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pH measurements in difficult media – Definitions, standards and procedures

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pH measurements in difficult media – Definitions, standards and procedures

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pH MEASUREMENTS IN DIFFICULT MEDIA – DEFINITIONS, STANDARDS AND PROCEDURES

FOREWORD

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IEC 62434, which is a technical report, has been prepared by subcommittee 65D: Analyzing equipment, of IEC technical committee 65: Industrial-process measurement and control.

The text of this technical report is based on the following documents:

Enquiry draft	Report on voting
65D/121/DTR	65D/124/RVC

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

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 the maintenance result date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

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- withdrawn,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

A bilingual version of this Technical report may be issued at a later date.

pH MEASUREMENTS IN DIFFICULT MEDIA – DEFINITIONS, STANDARDS AND PROCEDURES

1 Scope and object

This Technical Report concerns analyzers, sensor units and electronic units used for the determination of pH in non-aqueous solvents and aqueous organic solvent mixtures using glass electrodes. IEC 60746-1 includes further definition of the scope and provides for the general aspects of all electrochemical analyzers, including pH. It is worthwhile to remind that IEC 60746-2 contains specifications for simulators used for testing pH electronic units.

This technical report specifies the terminology, definitions, methodology, requirements for statements by manufacturers and performance tests for analyzers, sensor units and electronic units used for the determination of pH value in non-aqueous and aqueous-organic solvent mixtures.

2 Normative references

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, *Expression of performance of electrochemical analyzers – Part 1: General*

IEC 60746-2, *Expression of performance of electrochemical analyzers – Part 2: pH value*

3 General principles

3.1 Terms and definitions

The required definitions will be given following on the order of appearance of the relevant physical quantities in the text, and they comply with the pertinent IUPAC documents [1,2] [1] and IEC 60746-2.

3.2 Symbols

The meaning of each symbol used here is given immediately after its first appearance in the relevant equation and it is conform to the pertinent IUPAC documents [1,2] and IEC 60746-2.

3.3 pH value

3.3.1 General

A measure of the conventional hydrogen ion activity $a_{\mathrm{H+}}$ in solution given by the expression

$$\mathrm{pH} = -\log a_{\mathrm{H+}} = -\log(m_{\mathrm{H+}}\,\gamma_{\mathrm{H+}}) \tag{1}$$

where $\gamma_{\mathrm{H+}}$ is the activity coefficient of the H^+ ion at the molality $m_{\mathrm{H+}}$ (moles of H^+ per kg of solvent). pH is a dimensionless quantity; it is not correct to write the logarithm of a quantity other than a dimensionless number, and the full form of equation (1) is

---

[1] Numbers in square brackets refer to the bibliography.

$$\mathrm{pH} = -\log a_{\mathbf{H+}} = -\log(m_{\mathbf{H+}}\ \gamma_{\mathbf{H+}}/m^{\circ}) \qquad (2)$$

where m° = 1 mol kg^{-1} is the standard-state reference molality. This definition is in terms of the molal scale, which is that recommended by IUPAC for a key reason, i.e. the molality of a solution is temperature-independent, which saves much repetitive work of cell construction and filling. However, if one wants to treat pH in terms of the amount-of-substance concentration c (formerly "molarity") in mol dm^{-3}, the equation (2) would take the form

$$\mathrm{pH}_c = -\log(a_{\mathbf{H+}})_c = -\log(c_{\mathbf{H+}}\ y_{\mathbf{H+}}/c^{\circ}) \qquad (3)$$

where $y_{\mathbf{H+}}$ is the activity coefficient of H^+ at concentration $c_{\mathbf{H+}}$ (moles of H^+ per dm^3 of solvent). It is worthwhile to recall that pH and pH_c are interrelated by the equation

$$\mathrm{pH}_c = \mathrm{pH} - \log\,[\rho/(\mathrm{kg\ dm}^{-3})] \qquad (4)$$

where ρ is the relative density of the solvent.

Although equation (2), or alternatively (4), can be used to give an interpretation to pH values under certain limiting conditions, $a_{\mathbf{H+}}$ cannot be rigorously obtained by any method, for example from potential difference measurements, because it involves such a non-thermodynamic quantity as the single-H^+-ion activity coefficient $y_{\mathbf{H+}}$, and instead an operational definition is adopted in terms of pH values assigned to certain reference buffers (primary or secondary pH standards). The pH measurement is performed by measuring the potential difference (electromotive force) E_X between a pair of electrodes immersed in the sample at unknown pH_X in the (non-aqueous or aqueous-organic) solvent Z, according to the cell scheme:

Reference electrode in solvent Z	**Concentrated equitransferent salt bridge in solvent Z**	**Sample at unknown pH$_X$ in solvent Z**	**H$^+$–sensing electrode (hydrogen gas electrode, or glass electrode)**	(5)

and measuring the potential difference E_S with the same electrode pair, the same salt bridge of the same composition and solvent Z, and at the same temperature, in a reference buffer solution of known standard $\mathrm{pH}_{\mathrm{PS}}$ or $\mathrm{pH}_{\mathrm{SS}}$, according to:

Reference electrode in solvent Z	**Concentrated equitransferent salt bridge in solvent Z**	**Standard pH$_{\mathrm{PS}}$ or pH$_{\mathrm{SS}}$ in solvent Z**	**H$^+$–sensing electrode (hydrogen gas electrode, or glass electrode)**	(6)

E_X, E_S, etc. are all defined as the difference of the potential of the right-hand (glass electrode) minus the potential of the left-hand electrode (reference electrode). Considering the Nernstian expressions for E_X and E_S, the sought pH_X of the sample in question is given by:

$$\mathrm{pH}_\mathrm{X} = \mathrm{pH}_{\mathrm{SS}} - (E_X - E_S)/k + (E_{\mathrm{JX}} - E_{\mathrm{JS}})/k \qquad (7)$$

where k = 2,302 6 RT/F, and E_{JX} and E_{JS} are the liquid junction potentials (see 3.3.2) arising at the junctions between reference electrode and unknown pH_X and between reference electrode and the known standard $\mathrm{ph}_{\mathrm{PS}}$, respectively. The concentrated equitransferent salt bridge in solvent Z (see 3.6.5) duly minimizes E_{JX} and E_{JS}, so that their difference ($E_{\mathrm{JX}} - E_{\mathrm{JS}}$) (the so-called "residual liquid junction potential") can be ignored, and the following operational equation is now internationally endorsed for the determination of pH_X:

$$\mathrm{pH}_\mathrm{X} = \mathrm{pH}_{\mathrm{SS}} - (E_\mathrm{X} - E_\mathrm{S})/k \qquad (8)$$

At extreme acidities or alkalinities, or with high salinities (ionic strengths) of the sample, the residual liquid junction potential may be significant and requires careful consideration for the assessment of the accuracy level of the measured pH_X.

