
**Water quality — Determination of dissolved
oxygen — Electrochemical probe method**

*Qualité de l'eau — Dosage de l'oxygène dissous — Méthode
électrochimique 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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 5814 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This third edition cancels and replaces the second edition (ISO 5814:1990), which has been technically revised.

The main changes compared to the second edition are:

- a) a calibration procedure using water-saturated air is specified;
- b) the calibration procedure using air-saturated water is omitted.

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Water quality — Determination of dissolved oxygen — Electrochemical probe method

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This 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 according to this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies an electrochemical method for the determination of dissolved oxygen in water by means of an electrochemical cell which is isolated from the sample by a gas permeable membrane.

Measurement can be made either as a concentration of oxygen in milligrams per litre, percentage saturation (% dissolved oxygen) or both. The method measures oxygen in water corresponding to 1 % to 100 % saturation. However, 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 when strong algal growth is present, supersaturation of up to 200 % and above can occur.

The method measures oxygen in water with a saturation higher than 100 %, when special arrangements to prevent the outgassing of oxygen during the handling and measurement of the sample are made.

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 the preferred method 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^[1].

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.

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

Immersion of a probe, consisting of a cell enclosed by a selective membrane and containing the electrolyte and at least two metallic electrodes, in the water to be analysed.

NOTE The membrane is effectively impermeable to water and ionic dissolved matter, but is permeable to oxygen and a certain number of other gases.

One of the electrodes is made of a noble metal like gold or platinum. Oxygen is reduced at its surface by an electrochemical process. In order to make this process possible, a suitable electrochemical potential is established at this electrode. For polarographic probes, this is achieved by applying an external voltage related to a second electrode. Galvanic probes are able to build up the potential by themselves.

The current resulting from the reduction of oxygen is directly proportional to the rate of transport of oxygen through the membrane and the layer of electrolyte, and hence to the partial pressure of the oxygen in the sample at a given temperature.

Temperature has two different influences. The first relates to the variation of gas permeability of the membrane with temperature. So the primary signal of the probe has to be compensated with a built-in temperature sensor. Meters manufactured recently are able to do this automatically. The second is the temperature effect on the electrode reactions.

To calculate the percentage of saturation of samples in contact with an atmosphere, it is necessary to include the effective pressure. This can be performed manually or by implementing a pressure sensor for automatic compensation. Salinity can also be an influence.

4 Interferences

Gases and vapors such as chlorine, hydrogen sulfide, amines, ammonia, bromine, and iodine which diffuse through the membrane can interfere, if present, by affecting the measured current.

Other substances present in the sample can interfere with the measured current by causing obstruction, deterioration of the membrane or corrosion of the electrodes. These include solvents, oils, sulfides, carbonates, and biofilms.

5 Reagents

During analysis, use only reagents of recognized analytical grade.

5.1 **Water**, grade 2, as specified in ISO 3696, optionally from commercial sources.

5.2 **Sodium sulfite**, anhydrous, Na_2SO_3 or heptahydrate, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$.

5.3 **Cobalt(II) salt**, for example cobalt(II) chloride hexahydrate, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.

5.4 **Nitrogen gas**, N_2 , purity 99,995 % volume fraction or better.

6 Apparatus

6.1 **Measuring instrument**, comprising the components specified in 6.1.1 and 6.1.2.

6.1.1 **Measuring probe**, either of the galvanic type (e.g. lead/silver) or the polarographic type (e.g. silver/gold) with, if required, a temperature-sensitive compensating device.

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

6.2 **Thermometer**, graduated in at least 0,5 °C divisions.

NOTE Commonly a temperature sensor is integrated into the instrument (6.1).

6.3 **Barometer**, graduated to 1 hPa.

NOTE Usually the barometer is integrated into the instrument (6.1).

7 Sampling and analysis procedure

7.1 Sampling

7.1.1 General

Samples should always be handled so that transfer of oxygen between water sample and air is inhibited.

As a matter of principle, the oxygen concentration shall be measured directly on site in the water body to be analysed.

If direct measurement in the water body is not possible, the measurement can also be taken in a gas-tight connected flow-through device or immediately after sampling as a discrete sample.

Any discrete sampling procedure results 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 from taps

Connect an inert sampling tube, in a gas-tight fashion, to the tap and insert the sampling tube all the way down to the bottom of the sampling vessel. Ensure that the volume of water allowed to overflow is at least three times the capacity of the vessel.

7.1.4 Sampling with pumps

Only water-displacing submersible pumps should be used. Pumps that function according to the principle of air displacement are *not* suitable. Fill the sample vessel from the bottom, using a sampling tube, and allow the water to overflow. During sample transfer, the volume flow rate shall be controlled in order to guarantee a mainly laminar flow. Ensure that the volume of water allowed to overflow is at least three times the capacity of the vessel.

7.2 Measuring technique and precautions to be taken

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

- ensure the membrane is not damaged;
- allow an adequate polarization time;
- calibrate the system when necessary.

When a measurement is performed, ensure that the sample flows past the membrane with sufficient velocity according to the manufacturer's instructions. This can be achieved by natural streaming, movement of the sensor or stirring, e.g. with a magnetic stirrer. This is necessary to prevent loss of signal because of consumption of oxygen by the sensor.

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, which may affect the signal.

For storing and maintenance of the probe, consult the manufacturer's instructions.

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 of sodium sulfite (5.2) and about 1 mg of cobalt(II) salt (5.3) have been added to render the water free from oxygen. The solution is usable after an adequate reaction time.

