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Conveners: Vladimir Dobrovolskiy

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OIML R 54

RECOMMENDATION

Edition 202x (E)

pH SCALE FOR AQUEOUS SOLUTIONS

Echelle de pH des solutions aqueuses

OIML R 54 Edition 201x (E)



ORGANISATION INTERNATIONALE DE
METROLOGIE LEGALE

INTERNATIONAL ORGANIZATION OF
LEGAL METROLOGY

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Foreword

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This publication – reference OIML R 54, edition 201__ I – was developed by the OIML Technical Subcommittee TC 17/SC 3 pH-metry. The 2nd edition of the OIML R 54 (1981) «pH SCALE FOR AQUEOUS SOLUTION» was approved for final publication by the International Committee of Legal Metrology at its.....

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Bureau International de Métrologie Légale
11, rue Turgot – 75009 Paris – France
Telephone: 33 (0)1 48 78 12 82
Fax: 33 (0)1 42 82 17 27
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Internet: www.oiml.org

Introduction

Determination of the hydrogen pH is the most common method for controlling the composition of aqueous media, since the activity of hydrogen ions, pH, is one of the most important physicochemical (acid-base characteristics) properties of aqueous solutions.

Technological processes in the production of chemical reagents, fertilizers, agricultural and food products, household chemicals are carried out with constant monitoring of pH. That is why the vast majority of analytical laboratories in the world are equipped with various types of pH measuring instruments. Today the development of the chemical industry, nuclear energy, microelectronics, robotics, medicine and biotechnology, increasing demands on the effectiveness of environmental control and environmental protection measures require increasingly accurate pH measurement. This necessitates reliable measuring instruments that are traceable to the International System of Units (SI units), through national primary pH standards. The national primary pH standards need to have high metrological quality with low measurement accuracy to ensure reproducible pH measurements.

However, the pH scale indicated in the OIML R 54 Recommendation “pH Scale for Aqueous Solutions”, which has been in force since 1981, has some discrepancies with the results of more recent studies presented in the joint publication of the experts in 2002 [1]. Thus, the revision of the Recommendation has become relevant since 2002. Over the years, the pH scale has been studied in order to assess more accurately sources of uncertainty of primary pH measurements. This studies have been conducted through key comparisons within the framework of the Working Group on Electrochemical Analysis (EAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) of the International Committee for Weights and Measures (CIPM) of the International Bureau of Weights and Measures (BIPM).

This Recommendation is a revised version of OIML Recommendation R 54 “pH Scale for Aqueous Solutions” (1981, with the international comparisons between the leading metrology institutes in this area being taken into consideration. The Recommendation is harmonized with the International Recommendation IUPAC “Measurement of pH. Definition, standards, and procedures, IUPAC Recommendations 2002” [1], and takes into consideration Recommendations of some international standards [2-5].

The pH values of the scale have been specified by the primary measurement method of pH.

The primary method of measuring pH is applied in the electrochemical Harned cell, using a platinum/palladium coated platinum foil electrode, hydrogen gas and silver-silver chloride electrodes, in the pH range 3.5 – 10.3 in the temperature interval of 278.15 K to 323.15 K.

This Recommendation provides the primary pH standards of the OIML state-members with the pH Scale for metrological control.

pH Scale For Aqueous Solutions

1 Scope

- 1.1. This Recommendation cites the pH values Scale for primary pH standards reproducing this scale in the temperature interval of 278.15 K to 323.15 K.
- 1.2. The pH values of the Scale have been specified by the primary method of pH measurement.
- 1.3. The Scale is used for the calibration and verification of pH measuring equipment.
- 1.4. The Scale is appropriate for aqueous and dilute ionic strength (≤ 0.1 mol/kg) solutions.

2 Terms and definitions

For the purpose of this Recommendation, the following definitions apply.

2.1. pH, a single ion quantity [1]

is negative decimal logarithm of hydrogen ion relative activity a_H of solution:

$$pH = -\lg a_H = -\lg(m_H \gamma_H / m^0)$$

where: a_H is the relative (molality basis) activity and γ_H is the molal activity coefficient of the hydrogen ion H^+ at the molality m_H , and m^0 is the molality standard state exhibiting infinitely diluted behavior.

