

pH measurement —

Part 2: Specification for reference value standard solutions and operational reference standard solutions

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Foreword

This revision, in two Parts, of BS 1647 has been prepared under the direction of the Laboratory Apparatus Standards Committee. This Part together with Part 1, supersedes BS 1647:1961 which is withdrawn.

Part 1 of this standard explains the development of the standard and specifies the pH scale.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 16, an inside back cover and a back cover

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

0 Introduction

As specified in Part 1 of this standard, the reference value standard solution is an aqueous solution of potassium hydrogen phthalate with a molality of 0.5 mol/kg.

Operational pH standards are those assigned pH values at various temperatures based on the operational cell measurements specified in clause 4, where the operational reference standard is solution *X* and the reference value standard is solution *S*. Values assigned by this method for 15 operational reference standards are given in Table 1 for various temperatures in the range 0 °C to 60 °C. Above 60 °C values have been obtained by extrapolation of the smoothing equations given in Table 2.

NOTE 1 pH values of operational standards are based on the work reported elsewhere [1, 2], using liquid junctions formed under highly reproducible conditions.

NOTE 2 Within the pH range 3 to 9, pH values assigned to operational reference standard solutions using the cell without a liquid junction (the method described in Part 1 of this standard for assigning the pH to the reference value standard solution) are within ± 0.02 of those given in Table 1 because the residual liquid junction errors are small. Some useful values are tabulated in Table 3. Outside the pH range 3 to 9, differences may be appreciable and operationally-derived values are preferred. For work of low accuracy class, many of the values relating to solutions with specialist application found in the literature could be employed [3].

1 Scope

This Part of BS 1647 specifies the preparation of the reference value standard solution used as the basis of the pH scale specified in Part 1 of this standard and requirements for operational reference standard solutions suitable for calibration of pH meters against this pH scale. It also specifies accuracy classes for pH measurements.

NOTE The titles of the publications referred to in this Part of this standard are listed on the inside back cover.

2 Definitions

For the purposes of this Part of BS 1647 the definitions given in Part 1 of this standard apply.

3 Preparation of the reference value standard solution

The purity of the material used in the preparation of the reference value standard solution shall be such that the pH value of the solution, when determined by the method described in Appendix A, is 4.005 ± 0.003 at 25 °C.

The reference value standard solution shall be prepared as described in Appendix B.

NOTE Methods of independently checking the purity of the reference value standard material are described in Appendix C and Appendix D.

4 Operational reference standard solution

The pH values of the operational reference standard solutions at temperatures between 0 °C and 60 °C shall be in accordance with the following equation:

$$\text{pH}(X) = \frac{E(S) - E(X)}{k} + \text{pH}(S) \quad (1)$$

where

k is the slope factor;

pH(*S*) is the pH value of the reference value standard solution;

E(*S*) and *E*(*X*) are the electromotive forces of the operational cells

Reference electrode || *X* | *H*₂ | Pt

Reference electrode || *S* | *H*₂ | Pt

The electromotive forces *E*(*X*) and *E*(*S*) of the operational cells shall be measured consecutively, both cells being at the same temperature throughout, and the same reference electrode shall be used in each cell.

NOTE 1 The hydrogen electrodes in both cells may be replaced by a single glass electrode transferred between the cells, subject to limitations of the glass electrode (see B.2 in BS 1647-1:1984).

NOTE 2 The pH difference, pH(*X*) – pH(*S*), is calculated.

The pH values of the operational reference standard solutions between 60 °C and 95 °C shall be in accordance with the following equation:

$$\text{pH}(X) = A + B(T - 298.15) + C(T - 298.15)^2 + D(T - 298.15)^3 \quad (2)$$

where the constants *A*, *B*, *C* and *D* are given in Table 2.

NOTE 3 Values of pH at various temperatures are given in Table 1.

NOTE 4 The two cells both involve liquid junctions because the reference electrode consists of a calomel or silver/silver chloride electrode in contact with a solution of potassium chloride of fixed concentration. Provided that the filling solution of a single junction reference electrode has a high concentration of potassium chloride (not less than 3.5 mol/L KCl), or the bridge solution of a double junction reference electrode has a high concentration of potassium nitrate (not less than 1 mol/L), the actual concentration has a negligible effect on the determined value of pH(*X*). For work of the highest accuracy, it is essential that the junction be formed in a reproducible fashion within a capillary tube as described in F.2.4.

NOTE 5 If the test solution is chemically incompatible with the reference electrode filling solution, it is necessary to use a bridge solution in the form of a double junction reference electrode.

NOTE 6 Factors pertinent to the choice of reference electrode are described in BS 2586.

NOTE 7 The preparation of the operational standard reference solutions listed in Table 2 is described in Appendix E.

