



Designation: ~~E70~~—19 E70 – 24

## Standard Test Method for pH of Aqueous Solutions With the Glass Electrode<sup>1</sup>

This standard is issued under the fixed designation E70; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

*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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

~~D1193~~ Specification for Reagent Water

~~D1293~~ Test Methods for pH of Water

~~D5128~~ Test Method for On-Line pH Measurement of Water of Low Conductivity

~~D5464~~ Test Method for pH Measurement of Water of Low Conductivity

~~D6569~~ Test Method for On-Line Measurement of pH

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

<sup>1</sup> 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.

Current edition approved Nov. 1, 2019; Jan. 1, 2024. Published December 2019/January 2024. Originally approved in 1952. Last previous edition approved in 2015 as E70 – 07 (2015); E70 – 19. DOI: 10.1520/E0070-19; 10.1520/E0070-24.

<sup>2</sup> 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.

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

[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)<sup>3</sup>

[E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)

~~[E1910/E1910M Test Method for Agricultural pH Control Agents, Measurement of pH Change and Buffering Capacity](#)~~

2.2 *Other Documents:*<sup>4</sup>

[OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200](#)

### 3. Terminology

#### 3.1 Definitions:

3.1.1 ~~*pH*~~—*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.

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  $2 \times 10^{-12}$  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.

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

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

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.<sup>5</sup> 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.

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  $\pm 0.110\text{ }^{\circ}\text{C}$  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  $80\text{ }^{\circ}\text{C}$ , and sodium carbonate shall be ignited for 1 h at  $270\text{ }^{\circ}\text{C}$  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:

ASTM E70-24  
<https://standards.iteh.ai/catalog/standards/astm/fc2c4373-4b77-4fe5-ac2a-9a631fe8f3a9/astm-e70-24>  
**TABLE 1 pH(S) of Standard Solutions<sup>A,B</sup>**

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	...

<sup>A</sup> The compositions of the standard solutions are:

A—KH<sub>2</sub> citrate,  $m = 0.05\text{ mol kg}^{-1}$

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

C—KH<sub>2</sub>PO<sub>4</sub>,  $m = 0.025\text{ mol kg}^{-1}$ ; Na<sub>2</sub>HPO<sub>4</sub>,  $m = 0.025\text{ mol kg}^{-1}$

D—KH<sub>2</sub>PO<sub>4</sub>,  $m = 0.008695\text{ mol kg}^{-1}$ ; Na<sub>2</sub>HPO<sub>4</sub>,  $m = 0.03043\text{ mol kg}^{-1}$

E—Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>,  $m = 0.01\text{ mol kg}^{-1}$

F—NaHCO<sub>3</sub>,  $m = 0.025\text{ mol kg}^{-1}$ ; Na<sub>2</sub>CO<sub>3</sub>,  $m = 0.025\text{ mol kg}^{-1}$

where  $m$  denotes molality.

<sup>B</sup> 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.

<sup>5</sup> 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.

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 *Distilled Purity of Water*—The conductivity of the distilled water shall not exceed  $2 \times 10^{-6}$  S/cm mean Type I<sup>-1</sup>. For 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 ([Note 4](#)) 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.~~

~~Note 4—The water used for preparing the standard buffer solutions shall be Types I or II reagent water in accordance with Specification [D1193](#). Precautions shall be taken to prevent contamination of the distilled water with traces of the material used for protection against carbon dioxide.~~

~~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  $KH_2PO_4$  = 0.008695 mol/kg, molality of  $Na_2HPO_4$  = 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.

**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

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  $\pm 0.2^\circ\text{C}$  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 54) 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  $\pm 0.2^\circ\text{C}$  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 than 10.0, use an electrode designed for use at high alkalinities and observe the manufacturer's instructions.

8.4 If only an occasional pH determination is made, standardize the assembly each time it is used. In a long series of measurements, supplement initial and final standardizations by a check at intervals of 1 h, or longer if little or no change is found between successive standardizations.

## 9. Procedure

### 9.1 pH of Test Solutions:

9.1.1 Rinse the electrodes with Type 1 or Type 2 water. Fill the sample beaker with a sample aliquot sufficient to submerge electrodes and obtain a value for pH. In the case of well-buffered test solutions, one to three portions will usually be sufficient to yield pH values reproducible to  $\pm 0.02$  unit and that show drifts of less than  $\pm 0.01$  unit in  $\pm 1$  min or 2 min.

9.1.2 Measure the pH of water samples and slightly buffered solutions that are in equilibrium with the air as described in 9.1, except measure the pH of successive portions of water or test solutions, with vigorous agitation, until the observed results for two successive portions agree within 0.1 unit. Six or more portions may be necessary. The flow cell may also be used (see 9.2). If the water sample or the slightly buffered test solution is not in equilibrium with the carbon dioxide of the atmosphere, measure with external electrodes in a wide-mouth flask that has been flushed with carbon dioxide-free air, and protect the contents of the flask from exposure to air during the measurement.

