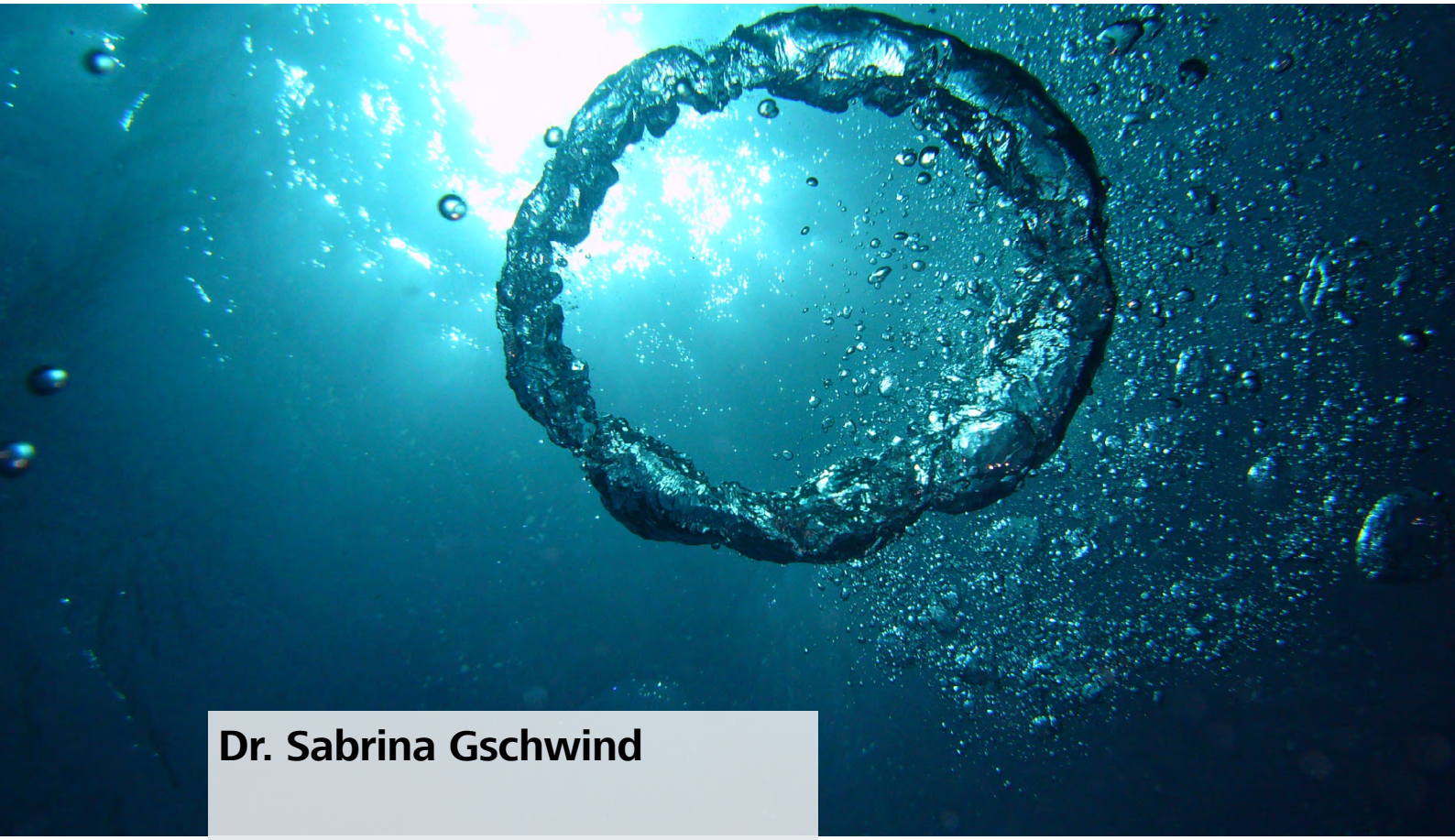
Determining dissolved oxygen in water: Titration or direct measurement?



