



Designation: E70 – 24

Standard Test Method for pH of Aqueous Solutions With the Glass Electrode¹

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This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 This test method specifies the apparatus and procedures for the electrometric measurement of pH values of aqueous solutions with the glass electrode. It does not deal with the manner in which the solutions are prepared. pH measurements of good precision can be made in aqueous solutions containing high concentrations of electrolytes or water-soluble organic compounds, or both. It should be understood, however, that pH measurements in such solutions are only a semiquantitative indication of hydrogen ion concentration or activity. The measured pH will yield an accurate result for these quantities only when the composition of the medium matches approximately that of the standard reference solutions. In general, this test method will not give an accurate measure of hydrogen ion activity unless the pH lies between 2 and 12 and the concentration of neither electrolytes nor nonelectrolytes exceeds 0.1 mol/L (M).

1.2 The values stated in SI units are to be regarded as standard. The values in parentheses are for information only.

1.3 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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2. Referenced Documents

2.1 ASTM Standards:²

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)³

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 Other Documents:⁴

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200

3. Terminology

3.1 Definitions:

3.1.1 *pH, n*—defined formally as the negative logarithm to the base 10 of the conventional hydrogen ion activity. See Appendix X1.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 For the purpose of this test method, the term “meter” shall apply to the instrument used for the measurement of potential (either in millivolts or in terms of pH units), the term “electrodes” to the glass electrode and the reference electrode, and the term “assembly” to the combination of the meter and the electrodes. The performance of the meter shall be differentiated from that of the electrodes.

4. Significance and Use

4.1 pH is, within the limits described in 1.1, an accurate measurement of the hydrogen ion concentration and thus is widely used for the characterization of aqueous solutions.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard’s Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, <http://www.access.gpo.gov>.

*A Summary of Changes section appears at the end of this standard

4.2 pH measurement is one of the main process control variables in the chemical industry and has a prominent place in pollution control.

5. Apparatus

5.1 *pH meters*—Many excellent pH meters are available from commercial sources. To some extent, the choice of meter will depend on the desired precision of measurement. The meter may operate on a null-detection principle or may utilize digital readout or a direct deflection meter with a large scale. Power may be supplied by batteries or a-c operation may be provided. The maximum grid current drawn from the glass electrode during measurement shall not exceed 2×10^{-12} A. Automatic or manual adjustment shall allow for changes in $F/(RT \ln 10)$ when the temperature of the assembly is altered. For referee work, or in case of dispute, meters capable of discriminating changes of pH to 0.01 unit (0.6 mV) or less shall be used.

5.2 Reference Electrodes and Glass Electrodes:

5.2.1 The silver-silver chloride electrode is suitable as reference electrodes in pH assemblies (Note 1 and 7.2). The design of the electrode shall permit a fresh liquid junction between the solution of potassium chloride and the buffer or test solution to be formed for each test and shall allow traces of solution to be readily removed by washing.

NOTE 1—Other reference electrodes of constant potential may be used, provided no difficulty is experienced in standardizing the assembly as described in Section 8. Combination pH electrodes with or without integrated temperature sensor are permitted for use with this test method.

5.2.2 The silver-silver chloride electrode also is used widely as a reference electrode and has replaced the mercury containing calomel electrode.

5.2.3 Commercial glass electrodes are designed for certain specific ranges of pH and temperature; consequently, the pH and temperature of the test solutions shall be considered in selecting the glass electrode for use. The pH response shall

conform with the requirements set forth in Appendix X2. The leads shall be shielded from the effects of body capacitance.

5.2.4 If the assembly is in intermittent use, the ends of the electrodes shall be immersed between measurements in a solution that follows the manufacturer's recommendation for electrode storage, (that is, 3 M KCL). If you do not have storage solution, you may use a pH 4 buffer solution as backup. For prolonged storage, follow the manufacturer's recommendations for electrode storage. Glass electrodes may be allowed to become dry (see Note 2), and reference electrodes shall be capped to prevent undue evaporation.