Modern probes typically achieve a stable response within 10 min to 15 min. However, different probes can have different response rates and the manufacturer's instructions should be consulted.

NOTE Cobalt(II) is used as catalyst for the reduction of oxygen by the sulfite. The zero checking and setting, if possible, can also be performed in a pure nitrogen atmosphere.

7.3.3 Calibration at saturation

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

NOTE 1 There are small differences between sensor currents in water and in air. Because of the sensor geometry, in water a so-called unmoved diffusion layer exists, which leads to a signal depression of ~2 %. Therefore, the calibration target is 102 % in water vapour-saturated air (refer to the manufacturer's instructions). This is commensurate with 100 % saturation in water.

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Replace the electrolyte and/or the membrane when the instrument can no longer be calibrated or when the response becomes unstable or slow (see the manufacturer's instructions).

NOTE 2 Values can be checked by the Winkler titration (see ISO 5813^[1]).

7.3.4 Linearity check

A linearity check (carried out in the laboratory versus Winkler test) is only necessary if there is a problem with the instrument. In that case, consult the manufacturer's instructions.

7.4 Determination

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

Ensure sufficient agitation of the water (see 7.2).

Completely immerse the measuring probe sensor in the sample, allowing an intensive contact of the membrane and the temperature sensor with the water.

Check the influencing variables, namely sample temperature, atmospheric pressure, and salinity of the sample.

NOTE Most instruments compensate for the temperature behaviour of the probe and 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. For information on how the solubility of oxygen is dependent on temperature, pressure and salinity, and for the correlation between conductivity and salinity, 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 $\rho_{O_2} = 1,5 \text{ mg/l}$.

EXAMPLE 2 $\rho_{O_2} = 18,1 \text{ mg/l}$.

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, expressed as a percentage, w_{O_2} , from

$$w_{O_2} = \frac{\rho_{O_2}}{\rho_{O_2,s}} \times 100 \quad (1)$$

where

ρ_{O_2} is the actual concentration, expressed in milligrams per litre, mg/l, of dissolved oxygen found in a water sample at an atmospheric pressure, p , in hectopascals, hPa, at a water temperature, θ , in degrees Celsius, °C;

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

Report the result to the nearest whole number. Give the water temperature θ and atmospheric pressure p at the measurement, and salinity S of the sample, if the latter has been taken into account.

EXAMPLE 1

$w_{O_2} = 3 \%$ $p = 1\,115 \text{ hPa}$; $\theta = 19,5 \text{ °C}$; $S = 35$

EXAMPLE 2

$w_{O_2} = 104 \%$ $p = 1\,005 \text{ hPa}$; $\theta = 22,1 \text{ °C}$; $S = 3$

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 (ISO 5814:2012);
- b) the identity of the water sample;
- c) the measuring conditions:
 - 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)

Physicochemical data for 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^[2]).

Table A.1 was calculated up to the conductivity of 5,4 S/m from the *International oceanographic tables* (see Reference [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 Atmospheric pressure and elevation

Table A.2 is used to estimate the true atmospheric pressure at certain elevations. The correspondence is based on the assumption that at sea level the atmospheric pressure is 1 013 hPa. After taking the atmospheric pressure depending on the elevation from Table A.2 or more precisely from a local weather service, enter this value into the instrument.

NOTE 1 The values given in Table A.2 are approximations derived according to the international atmospheric formula and can differ from other data obtained from other feasible equations.

NOTE 2 Corrections of the atmospheric pressure are only necessary if the instrument does not do this automatically.

Table A.2 — Elevation atmospheric pressure (example)

Elevation m	Atmospheric pressure hPa	Elevation m	Atmospheric pressure hPa
0	1 013	1 800	815
150	995	1 950	800
300	979	2 100	785
450	960	2 250	771
600	943	2 400	756
750	926	2 550	742
900	910	2 700	728
1 050	893	2 850	715
1 200	877	3 000	701
1 350	861	3 150	688
1 500	846	3 300	675
1 650	830	—	—

A.3 Solubility of oxygen in water

Table A.3 — Solubility of oxygen in water
equilibrated with water-saturated air at atmospheric pressure (1 013 hPa)
(for salinity see Table A.1)

Temperature °C	Salinity				
	0	9	18	27	36
	Oxygen solubility mg/l				
0	14,62	13,73	12,89	12,11	11,37
1,0	14,22	13,36	12,55	11,79	11,08
2,0	13,83	13,00	12,22	11,49	10,80
3,0	13,46	12,66	11,91	11,20	10,54
4,0	13,11	12,34	11,61	10,93	10,28
5,0	12,77	12,03	11,33	10,66	10,04
6,0	12,45	11,73	11,05	10,41	9,81
7,0	12,14	11,44	10,79	10,17	9,58
8,0	11,84	11,17	10,54	9,94	9,37
9,0	11,56	10,91	10,29	9,71	9,16
10,0	11,29	10,66	10,06	9,50	8,97
11,0	11,03	10,42	9,84	9,29	8,78
12,0	10,78	10,19	9,63	9,09	8,59
13,0	10,54	9,96	9,42	8,90	8,42
14,0	10,31	9,75	9,22	8,72	8,25
15,0	10,08	9,54	9,03	8,55	8,09
16,0	9,87	9,35	8,85	8,38	7,93
17,0	9,67	9,15	8,67	8,21	7,78
18,0	9,47	8,97	8,50	8,05	7,63
19,0	9,28	8,79	8,34	7,90	7,49