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Dissolved oxygen is a term describing the amount of oxygen molecules (O_2) which are dissolved in a liquid phase under certain conditions. In this white paper, two different methods for the analysis of dissolved oxygen, titration and direct measurement, are compared and contrasted to help analysts determine which method is more suitable for their specific applications. Here, we primarily focus on the determination of dissolved O_2 in water. However, the same principle applies for other liquid phases such as non-alcoholic or alcoholic beverages.

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What is dissolved oxygen?

Dissolved oxygen refers to the amount of free oxygen molecules (O_2) present in water or in other liquids. The amount of dissolved O_2 in water sources supplies a lot of information about the water quality, and it greatly influences all living organisms therein. Furthermore, it is an important factor in water purification. Oxygen has limited solubility in water, which is directly related to the atmospheric pressure and inversely related to water temperature and salinity.

Oxygen enrichment in water occurs via two main pathways:

- An exchange with the atmosphere, with further transport of oxygen into lower water layers
- Production of oxygen through the photosynthesis of plants and algae exposed to light

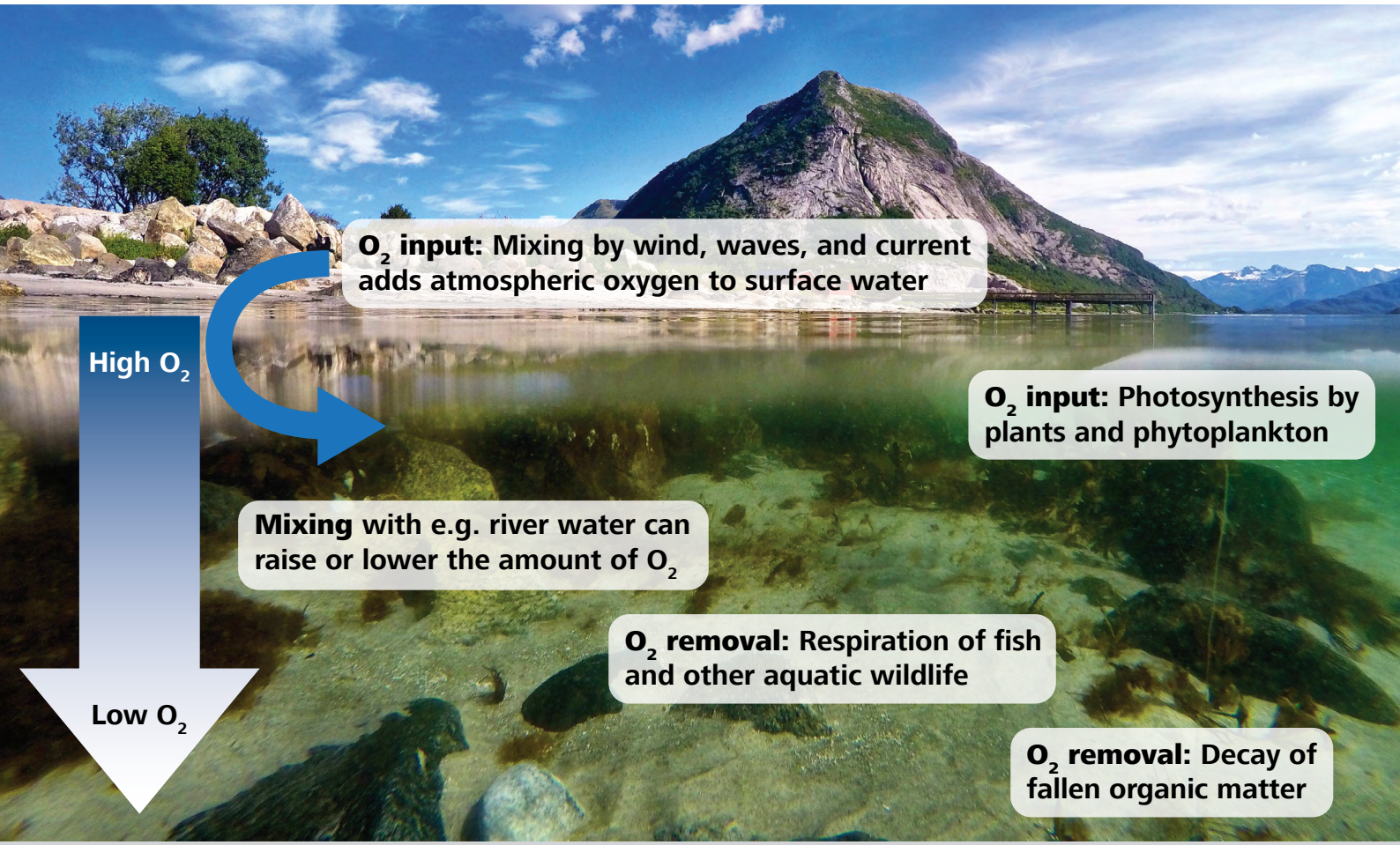
On the other hand, several natural processes in water consume oxygen:

