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Water quality — Determination of dissolved oxygen — Electrochemical probe method

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



Reference number
ISO 5814:1990(E)

Foreword

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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.

International Standard ISO 5814 was prepared by Technical Committee ISO/TC 147, *Water quality*.

This second edition cancels and replaces the first edition (ISO 5814:1984), of which it constitutes a minor revision.

Annexes A and B of this International Standard are for information only.

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Water quality — Determination of dissolved oxygen — Electrochemical probe method

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.

Depending on the type of probe employed, measurement can be made either as concentration of oxygen in milligrams per litre, percentage saturation (% dissolved oxygen) or both. The method measures oxygen in water corresponding to 0 % to 100 % saturation. However, most instruments permit measurement of values higher than 100 %, i.e. supersaturation.

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 waters containing iron and iodine fixing substances, all of which may interfere in the iodometric method specified in ISO 5813. Gases and vapours such as chlorine, sulfur dioxide, hydrogen sulfide, amines, ammonia, carbon dioxide, bromine and iodine which diffuse through the membrane, may interfere, if present, by affecting the measured current. Other substances present in the sample may interfere with the measured current by causing obstruction, or deterioration of the membrane or corrosion of the electrodes. These include solvents, oils, sulfides, carbonates and algae.

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

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publi-

cation, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5813:1983, *Water quality — Determination of dissolved oxygen — Iodometric method.*

3 Principle

Immersion of a probe, consisting of a cell enclosed by a selective membrane and containing the electrolyte and two metallic electrodes, in the water to be analysed. (The membrane is practically impermeable to water and ionic dissolved matter, but is permeable to oxygen and a certain number of the other gases and lyophobic substances.)

Because of the potential difference between the electrodes, caused by galvanic action or an external voltage, oxygen passing through the membrane is reduced at the cathode, while metal ions pass into solution at the anode.

The current so produced 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.

The permeability of the membrane to gases varies greatly with temperature, and compensation is required for readings taken at different temperatures of the sample. This can be done mathematically, for example, by the use of a suitable nomograph or computer program. The majority of modern instruments automatically compensate for temperature variation by inclusion of temperature-sensitive elements in the electronic circuitry. However, instruments reading directly in percentage solubility, unless provided with a pressure transducer in the circuitry to compensate for pressure differences, will

display an observed percentage reading. This is a reading with respect to atmospheric pressure and not the true reading if the pressure differs from atmospheric pressure.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

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

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

5 Apparatus

5.1 Measuring instrument, comprising the following components.

5.1.1 Measuring probe, either of the galvanic type (for example lead/silver) or the polarographic type (for example silver/gold) with, if required, a temperature-sensitive compensating device.

5.1.2 Meter, graduated to show the concentration of dissolved oxygen directly, and/or the percentage saturation with oxygen, or the current in microamperes.

5.2 Thermometer, graduated in divisions of $0,5^\circ\text{C}$.

5.3 Barometer, graduated in divisions of 10 Pa.

6 Procedure

When using the measuring instrument, the manufacturer's instructions should be followed.

6.1 Measuring technique and precautions to be taken

6.1.1 Never touch the active surface of the membrane with the fingers.

6.1.2 After changing the electrolyte and the membrane, or if the membrane has been allowed to dry out, wet the membrane and allow the reading to become stable before carrying out the calibration (see 6.2). The time required depends on that necessary for consumption of the oxygen dissolved in the electrolyte.

6.1.3 Ensure that air bubbles are not trapped in the probe when immersing it in the sample.

6.1.4 It is essential that the sample should flow past the membrane of the probe to prevent the occurrence of false readings due to depletion of the oxygen in the part of the sample in immediate contact with the membrane. Ensure that the flow rate is such that variations in readings are not produced, and consult the instrument manufacturer's instructions on this matter.

6.1.5 In the case of a discrete sample, carry out the determination in a vessel filled to overflowing, sealed to exclude air and containing a stirrer, for example a magnetic bar. Adjust the stirring rate such that the reading remains stable after reaching equilibrium, and there is no entrapment of air.