NOTE 2—New glass electrodes and those that have been stored dry shall be conditioned as recommended by the manufacturer. Requirements for the physical dimensions and shape of the electrodes and the composition of the internal reference solution are not considered part of this test method.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Commercially prepared solutions are acceptable for use.

6.2 *Buffer Solutions*—Commercially available, water-based buffer solutions with pH values of 4, 7, 9, 10 or other values to bracket the measurement of samples are acceptable for the standardization.

⁵ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 1 pH(S) of Standard Solutions^{A,B}

Temperature, °C	A	B	C	D	E	F
0	3.863	4.003	6.984	7.534	9.464	10.317
10	3.820	3.998	6.923	7.472	9.332	10.179
20	3.788	4.002	6.881	7.429	9.225	10.062
25	3.776	4.008	6.865	7.413	9.180	10.012
30	3.766	4.015	6.853	7.400	9.139	9.966
35	3.759	4.024	6.844	7.389	9.102	9.925
40	3.753	4.035	6.838	7.380	9.068	9.889
50	3.749	4.060	6.833	7.367	9.011	9.828
60	...	4.091	6.836	...	8.962	...
70	...	4.126	6.845	...	8.921	...
80	...	4.164	6.859	...	8.885	...
90	...	4.205	6.877	...	8.850	...

^A The compositions of the standard solutions are:

A—KH₂ citrate, $m = 0.05 \text{ mol kg}^{-1}$

B—KH phthalate, $m = 0.05 \text{ mol kg}^{-1}$

C—KH₂PO₄, $m = 0.025 \text{ mol kg}^{-1}$; Na₂HPO₄, $m = 0.025 \text{ mol kg}^{-1}$

D—KH₂PO₄, $m = 0.008695 \text{ mol kg}^{-1}$; Na₂HPO₄, $m = 0.03043 \text{ mol kg}^{-1}$

E—Na₂B₄O₇, $m = 0.01 \text{ mol kg}^{-1}$

F—NaHCO₃, $m = 0.025 \text{ mol kg}^{-1}$; Na₂CO₃, $m = 0.025 \text{ mol kg}^{-1}$

where m denotes molality.

^B For a discussion of the manner in which these pH(S) values were assigned, see Chapter 4 of the book by Bates, R. G., *Determination of pH, Theory and Practice*, John Wiley and Sons, Second edition, New York, 1973.

6.3 *Preparation of pH Buffers*—The pH(S) of six recommended standard solutions at several temperatures is listed in Table 1. The buffer solutions shall be prepared from highly purified materials sold specifically as pH standards (Note 3). Potassium hydrogen phthalate and the two phosphate salts shall be dried at 110 °C for 1 h before use, but borax and sodium bicarbonate shall not be heated above room temperature. Potassium dihydrogen citrate shall be dried for 1 h at 80 °C, and sodium carbonate shall be ignited for 1 h at 270 °C before use. The standard solutions shall be prepared as described in 6.6 – 6.11. They shall be preserved in bottles of chemically resistant glass or polyethylene and shall be replaced at an age of six weeks, or earlier if a visible change should occur in the solution.

NOTE 3—Six of the buffer salts can be obtained in the form of standard reference materials from the National Bureau of Standards. These materials are numbered as follows:

Buffer Salt	SRM No.
Potassium hydrogen phthalate	185
Potassium dihydrogen phosphate	186I
Disodium hydrogen phosphate	186II
Borax	187
Sodium bicarbonate	191
Sodium carbonate	192

The pH(S) values may vary slightly from one lot to another; consequently, the values given on the SRM certificate should be used in preference to those given in Table 2, if slight differences exist.

6.4 Commercial standard buffers are available. For the most exact measurements, the value of the commercial buffer should be verified using one of the recommended standard buffers in Table 1.

6.5 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type I or Type II. For the preparation of the citrate, phthalate, and phosphate solutions, the water need not be freed of dissolved carbon dioxide. The water used for the borax standard and the carbonate standard shall be boiled for 15 min or purged with air free of carbon dioxide and shall be protected with a soda-lime tube or equivalent while cooling and in storage. The pH of the carbon dioxide-free water shall be between 6.6 and 7.5 at 25 °C. The temperature of the water used to prepare the standards shall be within 2 °C of 25 °C. The amounts of the buffer salts given in 6.3 through 6.8 are weights in air near sea level determined with brass weights.

