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Water quality — Determination of dissolved oxygen — Optical sensor method

Qualité de l'eau — Dosage de l'oxygène dissous — Méthode optique à la sonde

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Water quality — Determination of dissolved oxygen — Optical sensor method

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies an optical method for the determination of dissolved oxygen in water using a sensor working on the basis of fluorescence quenching.

Measurement can be made either as a concentration of oxygen in milligrams per litre, percentage saturation (% dissolved oxygen), or both. Depending on the instrument used, detection limits of 0,1 mg/l or 0,2 mg/l can be reached according to the manufacturer's manual. Most instruments permit measurement of values higher than 100 %, i.e. supersaturation.

NOTE Supersaturation is possible when the partial pressure of oxygen is higher than in air. Especially in case of strong algae growth, supersaturation up to 200 % and more is possible.

If waters with a saturation higher than 100 % are measured, it is essential to make arrangements to prevent the outgassing of oxygen during the handling and measurement of the sample. Similarly, it is important that the transport of oxygen into the sample is prevented if the saturation is below 100 %.

The method is suitable for measurements made in the field and for continuous monitoring of dissolved oxygen as well as measurements made in the laboratory. It is one of the preferred methods for highly coloured and turbid waters, and also for analysis of waters not suitable for the Winkler titration method because of iron- and iodine-fixing substances, which can interfere in the iodometric method specified in ISO 5813.

The method is suitable for drinking waters, natural waters, waste waters, and saline waters. If used for saline waters such as sea or estuarine waters, a correction for salinity is essential for concentration measurement of oxygen.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Principle

Optical sensors that measure luminescence/fluorescence lifetime or luminescence/fluorescence phase shift are normally composed of a luminophore or fluorescent dye situated in a sensor cap, a light source [e.g. a light emitting diode (LED)], and a photodetector. The pulsed or modulated light from the source causes excitation of the luminophore, which is quenched in the presence of oxygen. The photodetector converts the resulting light emission into an electrical signal that can be sampled and processed to compute the phase shift or fluorescence or luminescence lifetime. This phase shift or excitation lifetime is used to quantify dissolved oxygen concentrations.

Temperature has two different influences. The first influence relates to the variation of the quenching process of the membrane with the temperature. So the primary signal of the probe has to be compensated with a built-in temperature sensor. State-of-the-art meters are able to do this automatically. The second influence is given by the sample and the temperature dependence of the solubility of oxygen in it. Also salinity can have a significant effect.

For calculating the percentage of saturation of samples being in contact with an atmosphere, it is necessary to take the atmospheric pressure into account. This can be performed manually or by implementing a pressure sensor for automatic compensation.

Most sensors have a second LED to be used as internal reference for compensation purposes.

4 Interferences

No interferences in waters as described in Clause 1.

5 Reagents

During analysis (i.e. for calibration), use only reagents of analytical grade.

5.1 Water, grade 2, as specified in ISO 3696.

5.2 Sodium sulfite, anhydrous, Na_2SO_3, or heptahydrate, $Na_2SO_3 \cdot 7H_2O$.

5.3 Cobalt(II) salt, for example cobalt(II) chloride hexahydrate, $CoCl_2 \cdot 6H_2O$.

5.4 Ascorbic acid.

5.5 Sodium hydroxide solution, NaOH, c = 1 mol/l.

5.6 Nitrogen gas, N_2, purity 99,995 % or better.

6 Apparatus

6.1 Measuring instrument, comprising the following components.

6.1.1 Measuring probe.

Probe designs vary in the wavelength of the excitation light and the luminophore or fluorescent dye.

6.1.2 Meter to show the mass concentrations of dissolved oxygen directly and/or percentage saturation with oxygen.

6.2 Thermometer, graduated to at least 0,5 °C.

NOTE Commonly, a temperature sensor is integrated into the instrument.

6.3 Barometer, graduated to 1 hPa.

NOTE Usually, the barometer is integrated into the instrument.

7 Procedure

7.1 Sampling

7.1.1 General

Normally, the oxygen concentration shall be measured directly on-site in the water body to be analysed.

If direct measuring in the water body is not possible, the measuring can also take place in a gastight connected flow-through device or immediately after fit for purpose sampling as a discrete sample.

Any discrete sampling procedure will result in a higher measurement uncertainty.

