

# INTERNATIONAL STANDARD

## NORME INTERNATIONALE

**Expression of performance of electrochemical analyzers –  
Part 4: Dissolved oxygen in water measured by membrane-covered  
amperometric sensors**

**Expression des qualités de fonctionnement des analyseurs électrochimiques –  
Partie 4: Oxygène dissous dans l'eau mesuré par des capteurs ampérométriques  
recouverts d'une membrane**



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INTERNATIONAL  
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ICS 19.080; 71.040.40

ISBN 978-2-8322-6274-0

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## INTERNATIONAL ELECTROTECHNICAL COMMISSION

**EXPRESSION OF PERFORMANCE OF  
ELECTROCHEMICAL ANALYZERS –****Part 4: Dissolved oxygen in water measured  
by membrane-covered amperometric sensors**

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International Standard IEC 60746-4 has been prepared by subcommittee 65B: Measurement and control devices, of IEC technical committee 65: Industrial-process measurement, control and automation.

This second edition cancels and replaces the first edition published in 1992. This edition constitutes a technical revision.

This edition includes the following significant technical changes with respect to the previous edition:

- a) terms and definitions have been revised to meet the requirements of ISO/IEC Directives Part 2:2016.
- b) ISO 5814:2012 is cited as reference for solubility tables of dissolved oxygen in water with variable salt content at different pressure and temperature.

The text of this International Standard is based on the following documents:

FDIS	Report on voting
65B/1128/FDIS	65B/1138/RVD

Full information on the voting for the approval of this International Standard can be found in the report on voting indicated in the above table.

This document has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC 60746 series, published under the general title *Expression of performance of electrochemical analyzers*, can be found on the IEC website.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under "<http://webstore.iec.ch>" in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

## EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS –

### Part 4: Dissolved oxygen in water measured by membrane-covered amperometric sensors

#### 1 Scope

This part of IEC 60746 is intended:

- to specify terminology, definitions and requirements for statements by manufacturers for analyzers, sensor units and electronic units used for the determination of dissolved oxygen partial pressure or concentration;
- to establish performance tests for such analyzers, sensor units and electronic units;
- to provide basic documents to support the applications of quality assurance standards [1]<sup>1</sup>.

This document applies to analyzers using membrane covered amperometric sensors. It applies to analyzers suitable for use in water containing liquids, ultrapure waters, fresh or potable water, sea water or other aqueous solutions, industrial or municipal waste water from water bodies (e.g. lakes, rivers, estuaries), as well as for industrial process streams and process liquids. Whilst in principle amperometric oxygen-analyzers are applicable in gaseous phases, the expression of performance in the gas phase is outside the scope of this document.

This document is applicable to analyzers specified for permanent installation in any location (indoors or outdoors) using membrane-covered amperometric sensors.

#### 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IEC 60746-1:2003, *Expression of performance of electrochemical analyzers – Part 1: General*

#### 3 Terms and definitions

For the purposes of this document, the terms and definitions given in IEC 60746-1 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

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<sup>1</sup> Numbers in square brackets refer to the Bibliography.

### 3.1 Oxygen sensor properties

#### 3.1.1

##### **membrane covered amperometric sensor**

sensor with a membrane covered metal cathode, a metal or metal/metal salt anode, optional auxiliary or reference electrodes and temperature sensors

Note 1 to entry: The electrochemical reduction of molecular oxygen occurs at the membrane-covered cathode. The metal or metal/metal salt anode provides a well-defined, electrochemically reversible oxidation reaction within the special filling electrolyte solution of the sensor. A gas-permeable membrane is employed to separate the electrolyte filling solution from the test medium to avoid contamination and to achieve a stable diffusion potential. In the case of applications in the gaseous phase the unit, volume fraction (v/v) are used.

Note 2 to entry: The cell can function as an electrochemical two-electrode cell, or as a potentiostatic three-electrode cell, or either as a galvanic cell. Within potentiostatic three-electrode cells, a high-impedance, current-free reference electrode is additionally implied to optimize the polarization voltage.

Note 3 to entry: Membrane-covered amperometric sensors are provided with temperature sensors located at the active sites of the electrode cells being in thermal contact with the media to be measured.

#### 3.1.2

##### **sensor sensitivity**

change in electrode current of the amperometric cell caused by the application of a partial pressure of oxygen

#### 3.1.3

##### **zero current of sensor**

current delivered by the sensor when the dissolved oxygen concentration or partial pressure is zero

Note 1 to entry: The zero current is expressed in  $\mu\text{A}$  or in  $\text{nA}$ .

#### 3.1.4

##### **polarization**

voltage to be applied to an amperometric cell during a time period to increase the stability of the sensor

#### 3.1.5

##### **stabilization time**

time period necessary for obtaining a stable measurement after reconnecting the sensor unit to the electronic unit for polarization purposes (see 3.1.4)

Note 1 to entry: Regeneration of the sensor with a new membrane or an electrolyte change or installation of a replacement sensor will require a subsequent stabilization time.

#### 3.1.6

##### **oxygen consumption**

electrochemical reduction of molecular oxygen at the cathode of amperometric oxygen sensors

### 3.2 Electronics

#### 3.2.1

##### **electronic unit**

electronic device of an electrochemical two-electrode cell comprises a stabilized DC voltage source and an electronic circuitry with a low impedance, direct current amplifier and optional microprocessor circuitries

Note 1 to entry: If the electronic unit of the analyzer comprises a microprocessor device, the detected amperometric signal will be digitised and evaluated to analyse the oxygen content.