The definition involves a single ion quantity, the activity of hydrogen ion, which is immeasurable by any thermodynamically valid method and requires a convention for its evaluation.

2.2. primary method of pH measurement [2, 6, 7]

- a primary method of measurement is a method having the highest metrological qualities, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units;
- a primary direct method measures the value of an unknown without reference to a standard of the same quantity;
- a primary ratio method measures the value of a ratio of an unknown to a standard of the same quantity; its operation must be completely described by a measurement equation.

2.3. primary pH standards

aqueous solutions of selected reference buffer solutions to which pH (PS) values have been assigned over the temperature interval of 278,15 K to 323,15 K from measurements on cells without transference, called Harned cells, by use of the Bates–Guggenheim convention [1]. These primary standards are capable of establishing good reproducibility and low uncertainty.

3 Instrumental (operational) definition of pH

3.1. The primary method of pH measurement, Harned cell [1]

The pH value can be determined from electrochemical data from the cell without transference using the hydrogen gas electrode, known as the electrochemical Harned cell:



and containing certified standard buffer and chloride ions, which are added in order to use the silver-silver chloride electrode.

3.2. The following six buffer solutions are recommended as primary pH standards [1]:

- I Solution of potassium hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, saturated at 298.15 K;
- II Solution of potassium hydrogen phthalate, 0.050 mol/kg $\text{KHC}_8\text{H}_4\text{O}_4$;
- III Solution of potassium dihydrogen phosphate and of sodium hydrogen phosphate, 0.025 mol/kg KH_2PO_4 + 0.025 mol/kg Na_2HPO_4 ;
- IV Solution of potassium dihydrogen phosphate and of sodium hydrogen phosphate, 0.009 mol/kg KH_2PO_4 + 0.030 mol/kg Na_2HPO_4 ;
- V Solution of disodium tetraborate decahydrate, 0.01 mol/kg $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$;
- VI Solution of sodium hydrogen carbonate and of disodium carbonate, 0.025 mol/kg NaHCO_3 + 0.025 mol/kg Na_2CO_3 .

3.3. Typical values of pH for the primary pH standards (buffer solutions) obtained using Harned cell in the temperature interval of 278.15 K to 323.15 K are given in Table 1.

3.4. The technical characteristics of the primary pH standards (buffer solutions) are presented in Annex A.

3.5. The primary pH method is described in Annex B.

Table 1 – Typical values of pH for the primary buffer solutions in the temperature interval of 278.15 to 323.15 K [1]

Temperature, K	The primary pH solutions					
	Potassium hydrogen tartrate $\text{KHC}_4\text{H}_4\text{O}_6$ saturated at 298.15 K	Potassium hydrogen phthalate, 0.050 mol/kg $\text{KHC}_8\text{H}_4\text{O}_4$	Potassium dihydrogen phosphate and of sodium hydrogen phosphate, 0.025 mol/kg KH_2PO_4 + 0.025 mol/kg Na_2HPO_4	Potassium dihydrogen phosphate and of sodium hydrogen phosphate, 0.009 mol/kg KH_2PO_4 + 0.030 mol/kg Na_2HPO_4	Disodium tetraborate decahydrate, 0.01 mol/kg $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	Sodium hydrogen carbonate and of disodium carbonate, 0.025 mol/kg NaHCO_3 + 0.025 mol/kg Na_2CO_3 –
	I	II	III	IV	V	VI
278.15	-	3.998	6.951	7.500	9.395	10.245
283.15	-	3.997	6.923	7.472	9.332	10.179
288.15	-	3.998	6.900	7.448	9.276	10.118
293.15	-	4.000	6.881	7.429	9.225	10.062
298.15	3.557	4.005	6.865	7.413	9.180	10.012
303.15	3.552	4.011	6.853	7.400	9.139	9.966
308.15	3.549	4.018	6.844	7.389	9.102	9.926
310.15	3.548	4.022	6.841	7.386	9.088	9.910
313.15	3.547	4.027	6.838	7.380	9.068	9.889
323.15	3.549	4.050	6.833	7.367	9.011	9.828

Note 1: Since there can be significant variations in the purity of samples of the same nominal chemical composition, batch-to-batch pH variations from 0.003 to 0.004 are typical.

