

INTERNATIONAL STANDARD

IEC
60746-2

Second edition
2003-01

Expression of performance of electrochemical analyzers –

Part 2: pH value

*Expression des qualités de fonctionnement
des analyseurs électrochimiques –*

*Partie 2:
Mesure du pH*

[IEC 60746-2:2003](#)

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

**EXPRESSION OF PERFORMANCE OF
ELECTROCHEMICAL ANALYZERS –**

Part 2: pH value

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International Standard IEC 60746-2 has been prepared by subcommittee 65D: Analysing equipment, of IEC technical committee 65: Industrial-process measurement and control.

This second edition cancels and replaces the first edition published in 1982 and constitutes a technical revision.

The text of this standard is based on the following documents:

FDIS	Report on voting
65D/90A/FDIS	65D/94/RVD

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

The contents of this second edition remain substantially unchanged.

The major change is that Annex B has been updated in line with recent IUPAC *Recommendations for the measurement of pH*.

This part of IEC 60746 shall be used in conjunction with IEC 60746-1, which includes further definition of the scope and provides for the general aspects of all electrochemical analyzers.

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

The committee has decided that the contents of this publication will remain unchanged until 2007. At this date, the publication will be

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- withdrawn;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

The contents of the corrigendum of May 2003 and July 2003 have been included in this copy.

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EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS –

Part 2: pH value

1 Scope

This International Standard is intended:

- to specify terminology, definitions and requirements for statements by manufacturers for analyzers, sensor units and electronic units used for the determination of the pH of aqueous solutions;
- to establish performance tests for such analyzers, sensor units and electronic units;
- to provide basic documents to support the applications of quality assurance standards ISO 9001, ISO 9002 and ISO 9003.

2 Normative reference

The following referenced documents are indispensable for the application 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 60746-1:2002, *Expression of performance of electrochemical analyzers – Part 1: General*

ISO 9001, *Quality management systems – Requirements*

ISO 9002, *Quality systems – Model for quality assurance in production, installation and servicing*

ISO 9003, *Quality systems – Model for quality assurance in final inspection and test*

3 Terms, definitions, symbols and abbreviations

3.1 Terms and definitions

For the purposes of this part of IEC 60746, the definitions given in Clause 3 of IEC 60746-1, as well as the following apply.

3.1.1

pH value

A measure of the conventional hydrogen ion activity a_{H^+} (see equation (1)), in an aqueous solution given by the expression:

$$pH = -\log a_{H^+}$$

It is measured with respect to pH values assigned to certain reference pH buffer solutions. The measurement is performed by determining the e.m.f., E , between a pair of electrodes immersed in the sample to be measured, according to the cell scheme:



and a measurement with the same electrode pair at the same temperature in a reference buffer solution of pH (S_1) according to

Reference electrode | Buffer (S_1) | pH electrode $E(S_1)$

The e.m.f.s $E(S_1)$, etc. are defined as the difference of the potential of the right-hand (pH) electrode minus the potential of the left-hand (reference) electrode.

The pH of the sample is then given ideally by:

$$\text{pH} = \text{pH}(S_1) - \frac{E - E(S_1)}{k} \quad (1)$$

where $k = 2,3026 R.T/F$, the theoretical, Nernstian, slope (see 3.1.2) .

Numerical values for k , the theoretical slope factor, at temperatures from 0 °C to 95 °C, are given in Annex A.

NOTE Measurements in non or partially aqueous media are beyond the scope of this document; the reader should refer to specialist texts.

3.1.2 practical slope factor and percentage theoretical slope

PTS

performance of the electrode pair may fall below the theoretical slope k exhibiting the practical slope k' which may be determined by replacing the sample with a second reference buffer solution of pH value pH (S_2) with an e.m.f. $E(S_2)$, then:

$$k' = \frac{E(S_2) - E(S_1)}{\text{pH}(S_1) - \text{pH}(S_2)} \quad (2)$$

NOTE The difference in pH value between the two reference buffer solutions should be as large as possible, however, solutions above pH 10 and below pH 3 should not generally be used (see Annex B).

The percentage theoretical slope (PTS) is given by:

$$PTS = \frac{100 k'}{k}$$

Equations (1) and (2) can be combined by substituting k' for k in equation (1) where:

$$\text{pH} = \text{pH}(S_1) - \frac{[E - E(S_1)] \cdot [\text{pH}(S_1) - \text{pH}(S_2)]}{E(S_2) - E(S_1)} \quad (3)$$

and the two reference buffers are usually chosen to bracket the pH of the sample.

3.1.3 pH sensor

the most commonly used pH sensor is the glass electrode, other potentiometric sensors, for example, the antimony electrode only being adopted when its use is precluded. The pH isfet (ion selective field effect transistor) sensor is an alternative to potentiometric sensors, necessitating manufacturer-specific instrumentation.

3.1.4 reference electrode

appropriate half-cell providing a stable potential at constant temperature against which the potential of the pH sensor is measured. Electrical contact with the sample is made at a liquid-junction with the reference electrolyte or an interposed bridge solution.

3.1.5**temperature compensator**

electrical sensor in thermal contact with the sample providing the means for temperature compensation

3.1.6**sensor unit**

insertion or flow-through housing into which pH and reference sensors, as well as usually, a temperature compensator (see 4.3.4) and possibly auxiliary devices (see 4.3.5) are fitted.

3.1.7**zero point pH**

pH value at which the e.m.f. of the electrode pair (sensor unit) is 0 V at a given temperature, unless otherwise stated, understood to be 25 °C.

3.1.8**isopotential pH, pH_i , of the electrode pair (sensor unit)**

pH, pH_i , at which the e.m.f., E_i , of the electrode pair is temperature invariant. It is a function of the temperature coefficients of the individual electrodes and provides temperature compensation for the electrode pair zero shift with appropriate instrumentation.

3.1.9**alkaline (or sodium) error of the glass electrode**

error of the e.m.f. caused by sensitivity of pH glass electrodes to alkali ions at high pH resulting in apparent low pH values. Major interferences are $Na^+ > Li^+ > K^+ > Ba^{2+}$. Errors increase with increasing alkali concentration, pH and temperature. The magnitude is dependent on the glass membrane composition.

3.1.10**reference buffer solution**

aqueous solution prepared according to a specific formula using recognized analytical grade chemicals and water having a conductivity no greater than $2 \mu S \cdot cm^{-1}$ at 25 °C (see Annex B)

3.1.11**solution ground (earth) electrode**

inert metal electrode required for differential input instrumentation as a comparison point against which glass and reference electrode potentials are determined. For other applications, it establishes the sample potential at instrument ground (earth)

3.1.12**simulator**

simulator providing Nernstian values of e.m.f.s (see 3.1.1 and Table A.1), representing pH values at selected temperatures through a high value series resistor representative of pH sensors.

The simulator comprises a stepped voltage source followed by a selectable series resistor.

The network is such that output voltage steps represent multiples, and may provide sub-multiples, of e.m.f. representing unit pH steps for selectable temperatures. The resistance of the voltage divider network should not exceed 10 k Ω and the selectable series resistor should be 1 000M Ω ($\pm 10\%$).

3.2 Symbols

a_{H^+} = hydrogen ion activity

pH = pH of the solution measured at temperature t

pH(S_1) = pH of the first reference buffer solution at temperature t

pH(S_2) = pH of the second reference buffer solution at temperature t