Note 2 to entry: To quantify the amperometric signal of the oxygen reduction, software-based algorithmic routines or data sets comprising solubility tables of oxygen in water (with consideration of temperature, pressure and salinity) [2] and a vapour pressure table of water are used.

### 3.2.2 auxiliary electronics

electronic devices provided for potentiostatic circuitries and for temperature and pressure transducers

Note 1 to entry: In electronic devices for three-electrode cells, additional potentiostatic circuitries are implemented.

## 3.3 Measurement units and solubility of oxygen

### 3.3.1 partial pressure

units for the expression of the oxygen partial pressure ( $p_{O_2}$ ):

millibar (mbar) or kilopascal (kPa)

Note 1 to entry: In the case of special applications, the units mm Hg (Torr) and inch Hg may be used with known conversion ratio [2].

Note 2 to entry: In the case of applications in the gaseous phase the unit, volume fraction (v/v) are used.

Volume fraction is the quotient of the volume of a specified component and the sum of the volumes of all components of a gas mixture before mixing, all volumes referring to the pressure and the temperature of the gas mixture. Volume fraction will be expressed in %. The volume fraction and volume concentration take the same value if, at the same state conditions, the sum of the component volumes before mixing and the volume of the mixture are equal. However, because the mixing of two or more non-ideal gases at the same state conditions is usually accompanied by a slight contraction (or, less frequently, a slight expansion), this is not generally the case.

[SOURCE: EN 50104:2010, 3.1.5]

### 3.3.2 concentration

units for expression of the dissolved oxygen concentration ( $c_{O_2}$ ):

parts per million (ppm) = milligram  $\cdot$  kg<sup>-1</sup>

parts per billion (ppb) =  $\mu$ g  $\cdot$  kg<sup>-1</sup>

Note 1 to entry: The mass of the test medium means in this case the mass of the sample water, including salts or other substances dissolved or suspended in it.

Note 2 to entry: Although ppm (parts per million) units are used in this document, it is sometimes convenient to use the units of milligrams per litre (mg  $\cdot$  dm<sup>-3</sup>) or of micrograms per litre ( $\mu$ g  $\cdot$  dm<sup>-3</sup>).

### 3.3.3 oxygen saturation index

unit for the expression of the dissolved oxygen in percent (%) to express the relative saturation of the actual oxygen concentration (parts per million), as fraction of the theoretical oxygen concentration (parts per million) of the air-saturated solution at the actual conditions of pressure, temperature and salinity

### 3.3.4 oxygen solubility

maximal possible dissolved oxygen concentration of the water sample in contact and equilibrium with air (air-saturated solution) at the actual conditions of pressure, temperature and salinity

Note 1 to entry: The oxygen solubility in water is dependent on other dissolved organic and inorganic compounds, dissolved electrolytes, salt-content in seawater (salinity) [2].

### 3.4 Test media

#### 3.4.1

##### test medium

stable mixture of gases (nitrogen, nitrogen + oxygen), saturated with water vapour or humidified reference air showing a known concentration or a known partial pressure of oxygen used for performance tests

Note 1 to entry: The concentration (see 3.3.2) or partial pressure or volume fraction (see 3.3.1) of dissolved oxygen and its uncertainty range shall be known.

#### 3.4.2

##### calibration solution

stable mixture of humidified (saturated with water vapour) gases (nitrogen, oxygen) or humidified reference air exhibiting a known stable concentration or partial pressure or volume fraction of oxygen (with traceable uncertainties) used for calibration of the analyzer

#### 3.4.3

##### zero oxygen solution

solution with dissolved gas (pure nitrogen) or dissolved molecular or ionogenic compounds (substitutes) used to eliminate the content of free oxygen or a gaseous phase (pure nitrogen) saturated with water vapour

## 4 Influence quantities for membrane covered amperometric sensors

### 4.1 Temperature

In addition to the temperature dependent solubility-effect of oxygen [2], the temperature has an impact on membrane-covered amperometric sensors owing to the temperature-dependent variation of the diffusion of oxygen molecules at the liquid interfaces of membrane-covered sensors.

### 4.2 Pressure

Pressure affects the dissolved oxygen saturation value, or respectively the maximal oxygen concentration or the oxygen partial pressure [2]. The air-pressure of the ambient media (calibration with water-vapour saturated air) or respectively the sample pressure has to be determined applying an appropriate pressure sensor or has to be manually entered at the electronic unit (see 3.2.1).

### 4.3 Dissolved substances

Dissolved inorganic substances (salts, acids, alkalies) as well as organic substances have an impact on the oxygen solubility in water.

In seawater, the salinity (salt content by weight) shall be considered in addition to the measured temperature by employing combined salinity-temperature tables in order to determine the correct oxygen solubility [2].

### 4.4 Flow

Membrane covered amperometric sensors show in principle a small, but intrinsic, oxygen-consumption, which requires an adjusted flow-rate given at rated operation conditions.

## 5 Procedure for specification

### 5.1 Zero and span drift

Statements shall be made on zero and span drift in accordance with IEC 60746-1:2003, 6.2.5