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Determination of pH value — Reference buffer solutions for the calibration of pH measuring equipment

Détermination de la valeur pH — Solutions tampons de référence pour l'étalonnage des appareils de mesure du pH

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Contents

Page

Foreword

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This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Determination of pH value — Reference buffer solutions for the calibration of pH measuring equipment

1 Scope

This document specifies reference buffer solutions for the calibration of pH measuring equipment.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

ISO 19396-1, *Paints and varnishes — Determination of pH value — Part 1: pH electrodes with glass membrane*

ISO 80000-9, *Quantities and units — Part 9: Physical chemistry and molecular physics*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 80000-9 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
pH
measure for the acidic or basic character of an aqueous solution

Note 1 to entry: Notation of pH: the "p" and the "H" are upright on one line.

Note 2 to entry: The acidic character is determined by the activity of the existing “hydrogen ions”.

3.2
pH value
decadal logarithm of the hydrogen ion activity multiplied with (−1)

$$\mathrm{pH} = -\lg\left(\frac{a_{\mathrm{H}^+}}{m^0}\right) = -\lg\left(\frac{m_{\mathrm{H}^+} \cdot \gamma_{m,\mathrm{H}^+}}{m^0}\right)$$

where

$a_{\mathrm{H^+}}$ is the activity of the hydrogen ion, in mol/kg;

m^0 is the standard molality (1 mol/kg);

$\gamma_{m,\mathrm{H^+}}$ is the activity coefficient of the hydrogen ion;

$m_{\mathrm{H^+}}$ is the molality of the hydrogen ion, in mol/kg.

Note 1 to entry: Molality is understood as moles per kilogram solvent.

Note 2 to entry: The pH value is not measurable as a measure of a single ion activity. Therefore, pH(PR) values of solutions of primary reference material are determined, which are approximate to it and can be attributed to it. This is based on a worldwide agreement, see ISO 80000-9:2009, Annex C.

4 Basic information

4.1 General

Reference buffer solutions are prepared using primary or secondary reference materials. The pH values of the reference buffer solutions are determined using the methods described in 4.2 and 4.3. The pH value of a reference buffer solution and the associated uncertainty of measurement are documented in a calibration certificate as the result of calibration. pH values of primary reference buffer solutions form the basis of pH measurements in practice and are generally determined by national metrology institutes. Secondary reference buffer solutions are commercially available. The reference buffer solutions prepared according to the methods described in Clause 5 serve as a material measure of the pH value.

4.2 pH values of primary reference buffer solutions

The pH value based upon the activity of single ions according to the formula in 3.2 cannot be measured. The pH value is assigned to reference buffer solutions outlined in Table 1. This is achieved using an electrochemical method of measurement that is based on the thermodynamic dependence of the potential of the platinum/hydrogen electrode on the hydrogen ion activity. Through the use of cells without transference, diffusion voltages arising from liquid junctions do not appear and therefore do not need to be considered when calculating the voltage of the cell. The cell (I) for this purpose shall consist of a platinum/hydrogen and a silver/silver chloride electrode, immersed in the reference buffer solution to which chloride in a low concentration $\left(m_{\mathrm{Cl^-}}\right)$ has been added.

$$\text{Pt|Ag|AgCl|reference buffer solution, pH(R), Cl}^- \left(m_{\mathrm{Cl^-}}\right) \text{|Pt, H}_2 \,(p_{\mathrm{H_2}} = 101\,325 \text{ Pa}). \qquad \text{(I)}$$

The pH value of the reference buffer solution is calculated according to Formula (1):

$$\mathrm{pH} = \lim_{m_{\mathrm{Cl^-}} \to 0} \left[\frac{\left(E - E^0\right)}{k} + \lg\left(\frac{m_{\mathrm{Cl^-}}}{m^0}\right) \right] + \lg\gamma_{\mathrm{Cl^-}} \qquad (1)$$

where

E is the voltage of cell (I);

E^0 is the standard potential of the Ag/AgCl electrode;

k is the Nernst slope ($k = RT(\ln 10) / F$);

m^0 is the standard molality (1 mol/kg);

m_{Cl^-} is the molality of the chloride ions in the solution;

γ_{Cl^-} is the activity coefficient of the chloride ion.

Chloride is added to the reference buffer solution in a minimum of three different molalities less than or equal to 0,02 mol/kg. To calculate the pH value, $m_{\mathrm{Cl}^-} \rightarrow 0$ is extrapolated according to Formula (1).