The cell diagrams (5) and (6), respectively, represent the well known “measure” and “calibration” configurations of the “pH operational cell”. Numerical values for k, the “Nernstian coefficient” or “theoretical slope factor”, at temperatures from (0 to 100) °C, are given in Annex A.

Upon aging, the glass electrodes show an irreversible decrease of the slope factor, which thus becomes the “practical slope factor” $k' < k$ and should consequently be accounted for in the operational equation (8). This is currently accomplished by the “bracketing standards procedure” (or “two standards calibration”). This requires use of two standards, one ($\mathrm{pH_{PS1}}$) below and one ($\mathrm{pH_{PS2}}$) above the expected $\mathrm{pH_X}$. The corresponding measurements of E_X, E_{S1}, and E_{S2}, are then combined to give the following equations:

$$k' = -(E_{S2} - E_{S1})/(\mathrm{pH_{S2}} - \mathrm{pH_{S1}}) \tag{9}$$

$$\mathrm{pH_X} = \mathrm{pH_{S1}} + (E_X - E_{S1})(\mathrm{pH_{S2}} - \mathrm{pH_{S1}})/(E_{S2} - E_{S1}) \tag{10}$$

3.3.2 Liquid junction potential

Electric potential difference arising across any junction between two electrolyte solutions of different insertion. This potential difference is, in current practice, minimized (even if by no means exactly) by insertion of a salt bridge (see 3.6.5). When the junction is between two solutions differing not only in the electrolyte composition, but also in the solvent (“heterosolvental junction”) the intervening liquid junction potential is composed of a *ionic* liquid junction potential (minimizable by insertion of an appropriate salt bridge – see 3.6.5) and a *solvental* liquid junction potential which can by no means be minimized and may amount to several tens of mV.

3.4 Standard reference buffer solutions (primary and secondary pH standards)

3.4.1 Reference buffer solution preparation

3.4.1.1 General

A reference buffer solution (pH standard) is prepared according to a specified formula, using recognized analytical-grade chemicals and solvents (non-aqueous or aqueous-organic) appropriately redistilled, if $\mathrm{pH_X}$ is required to not better than ±0,05. The pH value of reference buffer solutions may, because of the variation in the purity of available commercial chemicals, differ by as much ±0,01 from accepted values. For higher accuracy (for example to ±0,002), solutions may be prepared with chemicals that have been characterized and declared as Certified Reference Materials (CRM, see 3.4.1.4) by a national standards laboratory, and solvents (non-aqueous or aqueous-organic) characterized by the most severe procedures and tests (including conductivity, if applicable) of purification.

3.4.1.2 Primary standards ($\mathrm{pH_{PS}}$)

Certain substances which meet the criteria of:

a) preparation in highly pure state reproducibly, and availability as certified reference materials (see 3.4.1.4);

b) stability of solution over a reasonable period of time;

c) having low value of the residual liquid junction potential – see 3.3.2, shall be designated as *primary reference standards* ($\mathrm{pH_{PS}}$) in solution of specified concentration in the appropriate solvent Z.

The $\mathrm{pH_{PS}}$ values assigned to these primary standards are specifically derived from measurements on the following reversible cell (“Harned’s cell”):

Pt	**H_2 (gas, p = 101325 Pa)**	**$\mathrm{pH_{PS}}$ + KCl, in Z**	**AgCl**	**Ag**	**Pt**

(11)

whose structure (and that of the parallel cell (13)) is represented schematically in Figure 1. Best values of pH_{PS} for various standard buffer solutions in some 45 nonaqueous or aqueous-organic solvents at various temperatures are given in Annexes B, C and D, together with directions for proper preparation of the chemicals.

The potential difference E of cell (11), omitting to write the term $m° = 1\ \text{mol kg}^{-1}$ for convenience, is given by:

$$E = E° - k \log[m_{H+}\ m_{Cl-}\ \gamma_{H+}\gamma_{Cl-}] \tag{12}$$

where the standard potential difference $E°$ is derived separately from measurements on the cell (13):

Pt	**H_2 (gas, p = 101325Pa)**	**HCl (m), in Z**	**AgCl**	**Ag**	**Pt**

(13)

and calculated from equation (12) using $\gamma_{H+}\gamma C_{l}\text{-} = \gamma_{\pm}^2$ where $\gamma_{\pm}$ is the independently known mean ionic activity coefficient of HCl at molality m = 0,01 mol kg^{-1}. From equation (12) one gets:

$$pH = (E - E°)/k + \log(m_{Cl-}) + \log(\gamma_{Cl-}) \tag{14}$$

in which $\log(\gamma_{Cl-})$ is obtained from the IUPAC-endorsed Bates-Guggenheim equation (15) [1]:

$$\log(\gamma_{Cl-}) = -A_Z I^{1/2}/[1+1,5\ (I\ \varepsilon_W\rho_Z/\ \varepsilon_Z\rho_W)^{1/2}] \tag{15}$$

where I is the ionic strength of solution, A_Z is the classical Debye-Hückel constant appropriate to the (single or aqueous-organic) solvent Z, and ε and ρ are respectively permittivities and densities of the water (W) and the solvent Z as indicated by the subscripts. (If the solvent Z is water itself, equation (15) would reduce to $\log(\gamma_{Cl-}) = -A_W I^{1/2}/[1+1,5\ I^{1/2}]$, which is the form of Bates-Guggenheim equation used for the pH standardization in pure water medium [1]). The pH values obtained from (14) are found to vary slightly with m_{Cl-} due to the ionic interactions between the pH_{PS} buffer and KCl in the mixed electrolyte in cell (11). Therefore these pH values are plotted against m_{Cl-}, and the intercept at $m_{Cl-} = 0$ is finally recognized as primary standard pH_{PS}.

Values of the required ancillary quantities A_Z, $\gamma_{\pm}$, and $E°$ are available (see [1] and literature cited therein).

