

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*



Reference number
IEC 60746-2:2003(E)

Publication numbering

As from 1 January 1997 all IEC publications are issued with a designation in the 60000 series. For example, IEC 34-1 is now referred to as IEC 60034-1.

Consolidated editions

The IEC is now publishing consolidated versions of its publications. For example, edition numbers 1.0, 1.1 and 1.2 refer, respectively, to the base publication, the base publication incorporating amendment 1 and the base publication incorporating amendments 1 and 2.

Further information on IEC publications

The technical content of IEC publications is kept under constant review by the IEC, thus ensuring that the content reflects current technology. Information relating to this publication, including its validity, is available in the IEC Catalogue of publications (see below) in addition to new editions, amendments and corrigenda. Information on the subjects under consideration and work in progress undertaken by the technical committee which has prepared this publication, as well as the list of publications issued, is also available from the following:

- **IEC Web Site (www.iec.ch)**
- **Catalogue of IEC publications**
The on-line catalogue on the IEC web site (http://www.iec.ch/searchpub/cur_fut.htm) enables you to search by a variety of criteria including text searches, technical committees and date of publication. On-line information is also available on recently issued publications, withdrawn and replaced publications, as well as corrigenda.
- **IEC Just Published**
This summary of recently issued publications (http://www.iec.ch/online_news/justpub/jp_entry.htm) is also available by email. Please contact the Customer Service Centre (see below) for further information.
- **Customer Service Centre**
If you have any questions regarding this publication or need further assistance, please contact the Customer Service Centre:

Email: custserv@iec.ch
Tel: +41 22 919 02 11
Fax: +41 22 919 03 00

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 2003 — Copyright - all rights reserved

No part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

International Electrotechnical Commission, 3, rue de Varembe, PO Box 131, CH-1211 Geneva 20, Switzerland
Telephone: +41 22 919 02 11 Telefax: +41 22 919 03 00 E-mail: inmail@iec.ch Web: www.iec.ch



Commission Electrotechnique Internationale
International Electrotechnical Commission
Международная Электротехническая Комиссия

PRICE CODE

S

For price, see current catalogue

CONTENTS

FOREWORD	4
1 Scope	6
2 Normative reference	6
3 Definitions	6
4 Procedure for specification	8
4.1 Additional statements on sensor units and analyzers	9
4.2 Additional statements on electronic units	9
4.3 Statements on sensors	10
4.3.1 General	10
4.3.2 Reference electrodes	10
4.3.3 pH sensor	10
4.3.4 Temperature compensator	10
4.3.5 Auxiliary devices for sensor unit	10
5 Recommended standard values and ranges of influence quantities affecting the performance of electronic units	11
6 Verification of values	11
6.1 General aspects	11
6.2 Test procedures for electronic units	11
6.2.1 pH scaling	11
6.2.2 Isopotential pH, pH_i	12
6.2.3 Temperature compensation	12
6.3 Test procedures for sensor units	12
6.3.1 Zero point pH	12
6.3.2 Percentage theoretical slope, <i>PTS</i>	12
6.3.3 Isopotential pH, pH_i	12
6.4 Test procedures for analyzers	12
6.4.1 Intrinsic uncertainty	13
6.4.2 Linearity uncertainty	13
6.4.3 Repeatability	13
6.4.4 Output fluctuation	13
6.4.5 Warm-up time	13
6.4.6 Drift	13
6.4.7 Response times	13
6.4.8 Sample temperature	13
6.4.9 Primary influence quantities	13
Bibliography	21
Annex A (informative)	15
Annex B (informative) Reference buffer solutions: pH as a function of temperature	16
Annex C (normative) Alternative procedures for measuring response times: delay (T_{10}), rise (fall) (T_r , T_f) and 90% (T_{90}) times	19