6.1.6 In the case of a flowing sample, such as a water course, check the flow rate to ensure that it is sufficient. If not, either move the probe about in the sample or take a discrete sample and treat it as described in 6.1.5.

6.2 Calibration

The procedure is described in 6.2.1 to 6.2.3, but it is necessary to consult the instrument manufacturer's instructions.

6.2.1 Regulation

Adjust the electrical zero of the instrument, where applicable.

NOTE 1 Some instruments are zero compensated and need no adjustment.

6.2.2 Checking the zero

Check and, if possible, adjust the zero setting of the instrument by immersing the probe in 1 litre of water to which about 1 g of sodium sulfite (4.1) and about 1 mg of the cobalt(II) salt (4.2) have been added to render the water free from oxygen.

NOTE 2 Modern probes typically achieve a stable response in 2 min to 3 min. However, different probes can have different response rates and the manufacturer's instructions should be consulted.

6.2.3 Calibration at a value near saturation

Bubble air through water at a constant temperature so that its oxygen content is brought to saturation or near saturation. Leave for about 15 min at this temperature and determine the dissolved oxygen concentration, for example by the iodometric method specified in ISO 5813.

Regulate the instrument.

Immerse the probe in a bottle completely filled with the sample, prepared and standardized as de-

scribed. After allowing the probe to stabilize in the stirred solution for 10 min (see the note to 6.2.2), adjust the instrument reading to the known oxygen concentration of the sample, if necessary.

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

NOTES

3 If previous experience has shown that the bubbling time and the air flow rate used provide a sample saturated with air, the iodometric determination may be replaced by consultation of table A.1 and table A.2.

4 Many instruments allow calibration in air.

6.2.4 Linearity curve

Check the linearity before using the instrument for routine purposes and carry out checks at regular intervals.

Carry out these checks by preparing a range of distilled water samples of varying intermediate oxygen concentration. Completely fill three or four narrow-necked 250 ml bottles with distilled water and deoxygenate to varying extents by gently bubbling oxygen-free argon or nitrogen through each for an appropriate period. Take readings from time to time with the probe under test, until approximately the required concentration of dissolved oxygen is reached. Then determine the dissolved oxygen content by the probe and immediately afterwards determine the dissolved oxygen concentration by the iodometric method in ISO 5813.

If there is agreement between the two procedures across the range of dissolved oxygen concentrations, the probe can be said to show a linear response. Check any departure from linearity and, if necessary, consult the manufacturer of the probe.

NOTE 5 The reading of the instrument is usually linear for dissolved oxygen saturations up to 100 %.

6.3 Determination

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

After immersion of the probe in the sample, allow sufficient time for the probe to attain the water temperature and reach a stable reading. If necessary, because of the type of instrument used and the result required, check the water temperature and/or the atmospheric pressure.

7 Calculation and expression of results

7.1 Dissolved oxygen concentration

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

If the reading on the sample was made at a temperature different from that at which the instrument was calibrated, correct the value given by the instrument to allow for this. Some instruments make this correction automatically. This correction makes allowance for the difference in the solubility of oxygen at the two temperatures. Calculate the real value by multiplying the value read at the temperature at which the measurement was made by the ratio

$$\frac{\rho(\text{O})_m}{\rho(\text{O})_c}$$

where

$\rho(\text{O})_m$ is the solubility at the temperature of measurement;

$\rho(\text{O})_c$ is the solubility at the temperature of calibration.

Example:

Temperature of calibration	25 °C
Solubility at 25 °C	8,3 mg/l
Temperature at the time of the measurement	10 °C
Reading of the instrument	7 mg/l
Solubility at 10 °C	11,3 mg/l
Real value at 10 °C	$11,3/8,3 \times 7,0 = 9,5$ mg/l

NOTES

6 The values for $\rho(\text{O})_m$ and $\rho(\text{O})_c$, expressed in milligrams per litre, in the given example are obtainable from table A.1, column 2.

