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INTERNATIONAL STANDARD

NORME INTERNATIONALE

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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EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS –

Part 2: pH value

FOREWORD

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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.

This bilingual version (2012-12) corresponds to the monolingual English version, published in 2003-01.

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 French version of this standard has not been voted upon.

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*.

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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- withdrawn;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:

Reference electrode I Sample I pH electrode *E*

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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 I Buffer (S_1) I 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:

$$\mathrm{pH} = \mathrm{pH}(S_1) - \frac{E - E(S_1)}{k} \tag{1}$$

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:

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

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:

$$p\mathrm{H} = \mathrm{pH}(S_1) - \frac{[E - E(S_1)] \cdot [\mathrm{pH}(S_1) - \mathrm{pH}(S_2)]}{E(S_2) - E(S_1)} \tag{3}$$

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.

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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 kΩ and the selectable series resistor should be 1 000MΩ (±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*

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pH_i = pH at the isopotential point

E = e.m.f. in the measured sample at temperature t

$E(S_1)$ = e.m.f. in the first reference buffer solution at temperature t

$E(S_2)$ = e.m.f. in the second reference buffer solution at temperature t

E_i = e.m.f. at the isopotential point

F = the Faraday constant

R = the molar gas constant

t = temperature in degrees celsius

T = the temperature in kelvin of sample

k = the theoretical, Nernstian, slope of the electrode pair at temperature t

$k^{/}$ = the practical slope of the electrode pair at temperature t

4 Procedure for specification

See Clause 5 of IEC 60746-1, plus the following:

NOTE Uncertainties and uncertainty limits should be stated in pH values.

4.1 Additional statements on sensor units and analyzers

4.1.1 Type of sensor unit (i.e., flow-through or insertion unit).

4.1.2 Sensor unit dimensions, including mounting and connections.

4.2 Additional statements on electronic units

4.2.1 Number of digits and size of display, or for analogue instruments, scale width.

4.2.2 Output signal/signals, if adjustable, whether isolated from input and/or ground (earth) and permitted output load.

4.2.3 Temperature compensation range, compensator type and maximum permitted resistance of compensator plus connection cable; if only manual compensation available, it should be stated.

4.2.4 Percentage theoretical slope adjustment.

4.2.5 Zero point pH adjustment if provided and sensor pair zero point pH acceptance range.

4.2.6 Isopotential pH, pH_i, and adjustment, if provided.

4.2.7 Range of sample pH temperature coefficient adjustment, if provided.

4.2.8 Maximum allowable common mode input voltage.

4.2.9 If preamplifier may be separately mounted.

4.2.10 Input resistance

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4.3 Statements on sensors

4.3.1 General

4.3.1.1 Dimensions, including as appropriate, attached cable and/or connector type.

4.3.1.2 Rated temperature range.

4.3.1.3 Suitability of sensor pair for specific applications, for example, acidic fluoride samples, low conductivity and natural waters.

NOTE Combined sensors incorporating pH and reference electrodes are common, they may also include a temperature compensator.

4.3.2 Reference electrodes

4.3.2.1 Type of reference electrode, whether single or double junction variety and if sealed, gelled or refillable.

4.3.2.2 Reference electrolyte composition.

4.3.2.3 Type of junction between reference electrolyte or interposed bridge solution and sample.

4.3.2.4 If refillable, volume of reservoir and flow rate under stated hydrostatic pressure.

4.3.2.5 Nominal resistance at 25 °C.

4.3.3 pH sensor

4.3.3.1 Type, i.e., glass electrode, isfet or other.

NOTE For isfet sensor, state if preamplifier is available permitting its use with a conventional pH meter.

4.3.3.2 Zero point pH and isopotential pH, pH_i , with stated reference electrode.

4.3.3.3 Rated pH range.

4.3.3.4 Nominal sodium error at 25 °C in, for example, 1 M Na^+ solution at a stated pH in the upper region of the rated pH range.

4.3.3.5 Nominal resistance at 25 °C.

4.3.4 Temperature compensator

Type of compensator (for example, Pt 100).

4.3.5 Auxiliary devices for sensor unit

For example, devices for cleaning, pressurization of reference electrolyte.

4.3.5.1 Required power supply and consumption; compressed air pressure and consumption.

4.3.5.2 Volume and consumption of, for example, cleaning solutions.

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5 Recommended standard values and ranges of influence quantities affecting the performance of electronic units

See Annex A of IEC 60746-1.