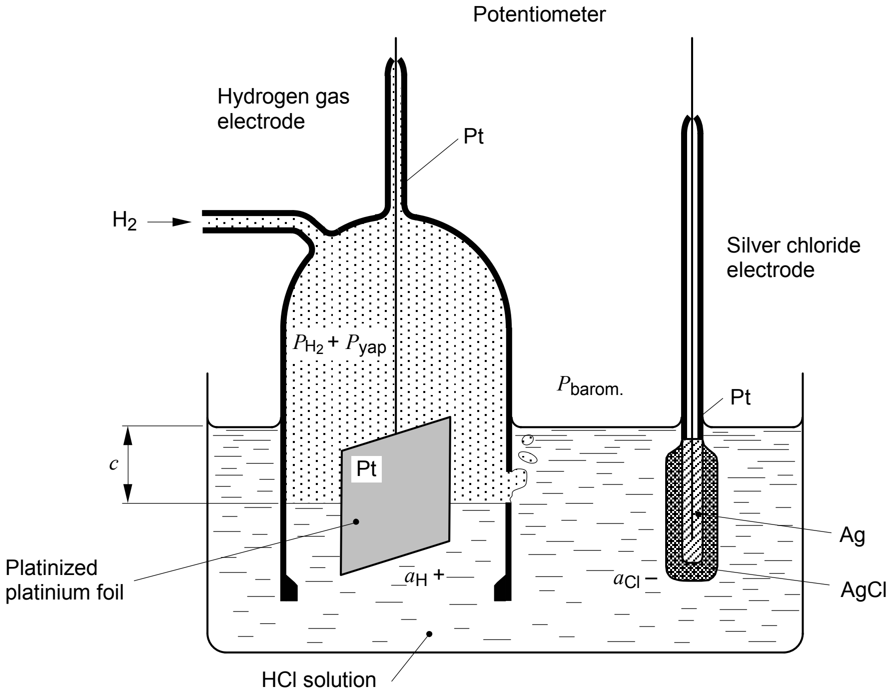

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Figure 1 – Schematic structure of the hydrogen gas electrode and of the AgCl electrode forming the cell (13)

3.4.1.3 Secondary standards (pH_{SS})

Certain substances which meet the criteria of:

a) preparation in highly pure state reproducibly;

b) stability of solution over a reasonable period of time, shall be designated as *secondary standards* (pH_{SS}) in solution of specified concentration in the general (non-aqueous or aqueous-organic) solvent Z.

The values of pH_{SS} can be assigned by comparison with the pH_{PS} values in cells with liquid junction of the type

Pt	**H_2**	**pH_{PS} in Z ¦¦ Salt bridge in Z ¦¦ pH_{SS} in Z**	**H_2**	**Pt**	(16)

where pH_{SS} may either have the same nominal composition of pH_{PS} or be of quite different composition, and it is desirable that the junctions be formed within capillary tubes so that the geometry of the liquid junction is well defined and the potential values reproducible. If E_{16} denotes the potential difference of cell (16), and the liquid junction potentials can be safely ignored, then the values of pH_{SS} are given by

$$pH_{SS} = pH_{PS} - E_{16}/k \tag{17}$$

An alternative IUPAC-endorsed method of obtaining pH_{SS} makes use of a variant of cell (11) in which the glass electrode (which is simply a H^+-sensing membrane electrode, namely a non-thermodynamic electrode) replaces the H^+-reversible hydrogen-gas electrode:

Pt	**Glass electrode**	**pH_{SS} + KCl, in Z**	**AgCl**	**Ag**	**Pt**	(18)

thus obtaining a non-reversible cell, of potential difference E_{18}. The procedure of processing the E_{18} data is wholly analogous to that described by the equations (12) to (15) above. The procedure followed (that based on cell (16) or that based on cell (18)) should be stated in any case.

3.4.1.4 Certified reference materials

Selected chemicals which were certified by a national metrological institution. Certainly, in order for a particular buffer to be considered a primary buffer solution, it should be of the highest metrological quality, in accordance with the definition of a primary standard. Therefore, the best conditions would be that the primary and the secondary standard materials should be accompanied by certificates from national metrological institutes in order for them to be described as Certified Reference Materials (CRMs).

3.4.1.5 Storage of standard pH buffers in certain solvents

When stocks of pH_{PS} or pH_{SS} buffer solutions in alcohols, glycols and glycerols (and in their mixtures with water) have been prepared for long-duration service or conservation, it is recommended to store them at freezer temperatures (≈ –15 °C) to prevent any undesired esterification.

3.4.2 Measurement of pH_X - Choice of the standard reference solutions

Unlike in the case of the purely aqueous solutions, where there is abundance of primary and secondary standards, for the general (non-aqueous or aqueous-organic) solvent Z there are few or no standards, with the only exceptions of methanol+water and ethanol+water mixtures, in which it is evident that electrochemists have concentrated their efforts almost exclusively. In fact, for aqueous mixtures with 2-propanol, ethylene glycol, glycerol, methylcellosolve, acetonitrile, 1,4-dioxane, dimethylsulfoxide, ethylene carbonate, propylene carbonate, and formamide, for a total of some 40 mixed solvent systems, beside the pure deuterium oxide solvent (D_2O, see Annex C), there are available the pH_{PS} values for the 0,05 mol kg^{-1} potassium hydrogen phthalate buffer [3 to 7], as collected in Annex B, plus sparse pH_{PS} values for a handful of other buffers to be seen in Annex D. Secondary standard pH_{SS} values for the same buffers mentioned above are now available in tetrahydrofuran+water mixtures [8] (Annex E). This very poor availability of pH standards, for now at least, impairs the possibility of applying the bracketing standards procedure (equations (9) and (10)) to compensate for deficiencies in the electrodes and measuring systems. Clearly, acquisition and systematisation of pH_{PS} as well as pH_{SS} values is overdue and urgently required.

3.5 Widths of normal pH scales or normal pH ranges in the general solvents Z

3.5.1 General

Each solvent Z has a parameter of great concern for the pH domain: this is the temperature-dependent autoprotolysis constant K_Z, which expresses the ability of Z to self-ionize to release H^+ ions. It is precisely the negative logarithm of K_Z, symbolized as $pK_Z = -\log K_Z$, at 25 °C that conventionally defines the **width of normal pH scale** (or **normal pH range**) in each solvent Z [**9**]. Values of pK_Z for a number of nonaqueous or aqueous-organic solvents can be found in the *ad hoc* IUPAC document [**10**]. The **midscale point (neutral pH point)** is 0,5 pK_Z. It is well known that in water $pK_Z = 14$, so that the normal pH scale in aqueous medium is 14 units wide, and the neutral point is at pH 7. Instead, in acetonitrile $pK_Z = 28$, and the neutral point is at pH 14; see Figure 2. Thus there emerges the problem of intercomparing pH values measured in different solvents Z: this is strictly linked with the determination of the so-called **primary medium effect on the H^+ ion**, which is described below.