7 For information on how the solubility of oxidation is dependent on the temperature, pressure and salinity, see annex A.

7.2 Dissolved oxygen concentration expressed as a percentage saturation

If required, calculate the percentage saturation of dissolved oxygen in water from:

$$\frac{\rho(\text{O})}{\rho(\text{O})_s} \times 100$$

where

$\rho(O)$ is the actual concentration, expressed in milligrams per litre, of dissolved oxygen found in a water sample at a pressure p , in kilopascals, and a temperature t , in degrees Celsius;

$\rho(O)_s$ is the theoretical concentration, expressed in milligrams per litre, of dissolved oxygen for that sample at a pressure p , in kilopascals, and a temperature t , in degrees Celsius, if the sample was saturated with moist air (see annex A).

8 Test report

The test report shall include the following information:

- a) a reference to this International Standard;
- b) the result and the method of expression used;
- c) the temperature of the water when the sample was taken and when the measurement was carried out;
- d) the atmospheric pressure when the sample was taken and when the measurement was carried out;
- e) the salinity of the water;
- f) the model of instrument used;
- g) any special details which may have been noted during the determination;
- h) details of any operations not specified in this International Standard, or regarded as optional.

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Annex A (informative)

Solubility of oxygen in water in relation to temperature, pressure and salinity

A.1 General

The solubility of oxygen in water at a given pressure varies with temperature, and similarly the solubility at a given temperature varies with the pressure. Additionally, there is a decrease in solubility with increasing salinity.

A.2 Solubility of oxygen in water as a function of temperature and salinity

A.2.1 Temperature effect

Column 2 of table A.1 gives the solubility, $\rho(O)_s$, of oxygen, expressed in milligrams per litre of oxygen in pure water, in the presence of air, saturated with water vapour and containing 20,94 % (V/V) of oxygen, at a total pressure of 101,325 kPa. The values given in column 2 are based on those published by Mortimer^[1].

A.2.2 Salinity effect

Column 3 of table A.1 gives the correction to be subtracted, $\Delta\rho(O)_s$, for each degree of salinity expressed in grams per kilogram of total salts in water. Thus the solubility of oxygen in water with a salinity of $w(\text{NaCl})$ in grams per kilogram is found by subtracting the value $w(\text{NaCl}) \cdot \Delta\rho(O)_s$, from the solubility of oxygen in pure water, at the same temperature, given in column 2 of table A.1. These salinity corrections are derived from tables published by UNESCO^[2] and are applicable to sea water or estuarine waters.

The salinity correction is, for practical purposes, linear up to a salinity of 35 g/kg. However, using these values for correction can give errors of up to about 1 % of the computed values for the solubility of oxygen in saline waters given by UNESCO^[2]. If accurate values are required, they can be conveniently found in the tables of oxygen solubility, expressed in milligrams per litre, computed by Gardener and Hughes^[3].

A.3 Correction for atmospheric pressure or altitude (see table A.2)

A.3.1 Atmospheric pressure

If the atmospheric pressure, p , at the time of sampling is not 101,325 kPa, then the solubility, $\rho'(O)_s$, for the pressure p , in kilopascals, is given by the equation

$$\rho'(O)_s = \rho(O)_s \times \frac{p - p_w}{101,325 - p_w}$$

where

$\rho'(O)_s$ is the solubility of oxygen in water, in milligrams per litre, at a pressure p , in kilopascals, and temperature t , in degrees Celsius;

$\rho(O)_s$ is the theoretical solubility of oxygen in water, in milligrams per litre, at 101,325 kPa and temperature t , in degrees Celsius;

p_w is the saturation vapour pressure of water, in kilopascals, in contact with air at temperature t , in degrees Celsius, see [4].

