



Designation: **E70–07 E70 – 07 (Reapproved 2015)**

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

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 reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

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 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 Specification for Reagent Water

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)³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

3. Terminology

3.1 *Definitions:*

3.1.1 *pH*—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.

¹ This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.01 on General Standards.

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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.

*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 saturated calomel electrode and the 3.5 mol/L (M) calomel electrode are suitable as reference electrodes in pH assemblies (**Note 1**). If the saturated electrode is used, a few crystals of solid potassium chloride shall be present in the chamber surrounding the electrode element at each temperature. 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 88.

5.2.2 The silver-silver chloride electrode also is used widely as a reference 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 Section 77. 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 in distilled water between measurements. The high-alkalinity type of glass electrode shall be stored in the borax buffer solution. For prolonged storage, glass electrodes may be allowed to become dry, 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 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 6.4 – 6.9. 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
<u>Buffer Salt</u>	<u>SRM No.</u>
<u>Potassium hydrogen phthalate</u>	<u>185</u>
<u>Potassium dihydrogen phosphate</u>	<u>186I</u>
<u>Disodium hydrogen phosphate</u>	<u>186II</u>
<u>Borax</u>	<u>187</u>
<u>Sodium bicarbonate</u>	<u>191</u>
<u>Sodium carbonate</u>	<u>192</u>

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.

6.2 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**.

6.3 *Distilled Water*—The conductivity of the distilled water shall not exceed 2×10^{-6} s · cm⁻¹. 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

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	...

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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.

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

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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 5.3 through 5.8 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.

6.4 *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.

6.5 *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.

6.6 *Phosphate, Standard Equimolal 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.

6.7 *Phosphate, Standard Solution D (1 + 3)* (molality of $KH_2PO_4 = 0.008695 \text{ mol/kg}$; molality of $Na_2HPO_4 = 0.03043 \text{ mol/kg}$); $pH(S) = 7.413$ at $25^\circ C$ —Dissolve 1.179 g of potassium dihydrogen phosphate and 4.302 g of disodium hydrogen phosphate in distilled water and dilute to 1 L.

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

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

7. Performance Tests of Meter and Electrodes

NOTE 5—Except for measurements of the highest precision, it will usually be unnecessary to perform the tests described in this section. In the usual pH measurement, the stability of the meter, the accuracy of the scale reading, and the pH response of the glass electrode over the range of the measurements are verified by checking the assembly with a series of standard buffer solutions.

7.1 *Assembly*—The assembly shall be judged to be performing satisfactorily if it furnishes, within acceptable limits of accuracy, the correct pH values for the standard buffer solutions listed in Table 2. When the electrodes are immersed in a buffer solution, the measured potential difference shall be substantially constant, and the cause of any instability shall be determined.

7.2 *Meter*—The meter shall be brought to electrical balance in accordance with the manufacturer's instructions. The performance shall then be tested by applying a known variable potential through a resistance of approximately 200 M Ω to the terminals of the meter, the high-resistance lead being connected to the terminal corresponding to the glass electrode. The source of potential may be a precision-type potentiometer with a range of 1100 mV or more and a limit of error not greater than 0.1 mV. The 200-M Ω resistor shall be properly shielded to avoid capacity pickup. Commencing with a value of zero, the applied potential shall be increased in increments of 100 mV, and the readings of the dial of the meter at balance shall be noted. The process shall be extended to cover the entire range of the meter. In no case shall the difference between the applied voltage and that indicated by the meter differ by more than 1 mV per increment of applied voltage.

NOTE 6—If the cumulative error at the end of the scale exceeds ± 3 mV, a calibration curve for the meter shall be constructed and corrections applied to each measurement of electromotive force or pH. Differences of electromotive force (volts) are converted to corresponding differences of pH by multiplying by $F/(RT \ln 10)$ (Table X1.1). Inasmuch as the meter is made to read correctly at the pH of the standard, the calibration correction to be applied to a pH measurement is the difference between the scale corrections at the pH of the standard and that of the unknown, with due regard for sign.

7.3 *Glass Electrodes*—The difference of potential between the glass electrode and the standard hydrogen gas electrode shall be measured when both electrodes are immersed in the same portion of various buffer solutions over the pH range in which the glass electrode is to be used. For these comparisons the cell shall be placed in a water bath thermostatically controlled to $\pm 0.1^\circ C$ near $25^\circ C$. The solutions used for this test shall be those listed in Section 6. The standards of pH 9.18 and below (at $25^\circ C$) shall be used to test electrodes of the general-purpose type. The borax and carbonate standards shall be used to test the high-alkalinity type of electrode. These buffer solutions shall be supplemented by a 0.1 mol/kg (M) carbonate-free solution of sodium hydroxide, the pH of which is approximately 12.8 at $25^\circ C$. The difference of potential between the general-purpose glass electrode and the hydrogen electrode shall be independent, within ± 1 mV, of pH changes in the range from 3.8 to 9.18 pH. The difference of potential between the hydrogen electrode and a glass electrode of the high-alkalinity type shall be the same, within ± 3 mV, at pH 12.8 as at pH 9.18.

8. Calibration and Standardization

8.1 Turn on the instrument, allow to warm up thoroughly, and bring to electrical balance in accordance with the manufacturer's instructions. Wash the glass and reference electrodes and the sample cup three times with distilled water. Allow the water to drain from the electrodes, but the sample cup may be dried gently with clean absorbent tissue. Note the temperature of the test (unknown) solution and adjust the temperature dial of the meter to the proper setting.

8.2 Select two standard solutions (Note 7) to bracket the anticipated pH, if possible, and warm or cool these standards as necessary to match within $2^\circ C$ the temperature of the unknown. Fill the sample cup with the first standard and immerse the electrodes. Set the dial of the meter to the pH(S) value of the standard at the appropriate temperature as read from Table 2 or interpolated in the data therein (see Note 3). Engage the operating button and rotate the standardizing knob or asymmetry potential knob until the meter is brought to balance. In direct-reading meters engage the operating-button, or turn the range switch to the proper position, and rotate the asymmetry potential knob until the reading of the dial corresponds to the known pH of the standardizing buffer solution. Fill the sample cup repeatedly with additional portions of the standard solution until the instrument remains in balance with ± 0.02 pH unit for two successive portions without a change in the position of the asymmetry potential knob. If the temperature of the electrodes differs appreciably from that of the solutions, use several portions of solution and immerse the electrodes deeply to assure that both electrodes and standard are at the desired temperature. In order to reduce the effects of thermal and electrical hysteresis, keep the temperature of electrodes, standard solutions, and wash water as close to that of the unknowns as possible.

8.2.1 Wash the electrodes and sample cup three times with distilled water. Place the second standard in the sample cup, adjust the instrument to the new balance point, and read the pH from the dial. Do not change the setting of the asymmetry potential knob.