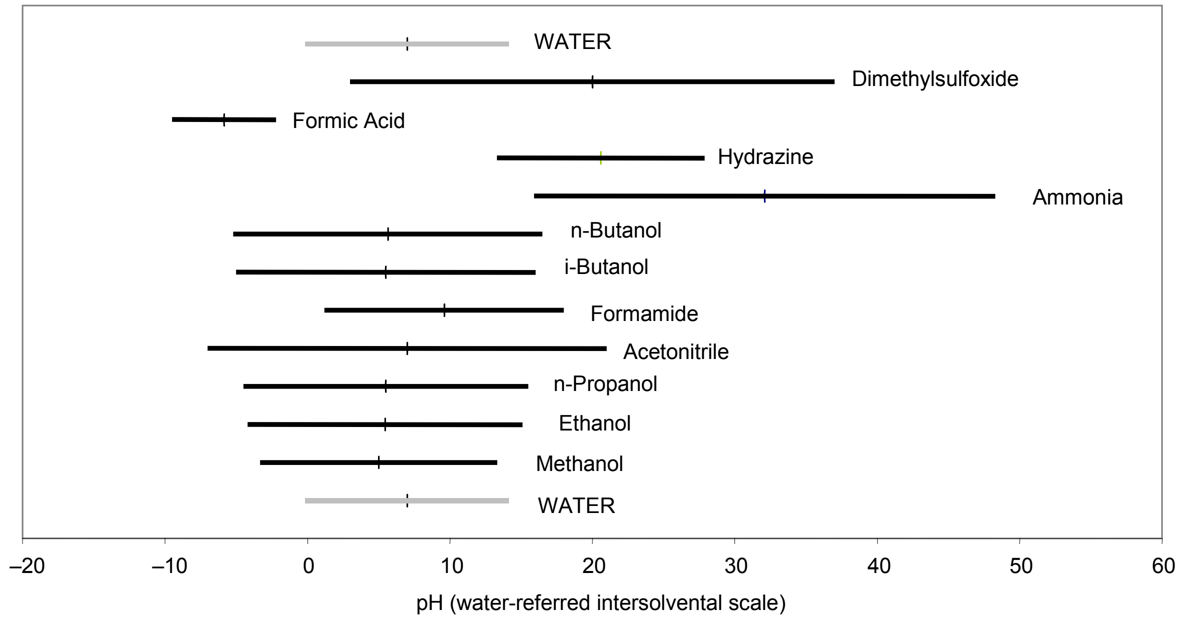

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Figure 2 – Intercomparing widths and relative positions of normal pH scales (with neutral points indicated by halving dots) in different solvents

3.5.2 Conditions for comparability of pH scales in different solvents Z with the aqueous pH scale: definition of an intersolvental scale of pH

Any pH_{PS} or pH_{SS} standard, and any pH value measured in solvent Z, is only valid for the pH scale in that solvent and are *not* physically comparable with pH_{PS} or pH_{SS} standards and any pH value measured in water. It can be shown [**9**] that, to make pH_Z (in solvent Z) physically comparable with pH_W (in water) on one **intersolvental pH scale**, pH_Z should be converted to $pH_{Z/W}$ as expressed by equation (20):

$$pH_{Z/W} = pH_Z - \log(\gamma_T) = pH_Z + [(E^\circ_H)_W - (E^\circ_H)_Z]/k \qquad (20)$$

where γ_T is the so-called "transfer activity coefficient" of H^+, or **primary medium effect upon H^+**, namely, $\log(\gamma_T)$ is a measure of the change of standard Gibbs free energy accompanying the transfer of the H^+ ion from water (W) to solvent Z. It is quantified in terms of the difference $[(E^\circ_H)_W - (E^\circ_H)_Z]$ of the standard **absolute** potential of the H^+–sensing electrode in W and Z, respectively. Since there cannot be any thermodynamically correct method of determining the above difference, recourse to extrathermodynamic methods or assumptions is unavoidable, and unfortunately there is remarkable discrepancy between the $\log(\gamma_T)$ values estimated by the various authors. Thus the conversion expressed by equation (20) is still belonging to the theoretical domain only, and to the users, each pH_Z scale is at this point not comparable with the aqueous pH_W scale. The situation depicted in Figure 2 represents the best overview available now but has only qualitative value.

3.5.3 Incorrect use of two-solvent cells for pH measurements

An improductive, but all too frequently tried, approach to obtaining a comparability of pH_Z with pH_W is that [see **11**] which is based on measuring the potential difference $(E_X)_Z$ of the cell (21):

Reference electrode in solvent Z	**Salt bridge in solvent Z**	**Sample at unknown pH_X in solvent Z**	**H^+–sensing electrode (hydrogen gas electrode, or glass electrode)**

(21)

the Nernstian expression of which is expressed by:

$$(E_X)_Z = U_Z - k\,(\mathrm{pH}_X)_Z + (E_{JX})_Z \tag{22}$$

after a deceptive “calibration” based on measuring the special potential difference $^*E_S$ of the two-solvent (“heterosolvental”) cell (23):

Reference electrode in solvent Z	**Salt bridge in solvent Z**	**Standard at known pH_{PS} in water**	**H^+–sensing electrode (hydrogen gas electrode, or glass electrode)**

which is expressed by

$$^*E_S = {}^*U - k\,(\mathrm{pH}_S)_W + {}^*E_{JS} \tag{23}$$

From equations (22) and (23), a new supposed “operational” equation is derived:

$$(\mathrm{pH}_X)_Z = (\mathrm{pH}_S)_W - [(E_X)_Z - {}^*E_S]/k \tag{24}$$

and relied upon as one ensuring pH_Z to be directly measurable and physically comparable with the aqueous standard $(\mathrm{pH}_S)_W$. However, subtraction of (23) from (22) to obtain (24) is illegitimate. In fact, U_Z and $^*U$ are quite different (and cannot be dropped in the difference) because of $(E^\circ_H)_W \neq (E^\circ_H)_Z$ and $(a_{H+})_W$ being not comparable with and $(a_{H+})_Z$; and the liquid junction potential $^*E_{JS}$ contains a *solvental* contribution not included in $(E_{JX})_Z$, so that they also cannot be dropped in the difference.