The activity coefficient of the chloride ions is estimated according to Formula (2) for solutions with an ionic strength of less than or equal to 0,1 mol/kg[2].

$$\lg\gamma_{\mathrm{Cl}^-} = -\frac{AI^{1/2}}{1+1{,}5\left(I/m^0\right)^{1/2}} \tag{2}$$

where

A is the Debye-Hückel constant;

γ_{Cl^-} is the activity coefficient of the chloride ion;

m^0 is the standard molality (1 mol/kg);

I is the ionic strength.

pH values of primary reference buffer solutions are often referred to as pH(R) (R = Reference). The expanded uncertainty of measurement U(pH) when determining a pH(R) value has been shown to be 0,002 to 0,005 at 25 °C depending on the primary reference buffer solution. As agreed, this uncertainty of measurement does not take into consideration the uncertainty of the Bates-Guggenheim convention for estimating the ionic activity of the chloride ion [see Formula (2)][3].

The expanded uncertainty of measurement of many pH(R) value measurements of primary reference buffer solutions prepared according to Clause 5 is U(pH) = 0,005 at 25 °C and U(pH) = 0,008 at 50 °C, due to the method of measurement and the purity and homogeneity of the materials used for different batches depending on the buffer solution. Accordingly, the pH(R) values of each batch can vary. Therefore, the pH(R) value is only valid for an individual batch with a corresponding calibration certificate. For buffer solution G, the expanded uncertainty of measurement of the pH(R) values is U(pH) = 0,006 at 25 °C and U(pH) = 0,01 for temperatures higher than 25 °C[4]. Contributions to uncertainty are a result of the method of measurement used as well as the purity and homogeneity of the material used.

Typical pH values of reference buffer solutions for the temperature range of 0 °C to 50 °C are given in Table 1.

4.3 pH values of secondary reference buffer solutions

The differential potentiometric method[5] is suitable for determining the pH values of secondary reference buffer solutions using primary reference buffer solutions with the same chemical composition. The isothermal cell used for this purpose (II) shall consist of two electrodes separated by a P 40 glass frit given in ISO 4793, and containing the primary and secondary standard buffer solutions and identical platinum hydrogen electrodes at exactly the same hydrogen pressure, i.e.

$$\mathrm{Pt, H_2}\left(p_{\mathrm{H_2}}\right)|\text{primary reference buffer, pH(R)}||\text{secondary reference buffer, pH}|\mathrm{Pt, H_2}\left(p_{\mathrm{H_2}}\right) \tag{II}$$

The cell voltage E of cell (II) is a measure of the difference in the pH values of the solutions and enables the pH(R) value of the secondary reference buffer solution to be determined using Formula (3), provided the absolute difference is |pH(R)-pH ≤ 0,02| and the pH of the solutions is between 3 and 11.

The diffusion voltage is then less than 10 % of the measured cell voltage and the cell is virtually without transference.

$$\mathrm{pH} = \mathrm{pH(R)} - E / k \tag{3}$$

where

k is the Nernst slope ($k = RT(\ln 10) / F$);

E is the voltage of cell (II).

Measured cell voltages are in the order of magnitude of a few hundred microvolts (μV). Consequently, pH differences down to 0,001 can be determined. The expanded uncertainty of measurement U of the pH value of the secondary reference buffer solution ranges from 0,003 to 0,006 at 25 °C when determining a single pH value depending on the type of secondary reference buffer solution, and is only slightly greater than that of the pH(R) values of primary reference buffer solutions determined using cell (I).

Table 1 — Typical values of primary and secondary reference buffer solutions

Reference buffer solution	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
Buffer material	Potassium tetraoxalate dihydrate $KH_3(C_2O_4)_2 \cdot 2\ H_2O$	Potassium hydrogen tartrate $KHC_4H_4O_6$	Potassium hydrogen phthalate $KHC_8H_4O_4$	Potassium dihydrogen phosphate + Disodium hydrogen phosphate KH_2PO_4 + Na_2HPO_4	Potassium dihydrogen phosphate + Disodium hydrogen phosphate KH_2PO_4 + Na_2HPO_4	Disodium tetraborate decahydrate $Na_2B_4O_7 \cdot 10\ H_2O$	Calcium hydroxide $Ca(OH)_2$	Potassium dihydrogen citrate $KH_2C_6H_5O_7$	Sodium carbonate + Sodium hydrogen carbonate Na_2CO_3 + $NaHCO_3$
Molality mol/kg	0,05	Saturated at 25 °C	0,05	0,025 (KH_2PO_4) + 0,025 (Na_2HPO_4)	0,008 695 (KH_2PO_4) + 0,030 43 (Na_2HPO_4)	0,01	Saturated at 25 °C	0,05	0,025 (Na_2CO_3) + 0,025 ($NaHCO_3$)
Temperature **°C**	**pH(R) values**								
0	1,666	—	4,000	6,984	7,534	9,464	—	3,863	10,317
5	1,668	—	3,998	6,951	7,500	9,395	13,207	3,840	10,245
10	1,670	—	3,997	6,923	7,472	9,332	13,003	3,820	10,179
15	1,672	—	3,998	6,900	7,448	9,276	12,810	3,802	10,118
20	1,675	—	4,000	6,881	7,429	9,225	12,627	3,788	10,062
25	1,679	3,557	4,005	6,865	7,413	9,180	12,454	3,776	10,012