While filling the sample vessel during sampling, oxygen uptake or oxygen stripping shall be minimized. Sample transfer shall occur without any turbulence, i.e. by maintaining a laminar flow.

7.1.2 Dip sampling (e.g. surface waters)

Take the sample by carefully and slowly dipping the sample vessel.

7.1.3 Sampling using faucets

Connect an inert sampling tube gastight to the faucet and insert the sampling tube all the way down to the bottom of the sampling vessel. Allow the water to overflow up to at least three times the volume of the vessel capacity.

NOTE A sampling vessel can be filled with water before the measurement of the oxygen concentration, provided that turbulence is avoided.

7.1.4 Sampling with pumps

Only water-displacing submersible pumps should be used. Pumps, which function according to the principle of air displacement, are not suitable. Fill up the sample vessel starting with the bottom, using a sampling tube, and discharge the water over an overflow. During sample transfer, the volume flow rate shall be controlled in order to guarantee a mainly laminar flow. Allow the water to overflow up to at least three times the volume of the vessel capacity.

7.2 Measuring technique and precautions to be taken

The measuring system shall be in a proper state as outlined in the manufacturer’s instructions. For example:

- the sensor cap shall not be damaged; small scratches mostly do not matter (refer to manual);
- the system has to be calibrated when necessary (refer to manual).

When a measurement is performed, ensure that the sample flows past the sensor cap with sufficient velocity to obtain a homogenous sample and a rapid reading. This can be achieved by natural streaming, movement of the sensor, or stirring e.g. with a magnetic stirrer (refer to manual).

Take care that there is no exchange of oxygen from a gas reservoir to the sample or vice versa. Therefore avoid formation of any air bubbles in the samples that are measured in a vessel. When measuring on-site, do not generate any air bubbles, as these can affect the signal.

For storing and maintenance of the probe, consult the manufacturer’s manual.

7.3 Calibration

7.3.1 General

The procedure is described in 7.3.2 to 7.3.3, but it is also necessary to consult the manufacturer's instructions.

Calibration at air saturation should be checked daily and after relevant changes of ambient conditions (i.e. temperature or pressure).

7.3.2 Checking the zero

If necessary, check and, if possible, adjust the zero setting of the instrument by immersing the probe in 1 l of water to which the equivalent of 1 g or more sodium sulfite is added (5.2) (the solution is usable after adequate reaction time, when a stable reading is achieved). About 1 mg of cobalt(II) salt (5.3) can be added to increase the reaction rate. Alternatively, 100 ml of an alkaline ascorbic acid solution can be used. The alkaline ascorbic acid solution is prepared by dissolving 2 g ascorbic acid (5.4) and 25 ml 1 mol/l NaOH (5.5) in 85 ml deionised water in a suitable vessel with stopper (for total 110 ml volume). Start stirring slowly; wait 3 min before use. Use a reagent that is applicable for checking the zero according to the manufacturer's manual.

WARNING — Water soluble cobalt(II) salts are toxic to humans and to aquatic life. Handling with care is necessary.

NOTE 1 Typical reaction times without cobalt(II) are 20 min, with cobalt(II) 5 min, and with alkaline ascorbic acid 30 min.

The zero checking and setting, if possible, can also be performed by using a pure nitrogen (5.6) atmosphere.

NOTE 2 Dry conditions are possible according to some manufacturer's manuals.

Modern probes typically achieve a stable response within some minutes. However, different probes can have different response rates and the manufacturer's instruction should be consulted. If stirring is required according to the manufacturer's manual, carry out the stirring in such a way that

a) the response time is minimized and

b) no oxygen from the atmosphere is mixed in.

7.3.3 Calibration at saturation

Perform the calibration in an applicable container according to the manufacturer's manual. Simple and effective calibration is possible in water vapour saturated air.

Replace the sensor cap when the instrument can no longer be calibrated, when the meter software does not accept the sensor cap response, or when the response becomes unstable or slow (see the manufacturer's instructions).

NOTE Values can be checked by the Winkler titration (see ISO 5813).

7.4 Determination

Carry out the determination on the water to be analysed according to manufacturer's instructions.

Gently agitate the sample, e.g. by stirring (see 7.2), if recommended by the manufacturer. Check the influencing variables like sample temperature, atmospheric pressure, and salinity of sample.

