test and then each week between 23:00 and 24:00. The values obtained in this manner form the basis of the following.



Result:

The electrochemical sensors measure within a range of 0.05 mg/L. No statement can be made whether sensor 3 or sensors 1 and 2 show slight drift.

In systematic terms, the optical sensor shows 0.1 to 0.15 mg/L higher readings than the mean value, also with the same fluctuation range, which could be referred to as an initial calibration error. However, the same finding is observed by several comparative measurements. One possible explanation may be the above mentioned difference between "dry" plant calibration and the water-soaked membrane.

One other possibility: In an aeration tank, the liquid phase and the gas phase are not in equilibrium. Each sensor therefore constantly generates a composite signal "β" comprised of the two phases. It might also be possible that the optode will generate a slightly higher signal than electrochemical sensors.

After 5 weeks, it cannot be determined which of the sensors provides higher stability. All signals were within fluctuation range of 0.05 mg/L and can therefore all be classified as very good. No maintenance was necessary.

The optical sensor is somewhat superior in applications in non flowing water combined with a short response time. Otherwise, it also shows changes in its measuring characteristics and requires corresponding maintenance and exhibits a significant number of uncertainties with regard to its signal formation.

References

[1] Clark, L. C., R. Wolf, D. Granger and Z. Taylor. 1953. Continuous recording of blood oxygen tensions by polarography. *J. of Appl. Physiol.*, 6: 189-193

[2] D. W. Lübbers and N. Opitz, *The pCO2/pO2 Optode: A New Probe for Measuring pCO2 and pO2 of Gases and Liquids*, *Z. Naturforsch.*, 30C (1975) 532-533

[3] www.hach.com > Hach Knowledge Base > Hach Frequently Asked Questions: By Product > Dissolved Oxygen Meters and Probes > Comparing results from HQ10 / HQ20 meters to other meters

[4] BMBF Project No. 02WU9907/0 and 02WU0338, Technical Information Library Hanover