Figure C.1 – Relation between T_{10} , T_r (T_f) and T_{90}19

Table A.1 – Values of the slope factor, $k = 2,3026 R.T/F$ 15

Table B.1 – Values of reference pH buffer solutions at various temperatures17

Table B.2 – Composition of reference pH buffer solutions18

INTERNATIONAL ELECTROTECHNICAL COMMISSION

**EXPRESSION OF PERFORMANCE OF
ELECTROCHEMICAL ANALYZERS –****Part 2: pH value**

FOREWORD

- 1) The IEC (International Electrotechnical Commission) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of the IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, the IEC publishes International Standards. Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. The IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.
- 2) The formal decisions or agreements of the IEC on technical matters express, as nearly as possible, an international consensus of opinion on the relevant subjects since each technical committee has representation from all interested National Committees.
- 3) The documents produced have the form of recommendations for international use and are published in the form of standards, technical specifications, technical reports or guides and they are accepted by the National Committees in that sense.
- 4) In order to promote international unification, IEC National Committees undertake to apply IEC International Standards transparently to the maximum extent possible in their national and regional standards. Any divergence between the IEC Standard and the corresponding national or regional standard shall be clearly indicated in the latter.
- 5) The IEC provides no marking procedure to indicate its approval and cannot be rendered responsible for any equipment declared to be in conformity with one of its standards.
- 6) Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. The IEC shall not be held responsible for identifying any or all such patent rights.

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.

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 | Sample | pH electrode E

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:

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

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

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

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.

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.

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 resistance¹. 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

$$PTS = \frac{100 \Delta pH_{\text{observed}}}{\Delta pH_{\text{actual}}}$$

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.

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

6.4.1 Intrinsic uncertainty**6.4.2 Linearity uncertainty**

Dependent upon the pH test range, this test procedure may have to be performed with fewer than five test solutions (see 6.2.2 of IEC 60746-1).

6.4.3 Repeatability**6.4.4 Output fluctuation****6.4.5 Warm-up time****6.4.6 Drift**

NOTE Drift is usually reported as a linear regression in two ways, short term over a period in the range 1 h to 24h and for a longer period in the range of 30 days to 100 days.

6.4.7 Response times

Procedures are given in Annex C, where Procedure A is the preferred and for flow-through sensor units, the only appropriate method.

6.4.8 Sample temperature

Errors caused by the variation of sample temperature shall be determined at two points in the measurement range near the lower and upper limits. Measurements shall be made at the reference sample temperature, then at the lowest temperature and repeated at the highest temperature of the test range.

NOTE The pH of solutions vary with temperature from approximately $(-0,04 \text{ to } +0,01) \text{ pH}^{\circ}\text{C}^{-1}$. Some electronic units incorporate solution temperature coefficient compensation..

6.4.9 Primary influence quantities

Response to the following influence quantities will generally need to be determined using test solutions near the upper and lower limits of the range. Influence quantities shall first be applied at the reference value, then near the lower and upper rated values. The final measurement shall be made when the quantity is returned to the reference value.

Variation in electrical supply characteristics usually affect the electronic unit only and may be tested with only one solution at the mid point of the span. These tests may be carried out on the electronics unit alone using a simulator.

- Vibration
- Supply voltage
- a.c. supply frequency or,
- d.c. supply ripple and impedance
- Electromagnetic compatibility
- Ambient temperature
- Humidity
- Sample flow-rate
- Sample pressure
- Sample outlet pressure

NOTE Sample pressure variation may affect the reference electrode. Pressure change results in an immediate offset, the magnitude a function of both the differential pressure across the liquid junction and the latter's nature. With non-refillable and gel-filled electrodes, the offset quickly dissipates. For reservoir-fed electrodes with pressure

equilibration between the reservoir and the sample line, the effect is eliminated: without such equilibration the offset will persist.

Additional influence quantities which may require verification are listed in IEC 60746-1.

Annex A

(informative)

Table A.1 – Values of the slope factor, $k = 2,3026 R.T/F$

t °C	k mV	t °C	k mV
0	54,199	50	64,120
5	55,191	55	65,112
10	56,183	60	66,104
15	57,175	65	67,096
20	58,167	70	68,088
25	59,159	75	69,081
30	60,152	80	70,073
35	61,144	85	71,065
40	62,136	90	72,057
45	63,128	95	73,049
$R = 8,314\ 41\ \text{J.K}^{-1}.\text{mol}^{-1}$ $F = 96\ 493,1\ \text{C.mol}^{-1}$ $T = \text{temperature in kelvin}$			

Annex B (informative)

Reference buffer solutions: pH as a function of temperature²

Reference buffer solution data to 50 °C are selected from the IUPAC 2002 *Recommendations for the measurement of pH* [1]³.