6 Verification of values

See Clause 6 of IEC 6046-1, plus the following:

6.1 General aspects

6.1.1 Glass electrodes shall be conditioned according to the manufacturer's instructions. At least 12 h hydration in a neutral or mildly acidic buffer solution shall be allowed for initial equilibration of new electrodes.

6.1.2 Reference pH buffer solutions shall be used for all tests unless otherwise agreed upon with the manufacturer (see 3.5 of IEC 60746-1 and Annex B) .

NOTE IUPAC recommended reference buffer solutions are tabulated in Annex B. Other reference pH buffer solutions may be used .

6.1.3 Test solutions shall be applied in a manner suited to the sensor unit.

6.1.3.1 Flow-through sensor units

Solutions shall be applied at a flow rate within the manufacturer's rated range.

6.1.3.2 Insertion sensor units

For measurements with more than one solution, unless otherwise indicated, the electrode pair (sensor unit) shall be rinsed with deionized water, thereafter pre-rinsing with the new solution prior to immersion. It is recommended that measurements shall be made in continuously stirred solutions to ensure homogeneity.

6.2 Test procedures for electronic units

Prior to testing the analyzer, the electronic unit shall be separately tested with a simulator such as that described in 3.1.12 and using either manual temperature control or a suitable resistor connected to the temperature compensator input.

6.2.1 pH scaling

If adjustable, set the isopotential control to the zero point pH, usually both are pH 7, and, if provided, cancel or adjust the sample pH temperature compensation to zero. If manually adjustable, set the percentage slope control to 100%. Adjust the manual or simulated temperature to 25°C or other reference temperature. Connect a simulator and check the scaling throughout pH 0 to pH 14 or the test pH range. At the scale length extremes, switch-in the series high resistance simulating that of the glass electrode as a check of the instrument's input impedance, an immediate transient should rapidly dissipate. Repeat the procedure for other temperatures within the test range (see Table A.1).

With the simulator, impose a lower percentage slope output (for example, at 25 °C for 90 % slope, 53,24 mV per pH unit) at 25 °C or other reference temperature to assess the percentage slope facility.

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6.2.2 Isopotential pH, pH_i

The electrode terminals, including solution earth if applicable, are shorted and the temperature set to 25°C, either manually or with a suitable variable resistance[1]. The display will indicate the zero point, usually pH 7 and identical to the isopotential pH, pH_i. Change the temperature setting from 0° to 50°C, ideally there will be no display variation.

6.2.3 Temperature compensation

Connect a simulator and adjust the temperature control to 25°C. Apply the appropriate simulated pH values for pH 0 and pH 14, or the test pH span. Repeat the procedure for other temperatures within the test temperature range.

NOTE For instruments with manually adjustable buffer control, repeat the test given in 6.2.2 before performing this test then readjust the buffer control so that no discernible variation is observed on repeating the test.

6.3 Test procedures for sensor units

6.3.1 Zero point pH

Standardize the analyzer in accordance with the manufacturer's instructions. If the instrument does not incorporate zero point pH registration, short the sensor inputs and the zero point pH of the electrode pair is displayed.

6.3.2 Percentage theoretical slope, *PTS*

$$PTS = \frac{100\ \Delta \mathrm{pH}_{\mathrm{observed}}}{\Delta \mathrm{pH}_{\mathrm{actual}}}$$

Standardize the analyzer in accordance with the manufacturer's instructions. Generally, two buffer solutions are required and the PTS of the electrode pair is registered. Alternatively, with the sensors in a buffer solution at about pH 4 and the percentage slope control, if fitted, set at 100 %, set the display to the appropriate value. Replace the buffer solution with a buffer solution at about pH 9 or pH 10. For those instruments with PTS adjustment, adjust to the appropriate pH value. For those instruments without PTS control, it may be calculated from the ratio of observed to actual pH buffer values by the above equation.

See also 3.1.2 for instruments with manually adjustable buffer control.

6.3.3 Isopotential pH , pH_i

For this test, the electronic unit is switched to voltage mode.

The e.m.f.s of the electrode pair in two buffer solutions, preferably bracketing the nominal isopotential pH, at two or more temperatures at least 20 °C apart. Plot the e.m.f.s against pH, the intersection point is the isopotential pH, pH_i, of the electrode pair.

6.4 Test procedures for analyzers

For applications where these tests are inappropriate, additional procedures may be agreed upon with the manufacturer.

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1 For instruments with manually adjustable buffer control, set the display to the isopotential point, which may be adjustable.

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