- Bacterial reduction of organic and inorganic material
- Consumption of oxygen by fish and other aquatic animals
- Other chemical and biological reactions

To assess the amount of dissolved oxygen and to draw conclusions from it, an accurate measuring method is necessary. Ideally, an in-situ measurement is performed by using a sensor. If a local assessment of the oxygen content is not possible and the water sample must be analyzed in a laboratory, different precautionary measures have to be applied.

The oxygen content of the sample **must not change** between sampling and analysis; therefore, microorganisms which consume oxygen have to be debilitated. The sample vessel must be completely filled to eliminate any headspace, prohibiting any reintroduction of oxygen after sampling. Also, both the pressure and the temperature need to be controlled.

In the next section, direct measurement and titration (according to Winkler) to assess the dissolved oxygen content will be discussed and compared.



How to determine the dissolved oxygen content

Winkler titration

The Winkler titration, first described in 1888 by Lajos Winkler [1], is the method of choice if the dissolved oxygen content is analyzed in the lab. This iodometric titration method is defined in several standards, such as **ISO 5813**, **EN 25813**, and **ASTM D888** for the assessment of dissolved oxygen in water.

This method is recommended for measurement of dissolved oxygen content **higher than 0.2 mg/L**. To eliminate interferences, modifications must be made.

Such interferences can include oxidizable organic substances (e.g., lignins, humic acids) and nitrites (at concentrations above 15 mg/L). In these cases the Winkler titration method must be modified: the Alsterberg (azide) procedure removes any present nitrite interferences and the Rideal-Stewart (permanganate) modification should be used in the presence of ferrous iron. Furthermore, if suspended matter is present which is capable of fixing or consuming iodine, the titration will give incorrect results. In this case, only direct measurement is recommended.

The most difficult part of the method is to preserve the dissolved oxygen content from the moment of sampling up until the analysis. Various measures have to be taken to achieve this.

First of all, special containers must be used for this purpose, identical to those needed for the determination of biological oxygen demand (BOD). These containers have a special opening and a stopper that seals well, omitting any entrainment of oxygen from the atmosphere. The sample must be preserved by fixing the amount of dissolved oxygen (i.e., making it unavailable for chemical and biological reactions) directly after sampling by adding both manganese and hydroxide ions in excess. This leads to the formation of manganese (III) hydroxide. If protected from light and temperature extremes (maintained within 10–20 °C), the sample may be stored for up to 24 hours.

Just before the titration is begun, the sample is acidified with sulfuric acid, and the manganese (III) hydroxide is reduced by iodide, which in turn is oxidized to iodine. The generated iodine is then titrated with thiosulfate solution. The amount of O_2 correlates to the obtained equivalence point: one mole of oxygen corresponds to four moles of thiosulfate.