Data for higher temperatures are from [2] .

Values were determined in cells without liquid junction.

Buffers and solutions A and J are useful at low and high pH, however, because of liquid junction errors, should not be used when measurements are made within the pH 3 to pH 10 range.

Other reference buffer solutions may be used for calibration and test solutions.

NOTE 1 For highest accuracy, solutions may be prepared with chemicals certified by a national metrological institution

NOTE 2 The IUPAC 2002 *Recommendations* replace those of 1985 and form the basis on which to provide traceability to SI that must include consideration of all uncertainties of pH measurement [1].

² Values are presented in Table B.1 and compositions in Table B.2.

³ Numbers in square brackets refer to the bibliography.

Table B.1 – Values of reference pH buffer solutions at various temperatures

Buffer	0 °C	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	37 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	95 °C
A ²	1,67	1,67	1,67	1,67	1,68	1,68	1,68	1,68	1,69	1,69	1,71	1,72	1,74	1,77	1,75	1,81
B ¹	--	--	--	--	--	3,557	3,552	3,549	3,548	3,547	3,549	3,55	3,57	3,60	3,63	3,65
C ¹	4,000	3,998	3,997	3,998	4,000	4,005	4,011	4,018	4,022	4,027	4,050	4,06	4,12	4,16	4,21	4,24
D ¹	6,984	6,951	6,923	6,900	6,881	6,865	6,853	6,844	6,841	6,838	6,833	6,84	6,85	6,86	6,88	6,89
E ¹	7,534	7,500	7,472	7,448	7,429	7,413	7,400	7,389	7,386	7,380	7,367	--	--	--	--	--
F ²	8,47	8,30	8,14	7,99	7,84	7,70	7,56	7,43	7,38	7,31	7,07	--	--	--	--	--
G ²	9,51	9,43	9,36	9,30	9,25	9,19	9,15	--	9,09	9,07	9,01	8,93	8,90	8,88	8,84	8,89
H ¹	9,464	9,395	9,332	9,276	9,225	9,180	9,139	9,102	9,088	9,068	9,011	8,97	8,93	8,91	8,90	8,89
I ¹	10,317	10,245	10,179	10,118	10,062	10,012	9,966	9,926	9,910	9,889	9,828	9,75	9,73	9,73	9,75	9,77
J ²	13,42	13,21	13,00	12,81	12,63	12,45	12,29	12,13	12,07	11,98	11,71	11,45	--	--	--	--
¹ Primary pH (PS) standard , 0° – 50° C [1] . ² Secondary pH (SS) standard , 0° – 50° C [1] .																

Table B.2 – Composition of reference pH buffer solutions

Buffer Solution	Substance	Molecular formula	Molality mol. kg ⁻¹	Mass g.dm ⁻³
A	Potassium tetroxalate	KH ₃ C ₄ O ₈ .2H ₂ O	0,05	12,620
B	Potassium hydrogen tartrate	KHC ₄ H ₄ O ₆	Saturated at 25°C	6,4
C	Potassium hydrogen phthalate	KHC ₈ H ₄ O ₄	0,05	10,12
D	Disodium hydrogen phosphate	Na ₂ HPO ₄	0,025	3,533
	+ Potassium dihydrogen phosphate	KH ₂ PO ₄	0,025	3,388
E	Disodium hydrogen phosphate	Na ₂ HPO ₄	0,030 43	4,302
	+ Potassium dihydrogen phosphate	KH ₂ PO ₄	0,008 69	1,179
F	Tris [†]	(CH ₂ OH) ₃ CNH ₂	0,016 67	1,999
	+ Tris hydrochloride	(CH ₂ OH) ₃ CNH ₂ .HCl	0,05	7,800
G	Disodium tetraborate	Na ₂ B ₄ O ₇ .10H ₂ O	0,05	19,012
H	Disodium tetraborate	Na ₂ B ₄ O ₇ .10H ₂ O	0,01	3,806
I	Sodium hydrogen carbonate	NaHCO ₃	0,025	2,092
	+ Sodium carbonate	Na ₂ CO ₃	0,025	2,640
J	Calcium hydroxide	Ca (OH) ₂	Saturated at 25 °C	1,5

[†] tris (hydroxymethyl) aminomethane

NOTE All reagents shall be of analytical grade and the conductivity of the water shall be no greater than 2µS cm⁻¹ (at 25°C).