NOTE 1 For information on how the concentration of oxygen is dependent on temperature, pressure, and salinity, see Annex A.

Immerse the measuring probe sensor in the sample, allowing an intensive contact of the sensor cap and the temperature sensor with the water.

NOTE 2 Most instruments compensate for the temperature behavior. In %-mode, they take into account the atmospheric pressure for the computation of the final reading. When using instruments without these automatic functions, the influence of temperature and pressure have to be considered by the user (see Annex A).

8 Calculation and expression of results

8.1 Dissolved oxygen concentration

Express the dissolved oxygen concentration, in milligrams of oxygen per litre, and report the result to the first decimal place.

EXAMPLE 1 $\rho(O_2) = 1{,}5$ mg/l.

EXAMPLE 2 $\rho(O_2) = 18{,}2$ mg/l.

8.2 Dissolved oxygen expressed as percentage saturation

Most instruments are equipped with an automatic calculation. If required, calculate the percentage saturation of dissolved oxygen in water from

$$w(O_2) = \frac{\rho(O_2)}{\rho(O_2)_{th}} \times 100 \qquad (1)$$

where

$w(O_2)$ is the percentage saturation of dissolved oxygen in water, expressed in percent, %;

$\rho(O_2)$ is the actual concentration, expressed in milligrams per litre, mg/l, of dissolved oxygen found in a water sample at a barometric pressure p, at a water temperature θ;

$\rho(O_2)_{th}$ is the theoretical concentration, expressed in milligrams per litre, mg/l, of oxygen for that sample at the barometric pressure p and the temperature θ, if the sample were saturated with moist air (see Annex A).

Report the result to the nearest whole number. The water temperature θ and barometric pressure p at the measurement, and salinity S of the sample when the latter was taken into account, shall be given (see Clause 9).

EXAMPLE 1 $w(O_2) = 3$ %

$p = 1\,115$ hPa; $\theta = 19{,}5$ °C; $S = 35$

EXAMPLE 2 $w(O_2) = 104$ %

$p = 1\,005$ hPa; $\theta = 22{,}1$ °C; $S = 3$

9 Test report

The test report shall contain at least the following information:

a) the test method used, together with a reference to this International Standard (i.e. ISO 17289:2014);

b) the identity of the water samples;

c) the measuring conditions (if necessary):
  - the temperature of the water when the sample was taken and when the measurement was carried out;
  - the atmospheric pressure when the sample was taken and when the measurement was carried out;
  - the salinity of the water;

d) the result in accordance with Clause 8;

e) all circumstances that might have influenced the result.

Annex A
(informative)

Physico-chemical data of oxygen in water

A.1 Salinity and conductivity

Use the values in Table A.1 if the conductivity meter in use does not measure salinity. Use a conductivity meter to determine conductivity at reference temperature (20 °C), then use Table A.1 to estimate the salinity to the nearest whole number.

If the conductivity meter is only able to display the conductivity at another reference temperature, the conductivity at 20 °C has to be calculated by a correction factor (see ISO 7888).

Table A.1 was calculated up to the conductivity of 5,4 S/m from the International Oceanographic Tables. [7]

Table A.1 — Correlation conductivity — Salinity

Conductivity S/m[b]	Salinity value[a]	Conductivity S/m[b]	Salinity value[a]	Conductivity S/m[b]	Salinity value[a]
0,5	3	2,0	13	3,5	25
0,6	4	2,1	14	3,6	25
0,7	4	2,2	15	3,7	26
0,8	5	2,3	15	3,8	27
0,9	6	2,4	16	3,9	28
1,0	6	2,5	17	4,0	29
1,1	7	2,6	18	4,2	30
1,2	8	2,7	18	4,4	32
1,3	8	2,8	19	4,6	33
1,4	9	2,9	20	4,8	35
1,5	10	3,0	21	5,0	37
1,6	10	3,1	22	5,2	38
1,7	11	3,2	22	5,4	40
1,8	12	3,3	23	—	—
1,9	13	3,4	24	—	—

[a] Salinity determined from conductivity at 20 °C.

[b] 1 S/m = 10 mmhos/cm.

A.2 Barometric pressure and elevation

Table A.2 is used to estimate the true barometric pressure at certain elevations. The correspondence is based on the assumption that at sea level the barometric pressure is 1 013 hPa. After taking the