However, a heterosolvental cell configuration of the type:

Reference electrode in water	**Salt bridge in water**	**Various samples at unknown $(\mathrm{pH}_X)_Z$’s in *same* solvent Z**	**H^+–sensing electrode in same solvent Z**	(25)

whose potential difference can be expressed as:

$$^*E_X = {}^*U - k\,(\mathrm{pH}_X)_Z + {}^*E_{JX} \tag{26}$$

can be **correctly** applied to measure $(\mathrm{pH}_X)_Z$ variations, $\Delta(\mathrm{pH}_X)_Z$, among various samples **in the same solvent Z**. In fact, as shown by equation (26), $\Delta(\mathrm{pH}_X)_Z = \Delta^*E_X/k$, because the heterosolvental terms (i.e. the constant $^*U$ and the liquid junction potential $^*E_{JX}$) cancel out in the difference. However, if the cell (25) is switched from solvent Z to another, different solvent Z’ (while retaining the same aqueous reference electrode), the Δ(pHX)Z’ values observed in Z’ are **not** physically correlatable with the $\Delta(\mathrm{pH}_X)_Z$ values observed in Z, because the solvental part of the liquid junction potential $^*E_{JX}$ is changed.

3.6 Electrodes and operating conditions

3.6.1 pH sensor (pH glass electrode)

The most commonly used pH sensor is the glass electrode [9], other potentiometric sensors, for example, the antimony electrode are only 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.

3.6.2 Hydrogen gas electrode

This is a thin foil of platinum electrolytically coated with finely divided deposit of platinum or palladium metal, which catalyses the electrode reaction $H^+ + e = ½\ H_2$ in solution saturated with hydrogen gas [9,12], see schematic representation in Figure 1. This electrode, which does not lend itself to routine measurements, is the precision H^+-sensing electrode, whose use is mandatory for thermodynamic studies or determinations of pH standards (see above).

However, in certain non-aqueous solvents (for example acetonitrile, dimethylsulfoxide) the hydrogen electrode does not work properly and should be replaced by another appropriate H^{+}-sensing electrode, for example the quinhydrone electrode described in 3.6.3.

3.6.3 Quinhydrone electrode

This is a wire of noble metal (platinum or gold) placed in a solution to which a small amount ($\approx$ 0,1 g) of quinhydrone has been added to saturate the solution with equimolal amounts of quinone and hydroquinone [9,12]. The quinhydrone electrode can replace the hydrogen electrode in certain nonaqueous solvents (for example acetonitrile, dimethylsulfoxide) where the hydrogen gas electrode shows erratic behaviour, for the purpose of determination of pH standards. Under certain conditions (neutral or acidic pH, absence of strong oxidizing and reducing agents and of large concentrations of added salts) the quinhydrone electrode may also replace the glass electrode for routine pH measurements.

3.6.4 Reference electrode

This is an appropriate half-cell providing a stable potential at constant temperature [12] 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 salt-bridge solution.

3.6.5 Salt bridge

3.6.5.1 General

This is a concentrated solution of a binary electrolyte MX having cation M^{+} and anion X^{-} of equal mobility ("equitransferent concentrated bridge" in common terminology, with $M^{+} = K^{+}$, NH_4^{+}, Rb^{+}, Cs^{+}, and $X^{-} = Cl^{-}$, Br^{-}, I^{-}, NO_3^{-}) to be inserted between the internal filling solution of the reference electrode and the sample solution at pH_X (or the reference standard at pH_{PS}) under study, of course *in the same solvent* Z, in order to minimize the residual liquid junction potential error [9,12], a common practice first introduced by Guggenheim [9,12,20]. Most popular examples are: saturated KCl, RbCl, CVsCl, and NH_4Cl in water or in several water-rich aqueous-organic solvents. Whenever possible, for example in the cases of the alkali halides mentioned above, the salt bridge directly constitutes the internal filling solution of the appropriate halide-reversible second-kind reference electrode ("built-in salt bridge") thus simplifying the electrode design and function. When the solvent changes from pure water to an aqueous-organic mixture or a pure nonaqueous solvent, the equitransference properties of some of the above MX salts may be lost. For instance, changing from pure water to pure formamide, the only acceptably equitransferent salt bridge is NH_4Cl whereas the others fail, as was demonstrated by a recent systematic study [18]. The appropriateness and efficiency of the NH_4Cl bridge extends also over the other amides and N-alkylamides of extremely high permittivities, and also to such mixed solvents as water+alcohol, water+glycol, and water+acetonitrile. When the halide-based salt-bridge is chemically incompatible with certain ions (for example the Ag^{+}, Tl^{+} or Hg^{2+} cations) of the sample solution, the Li_2SO_4 salt bridge [19] in conjunction with a Hg_2SO_4 or a Pb_2SO_4-based reference electrode can be used in certain solvents [19]. In commercial reference electrodes, the pertinent salt bridge is incorporated in the electrode design.

3.6.5.2 Second bridge, or bridge solution (of a double-junction reference electrode)

Another (concentrated) solution of an inert binary electrolyte having cation and anion of equal mobility, optionally interposed between regular salt bridge 3.6.5.1 and both the sample pH_X and standard pH_{PS} solutions, when there arises a chemical incompatibility (see also 3.6.5.1). Of course, the second bridge should be in the same solvent of the salt bridge 3.6.5.1. As second bridges, KNO_3, NH_4NO_3, $RbNO_3$, $CsNO_3$, Li_2SO_4, or Lithium Acetate can be used in water, but extended research is still needed to ascertain if, like Li_2SO_4 [19], they were also appropriate to nonaqueous or aqueous-organic solvents.

4 Solvent media of applicability

pH standardization in non-aqueous solvents and aqueous-organic solvent mixtures [1] shows a number of features some of which are shared with the pH standardization in aqueous solutions (see [2] and IEC 60746-2). In fact:

a) While water, with its relative permittivity of ≈78 at 25 °C, is a typical ionizing solvent, organic solvents range from benzene and 1,4-dioxane with relative permittivities of ≈2 and no ionizing power to N-methylacetamide with relative permittivity of ≈182 and strong ionizing power. Within the above range, there are several tens of non-aqueous solvents very popular in the areas of industrial chemistry, analytical chemistry, engineering and corrosion (i.e. alcohols, glycols, glycerols, ethers, amides, ketones, nitriles, etc.); and, of course, there are several hundreds of binary aqueous-organic solvent mixtures which are as important. In reality, an almost unlimited domain exists.