Note 2: Tabulated pH values are given as examples and it is recommended that actual pH values be taken from certificates, which are to accompany each batch of certified reference material.

Note 3: Recommended expanded uncertainty [7, 8] of pH measurements is in the order of $U(\text{pH}) \leq 0.003$ ($k = 2$) at 298.15 K. Recommended expanded uncertainty of pH measurements is in the order of $U(\text{pH}) \leq 0.005$ ($k = 2$) in the temperature interval of 278.15 K to 323.15 K (except 298.15 K).

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Annex A

Technical characteristics of the primary pH standards (Informative)

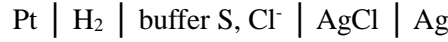
Table A – Technical characteristics of the primary pH standards

Name of chemical substances, included in the composition of buffer	Chemical formulations of substances	Mass to make 1kg buffer at 293.15 K g	Molality mol/kg	Nominal pH value at the temperature of 298.15 K measured in the Harned cell
Potassium hydrogen tartrate	$\text{KHC}_4\text{H}_4\text{O}_6$	9.5171	Saturated at 298.15 K	3.557
Potassium hydrogen phthalate	$\text{KHC}_8\text{H}_4\text{O}_4$	10.2000	0.050	4.005
Potassium dihydrogen orthophosphate	KH_2PO_4	3.4000	0.025	6.865
Disodium hydrogen orthophosphate	Na_2HPO_4	3.5500	0.025	
Potassium dihydrogen orthophosphate	KH_2PO_4	1.2240	0.009	7.413
Disodium hydrogen orthophosphate	Na_2HPO_4	4.2600	0.030	
Disodium tetraborate decahydrate	$\text{Na}_2\text{B}_4\text{O}_7 \times 10\text{H}_2\text{O}$	3.8120	0.010	9.180
Disodium carbonate	Na_2CO_3	2.6500	0.025	10.012
Sodium hydrogen carbonate	NaHCO_3	2.1000	0.025	

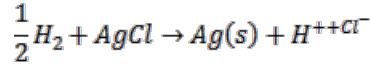
Annex B

The primary pH method (Informative)

Primary pH method is based on measurements of the potential difference of the Harned cell:



The application of Nernst equation to the spontaneous cell reaction:



yields the potential difference of the cell (corrected to 1 atm) as

$$E_1 = E^0 - k \times \lg[(m_{\text{H}} \gamma_{\text{H}}/m^0) \times (m_{\text{Cl}} \gamma_{\text{Cl}}/m^0)] \quad (1)$$

which can be rearranged to give the acidity function [9]:

$$p(a_{\text{H}} \gamma_{\text{Cl}}) = -\lg(a_{\text{H}} \gamma_{\text{Cl}}) = \frac{E_1 - E^0}{k} + \lg\left(\frac{m_{\text{Cl}}}{m^0}\right) \quad (2)$$

where: E^0 is the standard potential (Table B1) of ;

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

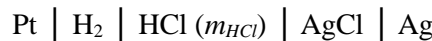
γ_{Cl} – the activity coefficient of the chloride ion at the molality m_{Cl} ;

T – thermodynamic temperature, K;

R – gas constant: $R = 8.314\,462\,618\,\text{J K}^{-1} \text{mol}^{-1}$ [10];

F – Faraday constant: $F = 96\,485.332\,123\,3\,\text{C mol}^{-1}$ [10].

The standard potential of the silver-silver chloride electrode is obtained from the potential difference of the Harned cell in which only HCl is present at a fixed molality (e.g., $m_{\text{HCl}} = 0.01\,\text{mol/kg}$). The application of the Nernst equation to HCl cell:



gives

$$E_2 = E^0 - 2K \times \lg\left(\frac{m_{\text{HCl}} \gamma_{\pm \text{HCl}}}{m^0}\right) \quad (3)$$

where: E_2 is the corrected to 1 atmosphere partial pressure of hydrogen gas potential difference of the cell;

$\gamma_{\pm \text{HCl}}$ is the mean ionic activity coefficient of HCl at the molality m_{HCl} [11].