(1) Chemical fixation:

$$O_2 + 4\ Mn(OH)_2 + 2\ H_2O \longrightarrow 4\ Mn(OH)_3$$

(2) Reduction of manganese (III) hydroxide:

$$2\ Mn(OH)_3 + 2\ I^- + 6\ H^+ \longrightarrow 2\ Mn^{2+} + I_2 + 6\ H_2O$$

(3) Redox titration:

$$I_2 + 2\ S_2O_3^{2-} \longrightarrow 2\ I^- + S_4O_6^{2-}$$

Figure 1. BOD bottle used for sampling ("Biological Oxygen Demand Bottle" *by Mameaw.piti. CC BY-SA 4.0*)

The redox titration can be performed either optically using starch as an indicator, or potentiometrically using a redox electrode. The second option improves accuracy, efficiency, and traceability. However, to achieve an accuracy of +/- 0.5 mg/L for the DO concentration, all sampling, preparation, and titration steps must be performed reproducibly and a certain amount of experience is necessary to achieve this.

The titration itself takes several minutes to be performed. Costs for all necessary chemicals (fixation, reduction, and titration) is approximately $40 USD per 100 titrations. Automation of the titration is rather difficult, as special vessels are used which have to be uncapped just prior to the titration. Therefore, high sample throughput is a challenge.

Dissolved oxygen measurement

For in-situ oxygen determination, a dissolved oxygen measurement is performed. For this, a DO meter is used, equipped with a sensor that changes its properties depending on the oxygen concentration. In the past, only electrochemical sensors were used. These days, optical sensors are much more frequently used due to their simplicity. Since electrochemical sensors are still common, the measurement principle is quickly described for a better overview.

Measurement with electrochemical sensors

Electrochemical DO sensors can be divided into three major classes according to their different output signals: current-type (galvanic or polarographic), conductance-type, and potentiometric-type. The most widely used electrochemical sensor in water analysis is the Clark-type sensor, which is based on the polarographic principle.

Developed by Leland Clark in 1953 [2], Clark-type sensors contain a cathode / anode pair (e.g., Pt cathode, Ag anode), an electrolyte solution, and an air-permeable film. When a voltage is applied to the cathode / anode pair, O_2 molecules which entered the electrolyte solution through the air-permeable film are reduced on the cathode. The generated current increases and will remain constant as long as new oxygen diffuses through the membrane. The resulting current is proportional to the diffusion of oxygen, and therefore to the oxygen concentration in the sample.

The following reactions occur on the cathode and anode:

(4) Cathode reaction:

$$O_2 + H_2O + 4e^- \longrightarrow 4\ OH^-$$

(5) Anode reaction

$$4\ Ag + 4\ X^- \longrightarrow 4\ AgX + 4\ e^-$$

This means that the electrolyte will be consumed and must be replaced often. Additionally, the cathode / anode pair has to be cleaned regularly. The membrane itself will be worn off, and exchange is necessary. The frequency of maintenance depends on the application, however, in most cases at least a monthly maintenance is required.

Measurement using an optical sensor

Currently, optical sensors for DO measurements are well accepted for the in-situ determination of dissolved oxygen, and are already mentioned in the standard **ISO 17289** as the method of choice. In other standards (**EN ISO 5814**, **ASTM D6764**), electrochemical probes are still mentioned. However, it is likely that this will change in the future.

Figure 2. Sensor membrane which incorporates the luminophore.