b) It is necessary to define the width of the “normal pH scale” (or “normal pH range”) (see 3.4) in each (non-aqueous or mixed) solvent for obvious comparison purposes. For example, if the above normal range in water is 14 pH units wide, with the neutrality point (midscale) at pH 7, in acetonitrile such normal range embraces 28 pH units, with the neutrality point at pH 14 (which is, of course, absolutely not physically comparable with pH 14 in water); etc.

c) Once each normal pH scale in each (non-aqueous or mixed) solvent is defined, it would be desirable to fix the relative positions of these pH scales (with their appropriate acidic and alkaline ends) with ultimate reference to water (because of obvious and undisputable key role of water with respect to any other solvent, or solvent mixture of water itself) so as to constitute one “intersolvental” scale of pH which would provide physically interrelated and comparable pH data. A sketch of the situation is to be seen in Figure 2, and a description of the key features is given in 3.4.

d) It is indispensable to provide for as many primary pH standards, $\mathrm{pH}_{\mathrm{PS}}$, as necessary to cover the normal pH scale in each (non-aqueous or mixed) solvent, within the usual range of temperatures. However, such $\mathrm{pH}_{\mathrm{PS}}$ standards are only available for a limited number of solvents so far, even if systematic determinations of primary standards ($\mathrm{pH}_{\mathrm{PS}}$) as well as secondary standards ($\mathrm{pH}_{\mathrm{SS}}$) are being carried out with promising speed in specialised laboratories.

e) IUPAC (International Union of Pure and Applied Chemistry) has recently recommended criteria and procedures [1] for the determination of the above primary and secondary pH standards in non-aqueous solvents and aqueous-organic solvent mixtures of relative permittivities higher than about 25 to 30 in the temperature range (0 to 100) °C, namely, under conditions of negligible or no ionic association in the solutions. The above range comprises nearly all such popular, ionizing solvents such as alcohols, glycols, glycerols, amides, nitriles, and their mixtures with water. The IUPAC-endorsed, [3] primary standards $\mathrm{pH}_{\mathrm{PS}}$ hitherto available are collected in the Annexes B, C and D.

5 Procedure for specification

See Clause 4 in IEC 60746-2.

6 Recommended standard values and ranges of influence quantities

All the relevant data are to be found in Annexes B, C, D, E, and F.

7 Verification of values

See Clause 4 in IEC 60746-2.

8 Other difficult media for pH determinations

Significant methodological difficulties in pH measurements are not only faced in the non-aqueous or aqueous-organic media dealt with in the previous clauses, but they also arise in special "aquatic" media such as the physiological solutions [9], the low-ionic-strength freshwaters [13], the estuarine waters [14], and seawaters and highly saline waters [15,16]. The difficulties caused by these media concern:

a) interpretation of acid-base equilibria interacting with other dissociative equilibria;
b) selection or adaptation of pH-metric standards;
c) choice and design of salt bridges at liquid junctions;
d) choice of reference electrodes;
e) type and design of operational pH-metric cells; (vi) control of influence quantities.

All these problems, and the related methodological recommendations, are dealt with exhaustively in specific IUPAC documents [13 to 16], and need not be redescribed here.

Annex A
(informative)

Values of the Nernstian slope factor $k = 2{,}3026\ RT/F$

See Table A.1

Table A.1 – Values of the Nernstian slope factor $k = 2{,}3026\ RT/F$

t / °C	k /V	t / °C	k /V
0	0,054 199	50	0,064 120
5	0,055 191	55	0,065 112
10	0,056 183	60	0,066 104
15	0,057 175	65	0,067 097
20	0,058 168	70	0,068 089
25	0,059 160	75	0,069 081
30	0,060 152	80	0,070 073
35	0,061 144	85	0,071 065
40	0,062 136	90	0,072 057
45	0,063 128	95	0,073 049
		100	0,074 041

Fundamental constants:

$R = 8{,}314\ 51$ J K^{-1} mol^{-1}

$F = 96\ 485{,}3$ C mol^{-1}

$T = (t + 273{,}15)$ = thermodynamic temperature in K

Annex B

(informative)

Values of primary pH-metric standards (pH_{PS}), with overall estimated standard errors δ, for the **0,05 *m* Potassium Hydrogen Phthalate buffer** in **aqueous-organic solvent mixtures** at various mass percent concentrations of nonaqueous component (with corresponding mole fractions *x*), at different temperatures *t*/°C [3 to 7].

		Mass percent of nonaqueous solvent in admixture with water										
		5	**10**	**15**	**20**	**30**	**40**	**50**	**64**	**70**	**80**	**84,2**
METHANOL	*X* **t/°C**		**0,058 8**		**0,123 2**			**0,359 9**	**0,499 9**			**0,749 8**
	10		4,254		4,490			5,151	5,488			6,254
	25		4,243		4,468			5,125	5,472			6,232
	40		4,257		4,472			5,127	5,482			6,237
	δ		±0,003		±0,003			±0,003	±0,003			±0,003
ETHANOL	*X* *t*/°C		**0,041 6**		**0,089 1**		**0,206 8**			**0,477 1**		
	–5		4,278		4,567		5,113			5,530		
	0		4,261		4,544		5,078			5,505		
	10		4,238		4,510		5,022			5,474		
	25		4,230		4,488		4,973			5,466		
	40		4,248		4,494		4,959			5,499		
	δ		±0,002		±0,002		±0,002			±0,002		
2-PROPANOL	*X* *t*/°C		**0,032 2**			**0,1139**		**0,230 6**		**0,411 6**		
	15		4,259			4,881		5,247		5,510		
	25		4,249			4,850		5,210		5,522		
	35		4,253			4,834		5,189		5,548		
	45		4,270			4,833		5,182		5,584		
	δ		±0,002			±0,002		±0,003		±0,004		

		Mass percent of nonaqueous solvent in admixture with water										
		5	**10**	**15**	**20**	**30**	**40**	**50**	**64**	**70**	**80**	**84,2**
1,2-ETHANE-DIOL [a]	X **t/°C**		**0,0312**			**0,1106**		**0,225 0**		**0,403 8**		
	–10		-			4,441		4,845		-		
	–5		-			4,432		4,827		-		
	5		4,122			4,419		4,802		-		
	15		4,121			4,416		4,790		5,254		
	25		4,127			4,419		4,790		5,238		
	35		4,139			4,421		4,799		5,241		
	45		4,156			4,450		4,817		5,261		
	δ		±0,002			±0,002		±0,002		±0,002		
2-METHOXY-ETHANOL [b]	X **t/°C**				**0,055 9**			**0,191 4**			**0,486 4**	
	–10				-			5,534			6,878	
	–5				4,546			-			-	
	0				4,526			5,470			6,819	
	10				4,515			5,422			6,757	
	25				4,505			5,380			6,715	
	35				4,508			-			6,716	
	37				-			5,363			-	
	45				4,514			-			-	
	δ				±0,003			±0,002			±0,003	
ACETO-NITRILE	X **t/°C**	**0,0226**		**0,071 9**		**0,1583**		**0,305 0**		**0,505 9**		
	15	4,163		4,533		5,001		5,456		6,159		
	25	4,166		4,533		5,000		5,461		6,194		
	35	4,178		4,542		5,008		5,475		6,236		
	δ	±0,005		±0,005		±0,005		±0,005		±0,005		