Annex C (normative)

Alternative procedures for measuring response times : delay (T_{10}), rise (fall) (T_r , T_f) and 90% (T_{90}) times

C.1 Procedure A

A recorder is connected to the output terminals of the analyzer. The sensor unit is placed in a flow-through cell (as similar as possible to that cell used in the application) and equipped with a two-way stopcock to supply alternately reference buffer solutions with low and high pH values. A reference buffer solution close to the minimum rated pH value is supplied until a constant reading on the recorder is obtained, then the two-way stopcock is switched to supply a reference buffer solution close to the maximum rated pH value and a mark made on the recorder chart. The maximum pH buffer solution is supplied until a constant reading is obtained. The stopcock is switched back to the minimum pH buffer solution and a second mark is made on the recorder chart. Again, the minimum pH buffer solution is supplied until a constant reading is obtained.

The flow rate of the solutions may be adjusted to the maximum specified by the manufacturer for the analyzer. The temperature of the solutions and sensor unit shall be constant within ± 1 °C and shall be reported with other results.

The values for delay time (T_{10}) and 90% time (T_{90}), for both increasing and decreasing step changes, rise time (T_r) and fall time (T_f) are determined from the chart speed. The larger of the two delay, rise or fall and 90% times are reported.

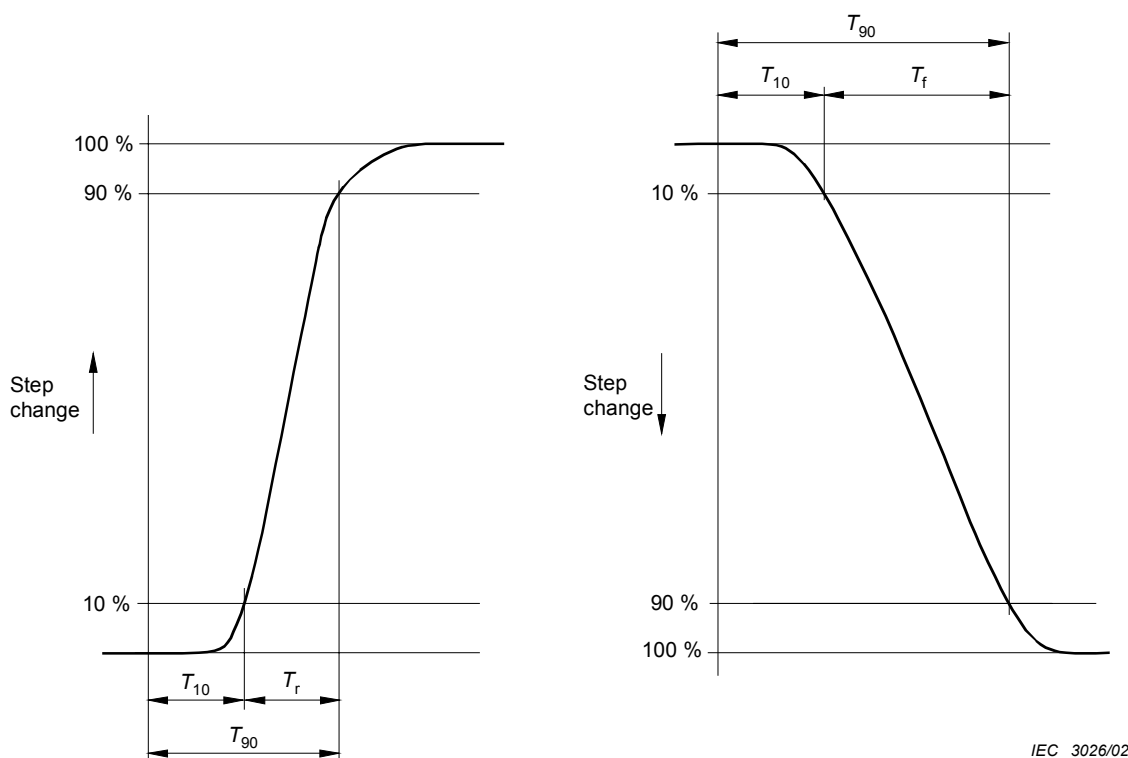


Figure C.1 – Relation between T_{10} , T_r (T_f) and T_{90}

IEC 3026/02

C.2 Procedure B

Similar to that described in C.1, except that the sensor unit is immersed alternately in two different tanks, one containing a stirred buffer solution close to the minimum rated pH value and the other containing a stirred buffer solution close to the maximum rated pH value. When transferring the sensor unit from one tank to the other, the sensor unit is shaken, not wiped or rinsed. The sensor unit is left in the tanks until constant readings are obtained.

Bibliography

- [1] Buck, R.P., Rondinini, S., Covington, A.K., Baucke, F.G.K., Camoes, M.F., Milton, M.J.T., Mussini, T., Naumann, R., Pratt, K.W., Spitzer, P., Wilson, G.S., *Recommendations for the measurement of pH*, J. Pure. Appl. Chem., 2002, 74, 2169-2200.
 - [2] Bates, R.G., *Determination of pH*, 2nd ed. J. Wiley, New York, 1973.
-



Standards Survey