Since p_w is usually small compared with p , a convenient approximation, $\rho''(O)_s$, for $\rho'(O)_s$, for practical purposes is given by the equation

$$\rho''(O)_s = \rho(O)_s \times \frac{p}{101,325}$$

Some of the values for $\rho'(O)_s$, in milligrams per litre, of oxygen for a pressure range of 111,5 kPa (1,1 atm) to 50,7 kPa (0,5 atm) and a temperature range of 0 °C to 40 °C are given in table A.2. These were derived from the equation:

$$\rho'(O)_s = \rho''(O)_s W$$

where the value of factor W is taken from Mortimer^[1] and is used for correcting the effect of water pressure, p_w .

A.3.2 Altitude

The mean atmospheric pressure as a function of altitude can be calculated by the Schmassmann equation

$$\log_{10} p_h = \log_{10} 101,3 - \frac{h}{18400}$$

where p_h is the mean atmospheric pressure, in kilopascals, at altitude h , in metres.

Table A.1 — Solubility of oxygen in water as a function of temperature and salinity

Temperature °C	Solubility of oxygen in water in equilibrium with air at 101,325 kPa [$\rho(O)_s$] mg/l	Correction to be subtracted for each degree of salinity expressed in grams per kilogram of total salts in water [$\Delta\rho(O)_s$] mg/l
0	14,62	0,087 5
1	14,22	0,084 3
2	13,83	0,081 8
3	13,46	0,078 9
4	13,11	0,076 0
5	12,77	0,073 9
6	12,45	0,071 4
7	12,14	0,069 3
8	11,84	0,067 1
9	11,56	0,065 0
10	11,29	0,063 2
11	11,03	0,061 4
12	10,78	0,059 3
13	10,54	0,058 2
14	10,31	0,056 1
15	10,08	0,054 5
16	9,87	0,053 2
17	9,66	0,051 4
18	9,47	0,050 0
19	9,28	0,048 9
20	9,09	0,047 5
21	8,91	0,046 4
22	8,74	0,045 3
23	8,58	0,044 3
24	8,42	0,043 2
25	8,26	0,042 1
26	8,11	0,040 7
27	7,97	0,040 0
28	7,83	0,038 9
29	7,69	0,038 2
30	7,56	0,037 1

Table A.2 — Solubility, $\rho'(O)_s$, of oxygen in water as a function of temperature and pressure

Temperature °C	Pressure [kPa (atm) ¹⁾]						
	111,5 (1,1)	101,3 (1,0)	91,2 (0,9)	81,1 (0,8)	70,9 (0,7)	60,8 (0,6)	50,7 (0,5)
	Solubility, $\rho'(O)_s$ (mg/l)						
0,0	16,09	14,62	13,14	11,69	10,21	8,74	7,27
5,0	14,06	12,77	11,48	10,20	8,91	7,62	6,34
10,0	12,43	11,29	10,15	9,00	7,86	6,71	5,58
15,0	11,10	10,08	9,05	8,03	7,01	5,98	4,96
20,0	10,02	9,09	8,14	7,23	6,30	5,37	4,44
25,0	9,12	8,26	7,40	6,56	5,70	4,84	4,00
30,0	8,35	7,56	6,76	5,99	5,19	4,60	3,62
35,0	7,69	6,95	6,22	5,47	4,75	4,01	3,28
40,0	7,10	6,41	5,72	5,03	4,34	3,65	2,96

1) Units at standard barometric pressure (normal atmospheric pressure at sea level): 101,325 kPa = 101,325 kN/m² = 1 atm = 760 mmHg.

Table A.3 — Variation of atmospheric pressure with respect to altitude

Altitude, h m	Mean atmospheric pressure, p_h kPa	Altitude, h m	Mean atmospheric pressure, p_h kPa
0	101,3	1 100	88,3
100	100,1	1 200	87,2
200	98,8	1 300	86,1
300	97,6	1 400	85,0
400	96,4	1 500	84,0
500	95,2	1 600	82,9
600	94,0	1 700	81,9
700	92,8	1 800	80,9
800	91,7	1 900	79,9
900	90,5	2 000	78,9
1000	89,4	2 100	77,9