Table 1 — pH values of operational reference standard solutions

Operational reference standard solution	Temperature (°C)												
	0	10	20	25	30	37	40	50	60	70	80	90	95
0.1 mol/kg potassium tetraoxalate	—	—	1.475	1.479	1.483	1.490	1.493	1.503	1.513	1.52	1.53	1.53	1.53
0.05 mol/kg potassium tetraoxalate	—	1.638	1.644	1.646	1.648	1.649	1.650	1.653	1.660	1.671 ^a	1.689 ^a	1.72	1.73
0.05 mol/kg sodium hydrogen diglycolate	—	3.470	3.484	3.492	3.502	3.519	3.527	3.558	3.595	—	—	—	—
Saturated potassium hydrogen tartrate	—	—	—	3.556	3.549	3.544	3.542	3.544	3.553	3.570 ^a	3.596 ^a	3.627 ^a	3.649 ^a
0.05 mol/kg potassium hydrogen phthalate	4.000	3.997	4.000	4.005	4.011	4.022	4.027	4.050	4.080	4.116	4.159	4.208	4.235
0.1 mol/L acetic acid + 0.1 mol/L sodium acetate	4.664	4.652	4.645	4.644	4.643	4.647	4.650	4.663	4.684	4.713	4.75	4.80	4.83
0.01 mol/L acetic acid + 0.01 mol/L sodium acetate	4.729	4.717	4.712	4.713	4.715	4.722	4.726	4.743	4.768	4.800	4.839 ^a	4.88	4.91
0.02 mol/kg piperazine orthophosphate	—	6.419	6.310	6.259	6.209	6.143	6.116	6.030	5.952	—	—	—	—
0.025 mol/kg disodium hydrogen orthophosphate + 0.025 mol/kg potassium dihydrogen orthophosphate	6.961	6.912	6.873	6.857	6.843	6.828	6.823	6.814	6.817	6.830	6.85	6.90	6.92
0.03043 mol/kg disodium hydrogen orthophosphate + 0.08695 mol/kg potassium dihydrogen orthophosphate ^c	7.506	7.460	7.423	7.406	7.390	7.369	—	—	—	—	—	—	—
0.04 mol/kg disodium hydrogen orthophosphate + 0.01 mol/kg potassium dihydrogen orthophosphate ^d	—	7.488	7.445	7.428	7.414	7.404	—	—	—	—	—	—	—
0.05 mol/kg Tris hydrochloride + 0.01667 mol/kg Tris ^b	8.399	8.083	7.788	7.648	7.513	7.332	7.257	7.018	6.794	—	—	—	—
0.05 mol/kg disodium tetraborate (borax)	9.475	9.347	9.233	9.182	9.134	9.074	9.051	8.983	8.932	8.898	8.88	8.84	8.89
0.01 mol/kg disodium tetraborate	9.451	9.329	9.225	9.179	9.138	9.088	9.066	9.009	8.965	8.932	8.91	8.90	8.89
0.025 mol/kg sodium hydrogen carbonate + 0.025 mol/kg sodium carbonate	10.27	10.154	10.045	9.995	9.948	9.889	9.866	9.800	9.753	9.728 ^a	9.725 ^a	9.75	9.77
Saturated calcium hydroxide	13.360	12.965	12.602	12.431	12.267	12.049	11.959	11.678	11.423	11.192 ^a	10.984 ^a	10.80	10.71

^a The last decimal figure is not significant but is included to facilitate smooth interpolation.^b NOTE Tris = Tris(hydroxymethyl) aminomethane.^c = ratio of 3.5 : 1.^d = ratio of 4 : 1.

Table 2 — Values of the constants for calculating pH values of operational reference standard solutions

$\text{pH}(X) = A + B(T - 298.15) + C(T - 298.15)^2 + D(T - 298.15)^3$				
Operational reference standard solution	Constant			
	A	$10^4 B$	$10^6 C$	$10^7 D$
0.1 mol/kg potassium tetraoxalate	1.4787	8.708	7.756	– 1.266
0.05 mol/kg potassium tetraoxalate	1.6462	3.184	– 8.733	3.136
0.05 mol/kg sodium hydrogen diglycolate	3.4924	18.871	27.983	0.4838
Saturated potassium hydrogen tartrate	3.5555	– 14.752	40.281	– 0.0301
0.05 mol/kg potassium hydrogen phthalate	4.0048	10.007	32.745	0
0.1 mol/L acetic acid + 0.1 mol/L sodium acetate	4.6435	– 0.7529	31.991	0.9828
0.01 mol/L acetic acid + 0.01 mol/L sodium acetate	4.7130	2.910	37.174	– 0.1575
0.02 mol/kg piperazine orthophosphate	6.2589	– 100.99	39.601	– 0.4978
0.025 mol/kg disodium hydrogen orthophosphate + 0.025 mol/kg potassium dihydrogen orthophosphate	6.8567	– 29.777	49.338	0.8568
0.03043 mol/kg disodium hydrogen orthophosphate + 0.08695 mol/kg potassium dihydrogen orthophosphate	7.4060	– 32.435	17.178	– 5.439
0.04 mol/kg disodium hydrogen orthophosphate + 0.01 mol/kg potassium dihydrogen orthophosphate	7.4277	– 31.767	80.661	14.713
0.05 mol/kg Tris hydrochloride + 0.01667 mol/kg Tris ^a	7.6484	– 274.70	96.190	– 2.493
0.05 mol/kg disodium tetraborate (borax)	9.1818	– 98.9233	75.587	0.9281
0.01 mol/kg disodium tetraborate	9.1793	– 87.021	81.179	– 2.189
0.025 mol/kg sodium hydrogen carbonate + 0.025 mol/kg sodium carbonate	9.9947	– 96.703	67.187	3.571
Saturated calcium hydroxide	12.4305	– 334.88	141.78	– 2.037
^a Tris = Tris(hydroxymethyl) aminomethane.				