		Mass percent of nonaqueous solvent in admixture with water										
		5	**10**	**15**	**20**	**30**	**40**	**50**	**64**	**70**	**80**	**84,2**
1,4-DIOXANE	X t/°C		0,022 2			0,080 6		0,169 7				
	15		**4,330**			**5,034**		**5,779**				
	25		4,329			5,015		5,782				
	35		4,337			5,007		5,783				
	45		4,355			5,008		5,783				
	δ		±0,002			±0,002		±0,002				
DIMETHYL-SULFOXIDE	X t/°C				**0,054 5**	**0,089 9**						
	–12				-	4,870						
	+25				4,471	4,761						
	δ				±0,002	±0,002						

[a] ethylene glycol.

[b] methyl cellosolve.

Values of primary pH-metric standards (**pH$_{PS}$**), with overall estimated standard errors δ, for the **0,05 *m* Potassium Hydrogen Phthalate buffer** in **aqueous-organic solvent mixtures** at various mass percent concentrations of nonaqueous component (with corresponding mole fractions *x*), at different temperatures *t*/°C [3 to 7].

		Mass percent of nonaqueous solvent in water mixture										
		8	**10**	**16**	**20**	**30**	**40**	**50**	**64**	**70**	**80**	**100**
	X ***t*/°C**	**0,017 5**		**0,037 6**								
ETHYLENE CARBONATE												
	25	4,145		4,301								
a)												
	δ	±0,003		±0,003								
	X ***t*/°C**	**0,015 1**		**0,032 5**								
PROPYLENE CARBONATE b)												
	25	4,177		4,347								
	δ	±0,005		±0,005								
GLYCEROL	***X*** ***t*/°C**				**0,046 6**		**0,115 4**					
	–5				4,165		-					
	0				4,158		-					
	10				4,158		4,406					
	25				4,172		4,420					
	40				4,451		4,451					
	δ				±0,002		±0,002					
FORMAMIDE	***X*** ***t*/°C**											**1,000 0**
	10											6,357
	25											6,325
	40											6,287
	55											6,241
	δ											±0,001

		Mass percent of nonaqueous solvent in water mixture										
		8	**10**	**16**	**20**	**30**	**40**	**50**	**64**	**70**	**80**	**100**
N-METHYL-FORMAMIDE	*X* ***t*/°C**							**0,233 7**				**1,000 0**
	18							4,525				6,138
	25							4,467				6,089
	40							4,433				6,103
	δ							±0,007				±0,007
N-METHYL-ACETAMIDE	*X* ***t*/°C**							**0,233 7**				**1,000 0**
	25							4,290				
	35							4,193				4,649
	40											4,314
	45							4,211				4,501
	50											4,623
								±0,009				±0,020

[a] 1,3-Dioxolan-2-one.

[b] 4-Methyl-1,3-dioxolan-2-one.

Annex C
(informative)

Values of primary pD-metric standards (**pD_{PS}**), with overall estimated uncertainty δ, for the **0,05 *m* Potassium Deuterium Phthalate buffer** in **Deuterium Oxide (D_2O)** at different temperatures *t*/°C

***t* /°C**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**
pD_{PS}	4,546	4,534	4,529	4,522	4,521	4,523	4,528	4,532	4,542	4,552
δ	± 0,007									

Annex D
(informative)

Values of primary standards (pH_{PS}) of various buffers for pH measurements in different solvents or aqueous–organic solvent mixtures at various temperatures. The concentrations of the organic components of the solvent mixtures are expressed in mass percent. [3,17,18]

BUFFERS		*ACETATE* **a**	*SUCCINATE* **b**	*PHOSPHATE* **c**	*TRIS+ TRIS HCl* **d**	*AmPy+ AmPy HCl* **e**			*OXALATE* *f*	*SUCCINATE* **g**
SOLVENT ***t*/°C**	**%**	**METHANOL**					**SOLVENT** ***t*/°C**	**%**	**METHANOL**	
10	**50**	5,518	5,720	7,937	8,436	9,116	**25**	**39,14**	2,374	
15	**50**	5,506	5,697	7,916	8,277	8,968	**25**	**43,30**		4,938
20	**50**	5,498	5,680	7,898	8,128	8,829	**25**	**64**		5,398
25	**50**	5,493	5,666	7,884	7,985	8,695	**25**	**70**	2,771	
30	**50**	5,493	5,656	7,872	7,850	8,570	**25**	**84,20**	3,358	
35	**50**	5,496	5,650	7,863	7,720	8,446	**25**	**84,40**		6,289
40	**50**	5,502	5,648	7,858	7,599	8,332	**25**	**90**	3,729	
							25	**94,20**		7,147
							25	**94,29**	4,133	
							25	**100**	5,79	8,75

BUFFERS	*ACETATE* **h**			*PHOSPHATE* **i**			*TRIS+***d** *TRIS* HCl	*SALICYLATE* **j**	*BARBITURATE* **k**			*OXALATE* **l**	*SUCCINATE* **g**
SOLVENT	**ETHANOL**									**SOLVENT**		**ETHANOL**	
% ***t*/°C**	**10**	**20**	**40**	**10**	**20**	**40**	**50**	**100**	**100**	***t*/°C**	**%**		
–10		5,075	5,498	7,376	7,638		8,912			**25**	**30**	2,298	4,668
–5	4,881	5,044	5,470	7,315	7,569		8,739			**25**	**50**	2,478	5,040
0	4,861	5,021	5,445	7,263	7,508		8,571			**25**	**71,89**	2,947	5,673
+5							8,411						
10							8,258						
15							8,114						
20							7,977						
25	4,822	4,967	5,395	7,104	7,310	7,597	7,845	8,31	13,23				