The IEC would like to offer you the best quality standards possible. To make sure that we continue to meet your needs, your feedback is essential. Would you please take a minute to answer the questions overleaf and fax them to us at +41 22 919 03 00 or mail them to the address below. Thank you!

Customer Service Centre (CSC)

International Electrotechnical Commission

3, rue de Varembe
1211 Genève 20
Switzerland

or

Fax to: **IEC/CSC** at +41 22 919 03 00

Thank you for your contribution to the standards-making process.

A Prioritaire

Nicht frankieren
Ne pas affranchir



Non affrancare
No stamp required

RÉPONSE PAYÉE

SUISSE

Customer Service Centre (CSC)
International Electrotechnical Commission
3, rue de Varembe
1211 GENEVA 20
Switzerland



Q1 Please report on **ONE STANDARD** and **ONE STANDARD ONLY**. Enter the exact number of the standard: (e.g. 60601-1-1)

.....

Q2 Please tell us in what capacity(ies) you bought the standard (tick all that apply). I am the/a:

- purchasing agent ☐
 librarian ☐
 researcher ☐
 design engineer ☐
 safety engineer ☐
 testing engineer ☐
 marketing specialist ☐
 other.....

Q3 I work for/in/as a:
(tick all that apply)

- manufacturing ☐
 consultant ☐
 government ☐
 test/certification facility ☐
 public utility ☐
 education ☐
 military ☐
 other.....

Q4 This standard will be used for:
(tick all that apply)

- general reference ☐
 product research ☐
 product design/development ☐
 specifications ☐
 tenders ☐
 quality assessment ☐
 certification ☐
 technical documentation ☐
 thesis ☐
 manufacturing ☐
 other.....

Q5 This standard meets my needs:
(tick one)

- not at all ☐
 nearly ☐
 fairly well ☐
 exactly ☐

Q6 If you ticked NOT AT ALL in Question 5 the reason is: (tick all that apply)

- standard is out of date ☐
 standard is incomplete ☐
 standard is too academic ☐
 standard is too superficial ☐
 title is misleading ☐
 I made the wrong choice ☐
 other

Q7 Please assess the standard in the following categories, using the numbers:

- (1) unacceptable,
 (2) below average,
 (3) average,
 (4) above average,
 (5) exceptional,
 (6) not applicable

- timeliness.....
 quality of writing.....
 technical contents.....
 logic of arrangement of contents
 tables, charts, graphs, figures.....
 other

Q8 I read/use the: (tick one)

- French text only ☐
 English text only ☐
 both English and French texts ☐

Q9 Please share any comment on any aspect of the IEC that you would like us to know:

.....



ISBN 2-8318-6765-7



ICS 71.040; 19.040