6.6 *Citrate, Standard Solution A* (molality = 0.05 mol/kg; pH(S) = 3.776 at 25 °C)—Dissolve 11.41 g of potassium dihydrogen citrate in distilled water and dilute to 1 L.

6.7 *Phthalate, Standard Solution B* (molality = 0.05 mol/kg; pH(S) = 4.008 at 25 °C)—Dissolve 10.12 g of potassium hydrogen phthalate in distilled water and dilute to 1 L.

6.8 *Phosphate, Standard Equimolar Solution C* (molality of each phosphate salt = 0.025 mol/kg; pH(S) = 6.865 at 25 °C)—Dissolve 3.388 g of potassium dihydrogen phosphate and 3.533 g of disodium hydrogen phosphate in distilled water and dilute to 1 L.

6.9 *Phosphate, Standard Solution D (1 + 3)* (molality of KH₂PO₄ = 0.008695 mol/kg, molality of Na₂HPO₄ = 0.03043 mol/kg); pH(S) = 7.413 at 25 °C)—Dissolve 1.179 g of potassium dihydrogen phosphate and 4.302 g of disodium hydrogen phosphate in distilled water and dilute to 1 L.

6.10 *Borax, Standard Solution E* (molality = 0.01 mol/kg; pH(S) = 9.180 at 25 °C)—Dissolve 3.80 g of sodium tetraborate decahydrate (borax) in distilled water and dilute to 1 L.

6.11 *Carbonate, Standard Solution F* (molality of each carbonate salt = 0.025 mol/kg; pH(S) = 10.012 at 25 °C)—Dissolve 2.092 g of sodium bicarbonate and 2.640 g of sodium carbonate in distilled water and dilute to 1 L.

7. Hazards

7.1 Consult current OSHA regulations, suppliers' Safety Data Sheets, and local regulations for all materials used in this test method.

7.2 The use of the more toxic calomel (mercuric chloride) electrodes has been almost completely eliminated in commercial laboratories in the United States. They have been supplanted for the most part by safer silver-silver chloride reference electrodes, and to a smaller extent, by redox coupled systems such as an iodide salt system. Therefore, for safety reasons, it is recommended to use the safer, newer reference electrodes than the calomel reference electrode.

8. Calibration and Standardization

8.1 Set up the instrument in accordance with the manufacturer's instructions. Rinse the glass and reference electrodes with Type 1 or Type 2 water into a container. Allow the water to drain from the electrodes. Set the meter temperature setting to the ambient temperature of the lab and buffers.

8.2 Warm or cool test specimen to agree within 2 °C of buffer solutions used to calibrate the instrument. Follow the manufacturer's instructions for the calibration sequence taking care to rinse the electrodes after each measurement of buffer or standard solution. Calibrate the instrument with at least two standard solutions (Note 4) to bracket the anticipated pH, if possible. In order to reduce the effects of thermal and electrical hysteresis, keep the temperature of electrodes, standard solutions, and wash water within 2 °C or as close as possible. The calibration slope shall be in the 95 % to 100 % range, or the electrode will have to be cleaned or replaced.

NOTE 4—It is recommended to calibrate with three buffer solutions and reverify middle buffer meets method precision in order to detect a faulty glass electrode or incorrect temperature compensation. A procedure to test the pH electrode performance is found in Appendix X1.

8.3 If the anticipated pH of the test solution is less than 3.8, use the phthalate solution or appropriate commercial buffer for the initial standardization and the citrate solution as the second standard. If the anticipated pH of the test solution is greater

TABLE 2 Bias of pH Measurements

Nominal pH	Hydrogen Electrode	Glass Electrode	Difference
3.7	3.715	3.73	+ 0.015
6.5	6.519	6.53	+ 0.011
8.2	8.174	8.18	+ 0.006
8.4	8.478	8.45	- 0.028