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INTERNATIONAL ELECTROTECHNICAL COMMISSION
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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*   withdrawn,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.

iTeh STANDARD PREVIEW
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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_{H+} in solution given by the expression

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

where γ_{H+} is the activity coefficient of the H^+ ion at the molality m_{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

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

$$pH = -\log a_{H+} = -\log(m_{H+}\, \gamma_{H+}/m°) \tag{2}$$

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

$$pH_c = -\log(a_{H+})_c = -\log(c_{H+}\, y_{H+}/c°) \tag{3}$$

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

$$pH_c = pH - \log [\rho/(kg\ dm^{-3})] \tag{4}$$

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_{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_{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 pH_{PS} or pH_{SS}, according to:

Reference electrode in solvent Z	Concentrated equitransferent salt bridge in solvent Z	Standard pH_{PS} or pH_{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:

$$pH_X = pH_{SS} - (E_X - E_S)/k + (E_{JX} - E_{JS})/k \tag{7}$$

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 ph_{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 $(E_{JX} - E_{JS})$ (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:

$$pH_X = pH_{SS} - (E_X - E_S)/k \tag{8}$$

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 (pH_{PS1}) below and one (pH_{PS2}) above the expected pH_X. The corresponding measurements of E_X, E_{S1}, and E_{S2}, are then combined to give the following equations:

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

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

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 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 (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* (pH_{PS}) in solution of specified concentration in the appropriate solvent Z.

The 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) | pH_{PS} + KCl, in Z | AgCl | Ag | Pt | (11) |
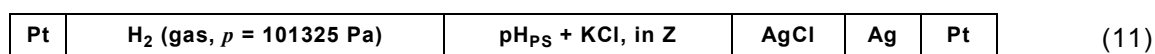
whose structure (and that of the parallel cell (13)) is represented schematically in Figure 1. Best values of pH_{PS} for various standard buffer solutions in some 45 nonaqueous or aqueous-organic solvents at various temperatures are given in Annexes B, C and D, together with directions for proper preparation of the chemicals.

The potential difference E of cell (11), omitting to write the term $m° = 1$ 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 $\gamma_{H+}\gamma_{Cl-} = \gamma_{\pm}^2$ 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).
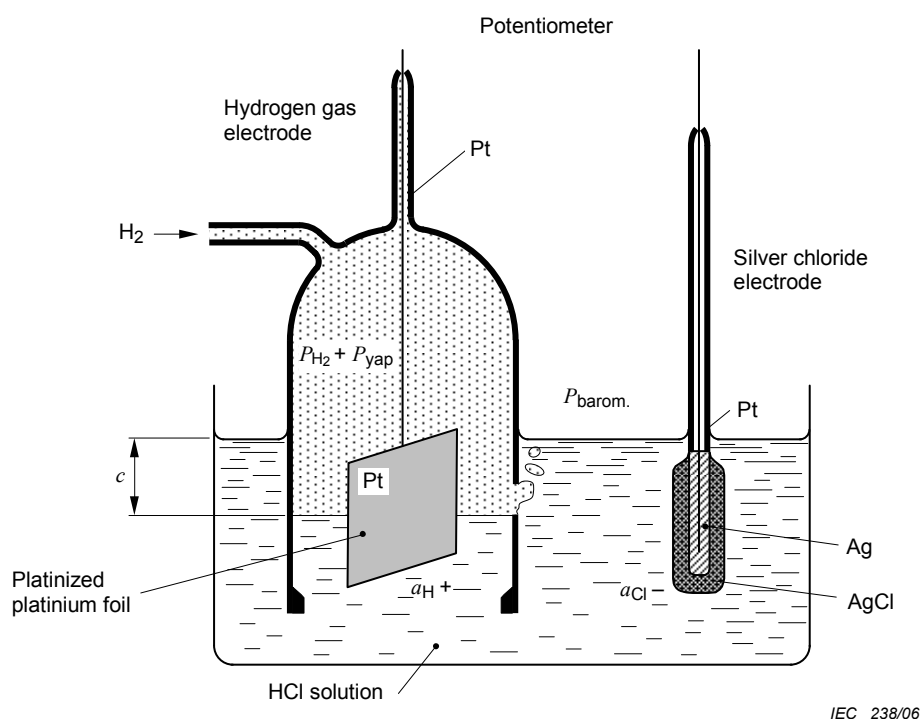
Figure 1 – Schematic structure of the hydrogen gas electrode and of the AgCl electrode forming the cell (13)

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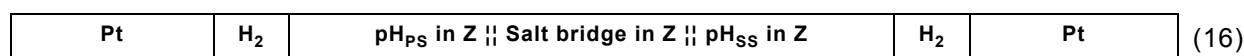
where pH$_{SS}$ may either have the same nominal composition of pH$_{PS}$ or be of quite different composition, and it is desirable that the junctions be formed within capillary tubes so that the geometry of the liquid junction is well defined and the potential values reproducible. If E_{16} denotes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

$$pH_{SS} = pH_{PS} - E_{16}/k \qquad (17)$$

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 ($\approx$ −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 system-atisation 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.