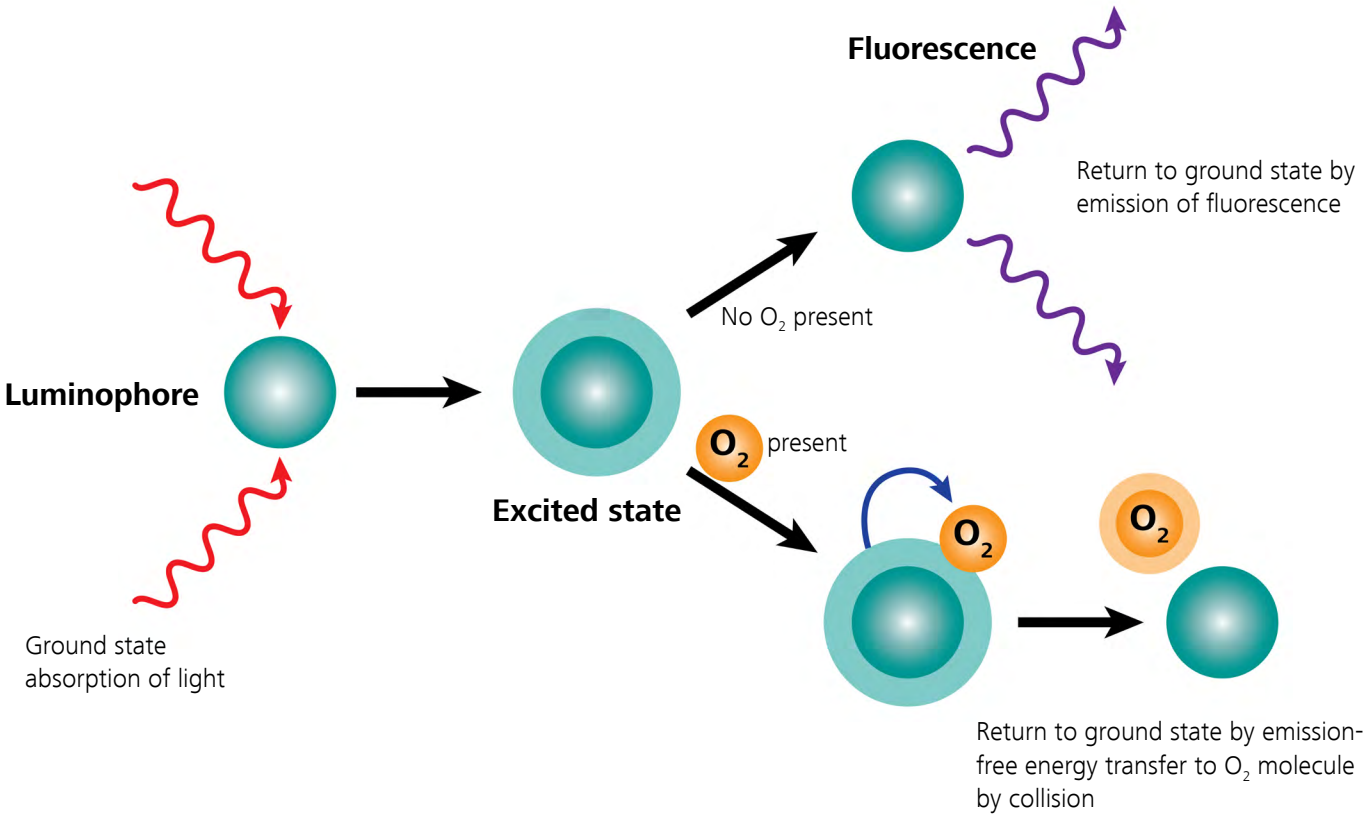
Optical sensors are based on the fluorescence quenching principle. The DO sensitive membrane incorporates a fluorescent substance, a «luminophore», which is excited by absorption of light at a specific wavelength, and releases energy after a certain timeframe to return to the ground state (emission of fluorescence).

When dissolved oxygen is present in the sample, the oxygen collides with the fluorescent substrate, and the transition to the ground state occurs without emission of radiation. The content of dissolved oxygen can be determined according to the fluorescence intensity or the fluorescence lifetime.

For calculation of the dissolved oxygen content, the Stern-Volmer equation is applied.

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[O_2]$$

I_0 and τ_0 represent the fluorescence intensity and fluorescence lifetime under anaerobic conditions, I and τ are the fluorescence intensity and lifetime when oxygen is present. K_{SV} represents the Stern-Volmer constant and $[O_2]$ is the concentration of dissolved oxygen.



Currently, modern optical sensors measure the phase shift of modulated light resulting from the reaction of the fluorescent substrate with oxygen, as this value remains stable over a long period of time. Intensity measurements are easily biased by changes in the excitation light source intensity, ambient scattering, and other matrix effects and are therefore prone to enhanced variability and drift. Additionally, degeneration of the luminophore will require more frequent calibration. For this reason, the intensity of the signal is mainly used to monitor the performance of the luminophore to check its quality.