BUFFERS	*TES+* Na*TES* ***m***		*PHOSPHATE* ***i***		*PHOSPHATE* ***n***			*CITRATE* ***o***	*PHOSPHATE* ***p***	*CARBONATE* ***q***
SOLVENT	**DIMETHYLSULFOXIDE**						**SOLVENT**	**DEUTERIUM OXIDE**		*****
% **t/°C**	**20**	**30**	**20**	**30**	**20**	**30**	**%** **t/°C**	**100**	**100**	**100**
–12		8,210					**5**	4,378	7,539	10,998
–5,5	7,889						**10**	4,352	7,504	10,924
0	7,649	7,860					**15**	4,329	7,475	10,855
+25	7,106	7,128	7,407	7,710	7,959	8,266	**20**	4,310	7,449	10,793
							25	4,293	7,428	10,736
							30	4,279	7,411	10,685
							35	4,268	7,397	10,638
							40	4,260	7,387	10,597
							45	4,253	7,381	10,560
							50	4,250	7,377	10,527

BUFFERS	*PHOSPHATE* ***r***	*PHOSPHATE* ***s***	*PHOSPHATE* ***s***
SOLVENT	**FORMAMIDE**		**N-METHYL FORMAMIDE**
% **t/°C**	**100**	**100**	**50**
10	9,326	9,727	
18			7,511
25	9,157	9,475	7,489
30			7,064
40	8,925	9,203	
55	8,690	8,982	

LEGEND TO ANNEX D

a: Acetic acid (0,05m) + Sodium acetate (0,05m) + NaCl (0,05m);

b: NaHSuccinate (0,05m) + NaCl (0,05m);

c: KH_2PO_4 (0,02m) + Na_2HPO_4 (0,02m) + NaCl (0,02m);

d: TRIS = Tris(hydroxymethyl)-aminomethane (0,05m), TRIS HCl = TRIS hydrochloride (0,05m);

e: AmPy = 4-Aminopyridine (0,06m), AmPy HCl = 4-Aminopyridinium chloride (0,06m);

f: Oxalic acid (0,01m) + Ammonium oxalate (0,01m);

g: Succinic acid (0,01m) + Lithium succinate (0,01m);

h: Acetic acid (0,05m) + Sodium acetate (0,05m);

i: KH_2PO_4 (0,025m) + Na_2HPO_4 (0,025m);

j: Salicylic acid (0,01m) + Lithium salicylate (0,01m);

k: Diethylbarbituric acid (0,01m) + Lithium diethylbarbiturate (0,01m);

l: Oxalic acid (0,01m) + Lithium oxalate (0,01m);

m: TES = N-tris(hydroxymethyl)methyl-2-aminoethane sulfonic acid (0,070m) + Na TES = Sodium salt of TES (0,030m);

n: KH_2PO_4 (0,008 695m) + Na_2HPO_4 (0,030 43m);

o: $KD_2C_6H_5O_7$ (0,05m);

p: KD_2PO_4 (0,025m) + Na_2DPO_4 (0,025m);

q: $NaDCO_3$ (0,025m) + Na_2CO_3 (0,025m);

r: KH_2PO_4 (0,01m) + Na_2HPO_4 (0,01m);

s: KH_2PO_4 (0,003 478m) + Na_2HPO_4 (0,012 172m).

For the buffers **a, b, c, d,** and **e** the original works furnish pH_{PS} values also at buffer molalities other than the mid molalities quoted above.

The standard values in deuterium oxide (heavy water) are in terms of pD_{PS}.

Annex E
(informative)

Secondary standard values pH_{SS} for various buffer solutions in tetrahydrofuran+water solvent mixtures at 25 °C [**8**]: standard deviations $\delta \leq 0,01$. Tetrahydrofuran (THF) = C_4H_8O = diethylene oxide = tetramethylene oxide) [8].

	pH_{SS}				
Buffers	**CITRATE**	**PHTHALATE**	**TETRABORATE**	**CARBONATE**	**ACETATE**
THF mass %					
0	3,773	4,005	9,18	10,012	4,654
10	3,93	4,26	9,53	10,53	4,83
20	4,10	4,62	9,77	11,42	5,02
30	4,30	4,93	10,18	11,59	5,28
40	4,57	5,31	10,54	11,82	5,62
50	4,76	5,56	10,87	12,10	5,84
60	5,04	5,86	-	-	6,33
70	-	6,17	-	-	-
Buffer composition	Potassium dihydrogen citrate 0,05 $mol \cdot kg^{-1}$	Potassium hydrogen phthalate 0,05 $mol \cdot kg^{-1}$	Sodium tetraborate 0,01 $mol \cdot kg^{-1}$	$NaHCO_3$ 0,025 $mol \cdot kg^{-1}$ + Na_2CO_3 0,025 $mol \cdot kg^{-1}$	Acetic acid 0,1 $mol \cdot dm^{-3}$ + Sodium acetate 0,1 $mol \cdot dm^{-3}$

Annex F
(informative)

Secondary standard values pH$_{SS}$ for various buffer solutions in formamide, in N-methylacetamide + water, and in glycerol + water solvent mixtures at various temperatures t [17,18]: standard deviations $\delta \le 0{,}01$.

	pH$_{SS}$				
BUFFERS	**TETROXALATE**	**TARTRATE**	**PHOSPHATE**	**CITRATE**	***t*/°C**
SOLVENTS					
Formamide	1,242			5,107	25
50 mass % **N-Methyl-Acetamide**	1,611	3,981	7,941		25
	1,640	3,896	7,770		35
	1,686	3,866	7,705		45
20 mass % **Glycerol**	1,745	3,881	7,604		−5
	1,709	3,837	7,547		0
	1,669	3,764	7,457		10
	1,733	3,811	7,463		25
	1,760	3,797	7,382		40
40 mass % **Glycerol**	1,886	4,149	7,698		−10
	1,856	4,074	7,642		10
	1,975	4,024	7,624		25
	1,888	4,069	7,601		40
Buffer composition	$KH_3C_4O_8 \cdot 2H_2O$ 0,05 m	$KHC_4H_4O_8$ sat. sol.	Na_2HPO_4 0,030 43 m + KH_2PO_4 0,030 43 m	KH_2Citrate 0,05 m	

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The net pressure pH2 of the hydrogen gas is pH2 = pBAROM − pVAP + C, and should be normalized to pH2 = 101,325 kPa by the procedure described in [9]. To prevent H2 from diffusing onto, and chemically reacting with, the AgCl electrode, in common practice the two electrode compartments are separated by a suitable porous glass frit or a closed stopcock. If the HCl solution is replaced by the mixed (Primary Buffer + KCl) solution, this would also be the structure of cell (11).

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