The effect of the chloride on the electromotive force of Harned cell is eliminated by using at least three buffer solutions with varying chloride contents m_{Cl} and by linear extrapolation to zero chloride, yielding the empirical function:

$$-\lg(a_{\text{H}} \gamma_{\text{Cl}}) = -\lg(a_{\text{H}} \gamma_{\text{HCl}})^0 + S \times m_{\text{Cl}} \quad (4)$$

where: $(a_{\text{H}} \gamma_{\text{HCl}})^0$ is the limiting acidity function;

S is the experimental, temperature-dependent constant.

Primary standard pH value of certified buffer is calculated from the following formula:

$$pH(PS) = -\lg a_H = -\lg(a_H \gamma_{Cl})^0 + \lg \gamma_{Cl}^0 \quad (5)$$

using the trace activity coefficient of the chloride ion $\lg \gamma_{Cl}^0$. The latter (like the activity coefficient of the hydrogen ion) is an immeasurable quantity, but can be calculated adopting the Bates-Guggenheim convention [10]:

$$\lg \gamma_{Cl}^0 = -A \times I^{\frac{1}{2}} / (1 + 1.5) I^{\frac{1}{2}} \quad (6)$$

where: A is the Debye-Hückel temperature-dependent constant (Table B1);

I is ionic strength of the buffer (see Table B2).

Although the resulting pH value is a conventional quantity it can be incorporated into the SI units under condition that pH uncertainty, the uncertainties of mean ionic activity coefficient of HCl and of trace activity coefficient of the chloride ion are taken into account.

4.1. Table B1 – Standard potential E° and coefficient A as a function of temperature

Temperature K	The standard potential (E°)	The Debye-Hückel temperature-dependent constant (A)
278.15	0.234 13	0.495 2
283.15	0.231 42	0.498 8
288.15	0.228 57	0.502 6
293.15	0.225 57	0.506 6
298.15	0.222 34	0.510 8
303.15	0.219 04	0.515 0
308.15	0.215 65	0.519 6
313.15	0.212 08	0.524 2
323.15	0.204 49	0.534 1

4.2. Table B2 – Ionic strength I of buffer solutions as a function of temperature

Buffer solution	Molality mol/kg	Temperature K	Ionic strength (I) mol/kg
Potassium tetraoxalate	0.050	278.15	0.077 0
		283.15	0.076 7
		288.15	0.076 5
		293.15	0.076 3
		298.15	0.076 0
		303.15	0.075 8
		308.15	0.075 5
		313.15	0.075 3
		318.15	0.075 1
		323.15	0.074 9
Potassium hydrogen phthalate	0.050	273.15-333.15	0.053 5
Potassium dihydrogen phosphate +	0.025	278.15-323.15	0.100 0
Disodium hydrogen phosphate	0.025		
Potassium dihydrogen phosphate +	0.008 695	278.15-323.15	0.100 0
Disodium hydrogen phosphate	0.030 43		
Sodium tetraborate	0.010	278.15-323.15	0.020 0

4.3. Table B2 (cont.) – Ionic strength I of buffer solutions as a function of temperature

Buffer solution	Molality mol/kg	Temperature K	Ionic strength (I) mol/kg
Sodium hydrogen carbonate + Sodium carbonate	0.025	278.15	0.100 0
		283.15	0.099 9
		288.15	0.099 9
		293.15	0.099 9
		298.15	0.099 9
	0.025	303.15	0.099 8
		308.15	0.099 8
		313.15	0.099 7
		318.15	0.099 6
Calcium hydroxide	solution saturated at 298.15 K	323.15	0.099 5
		278.15	0.053
		283.15	0.051
		288.15	0.050
		293.15	0.050
		298.15	0.049
		303.15	0.049
		308.15	0.048
		313.15	0.048
		318.15	0.048
		323.15	0.047