The luminescence lifetime τ is calculated using the phase shift φ of a fixed frequency (f) modulated light wave.

$$\tan \varphi = 2 \pi \times f \times \tau$$

Any calculation of the oxygen content is made directly by the measurement device, and the oxygen content is displayed in the desired unit of measure. Single measurements take **less than a minute** to reach a stable value. For some sensors, a response time below 30 seconds can be achieved.

This sensor does not need too much maintenance — only the cap containing the luminophore can deplete. Depending on the frequency of usage, the cap has to be replaced annually.

In **Table 1**, advantages and disadvantages of the three presented methods are summarized.

Table 1. Comparison of Winkler titration and DO measurement with an electrochemical or optical sensor.

	Pro	Con
Winkler titration **ISO 5813** **EN 25813** **ASTM D888** **EN ISO 5815-1** **ISO 5815-2**	• High accuracy (< 0.5 mg/L)	• Analysis time takes several minutes • No continuous or in-situ detection possible, sample has to be brought to the lab • Various chemicals necessary, cost approximately $40 USD per 100 titrations • Influence of iron, nitrite, free chlorine, organic material • Limit of detection approximately 0.2 mg/L
Electrochemical sensor **EN ISO 5814** **ASTM D6764** **EN ISO 5815-1** **ISO 5815-2**	• Sensitive to low concentrations • Can be used for in-situ or continuous DO measurements • Widely accepted application	• Detection process consumes oxygen • Frequent maintenance: exchange of membrane and electrolyte • Polarization of electrode takes up to 15 minutes • Easily affected by water quality and electromagnetic interferences • Influence of H_2S, SO_2, CO_2
Optical sensor **ISO 17289**	• Low maintenance • Does not consume oxygen • Easy to clean • Can be used for in-situ or continuous DO measurements • High accuracy: < 0.15 mg/L at DO concentrations between 0–20 mg/L • Fast response time, analysis takes < 1 minute	• Sensitive to ambient light • Above a DO concentration of 20 mg/L, errors up to 10% are possible

Oxygen measurement has a significant advantage because measurements can be performed in-situ and onsite. Compared to titration, a DO measurement takes about 10% of the time, the device can be operated by non-trained users, and no chemicals are used (nor is any waste generated).

Furthermore, optical sensors are **more robust** and **require less maintenance** compared to electrochemical sensors. Electrochemical sensors must be maintained frequently; the electrolyte and membrane have to be replaced regularly and they are more sensitive to water quality and electromagnetic interferences. Additionally, other gases such as H_2S, SO_2, or CO_2 can negatively influence the measurement.

In summary, optical DO measurement is **faster**, **easier**, **cheaper**, and **more ecological** than DO measurements with electrochemical sensors or titration of O_2 according to Winkler. Titration is only recommended when accurate results are necessary for DO concentrations larger than 20 mg/L.

References

[1] Winkler, L. Die Bestimmung des im Wasser gelösten Sauerstoffes. *Berichte der Deutschen Chemischen Gesellschaft.* **1888**, *21*, 2843–2855. https://doi.org/10.1002/cber.188802102122

[2] Clark, L.; Wolf, R.; Granger, D.; Taylor, Z. Continous recording of blood oxygen tensions by polarography. *J. Appl. Physiol.* **1953**, *6*, 189–193. https://doi.org/10.1152/jappl.1953.6.3.189

Additonal Literature

EN 25813: Water quality – Determination of dissolved oxygen – Iodometric method

ISO 5813: Water quality – Determination of dissolved oxygen – Iodometric method

EN ISO 5814: Water quality – Determination of dissolved oxygen – Electrochemical probe method

EN ISO 5815-1: Water quality – Determination of biochemical oxygen demand after n days (BODn) – Part 1: Dilution and seeding method with allylthiourea addition

ISO 5815-2: Water quality – Determination of biochemical oxygen demand after n days (BODn) – Part 2: Method for undiluted samples

ISO 17289: Water quality – Determination of dissolved oxygen – Optical sensor method

ASTM D888: Standard Test Methods for Dissolved Oxygen in Water

ASTM D6764: Standard Guide for Collection of Water Temperature, Dissolved-Oxygen Concentrations, Specific Electrical Conductance, and pH Data from Open Channels

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