### 9.2 pH of Flowing Streams:

9.2.1 Flow cells and electrode units for immersion in flow channels are an important feature of industrial pH control. In conjunction with electronic recorders and recorder-controllers, they provide the continuous measurements necessary for fully automatic regulation of pH. The flow cell is particularly advantageous for the determination of the pH of water or of sparingly buffered solutions. Simple dip measurements without agitation are subject to appreciable errors due to inadequate washing of the electrodes, solubility of the glass, and absorption of carbon dioxide during the measurement. A rapid flow of solution past the electrode maintains a clean glass interface, retards the tendency for fine solids to collect at the surface, minimizes errors resulting from solubility of the glass, and protects the sample from atmospheric contaminants.

9.2.2 *Flow Cell*—The flow unit may be of metal, glass, rubber, or plastic. If metal pipe connections are employed, they shall all be of the same metal. The volume of the unit shall be small, to permit a high rate of flow. If the cell is not provided with a resistance

thermometer for automatic temperature compensation (or if it is used in conjunction with a meter not equipped to utilize this feature), arrangements for monitoring the temperature of the solutions shall be provided. The unit and the leads shall be free from the effects of body capacitance.

**9.2.3 Standardization and pH Determination**—If the assembly is in continuous use, standardize it daily in accordance with the instructions given in Section 88. Use two standards in order to check the proper functioning of the electrodes. For a precision greater than  $\pm 0.1$  pH unit below pH 9, the temperature of the standard should be within  $2^{\circ}\text{C}$  of that of the flowing solution. For the measurement of pH, carefully observe the instructions furnished by the manufacturer of the meter or recorder.

**9.2.4 pH of Water and Slightly Buffered Solutions**—Maintain a flow rate sufficient to change the solution in the cell five times per minute. Do not read the pH of water or of a slightly buffered solution until the flow of water or test solution has been continued for at least 15 min following immersion of the electrodes in the standard buffer solution, or until a drift of less than 0.1 pH unit in 2 min is observed. If the pH of the flowing solution is changing, the glass electrode measurement may lag considerably behind the true pH.

## 10. Report

10.1 Report the pH to 0.01 unit and the temperature of the test solution to the nearest  $\pm 0.1^{\circ}\text{C}$ .

## 11. Precision and Bias<sup>6</sup>

**11.1 Intermediate Precision (formerly called Repeatability)**—The following criteria should be used for judging the acceptability of results obtained using separate glass and calomel electrodes (Duplicate results by the same operator should not be considered suspect (95 % confidence limit) unless they differ by more than 0.02 pH unit. **Notes 6 and 7**):

**11.1.1 Repeatability (Single Analyst)**—The standard deviation for a single determination has been estimated to be 0.006 pH unit at 106 dF. The 95 % limit for the difference between two such runs is 0.02 pH unit.

**11.1.1 Laboratory Precision (Within-Laboratory, Between-Days Variability)**—The standard deviation of results, each the average of duplicates, obtained by the same analyst on different days, has been estimated to be 0.022 pH unit at 53 dF. The 95 % limit for the difference between two such averages is 0.06 pH unit.

**11.1.2 Reproducibility (Multilaboratory)**—The standard deviation of results, each the average of duplicates, obtained by analysts in different laboratories, has been estimated to be 0.040 pH unit at 12 dF. The 95 % limit for the difference between two such averages is 0.11 pH unit.

**NOTE 5**—The above precision estimates are based on an interlaboratory study performed in 1973 on four buffer solutions having pH values of approximately 3.7, 6.5, 8.2, and 8.4. Fourteen laboratories analyzed each solution in duplicate and replicated the analysis on another day for a total of 224 determinations. A variety of commercial meters equipped with glass and calomel electrodes were used in this study. Practice E180 was used in developing these precision estimates.

**11.2 Bias**—The pH values of the buffer solutions, as determined using a hydrogen electrode at  $25^{\circ}\text{C}$ , are compared with the average values obtained using this test method in **Table 2**.

**11.3** The following limited interlaboratory study by ten laboratories in one company suggests that the precision obtainable with new combination electrodes is comparable to that in the 1973 study using separate electrodes.

**11.3.1** In 1994, a standard buffer solution of pH 4.63 was sent each laboratory which measured the pH once per day for three days. Each laboratory made the measurements using both a new and an old electrode. The results were analyzed using the techniques in Practice E691. Because of the design, no estimates for repeatability are possible. The estimates for Laboratory Precision and Repeatability are given in **Table 3**.

**NOTE 6**—These estimates of precision apply to optimum conditions, namely for pH measurements of well-buffered aqueous solutions. The precision attainable in measurements of the pH of water and other poorly buffered solutions will, in general, be of a considerably lower order.

<sup>6</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting RR:E15-1019. Contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org).