



Standard Test Methods for pH of Water¹

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

1. Scope

1.1 These test methods cover the determination of pH by electrometric measurement using the glass electrode as the sensor. Two test methods are given as follows:

Test Method A—Precise Laboratory Measurement	Sections 8 to 15
Test Method B—Routine or Continuous Measurement	16 to 24

1.2 Test Method A covers the precise measurement of pH in water utilizing at least two of seven standard reference buffer solutions for instrument standardization.

1.3 Test Method B covers the routine measurement of pH in water and is especially useful for continuous monitoring. Two buffers are used to standardize the instrument under controlled parameters, but the conditions are somewhat less restrictive than those in Test Method A. For on-line measurement, also see Test Method [D6569](#) which provides more detail.

1.4 Both test methods are based on the pH scale established by NIST (formerly NBS) Standard Reference Materials.²

1.5 Neither test method is considered to be adequate for measurement of pH in water whose conductivity is less than about 5 μ S/cm. Refer to Test Methods [D5128](#) and [D5464](#).

1.6 Precision and bias data were obtained using buffer solutions only. It is the user's responsibility to assure the validity of these test methods for untested types of water.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *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.*

¹ These test methods are under the jurisdiction of ASTM Committee [D19](#) on Water and are the direct responsibility of Subcommittee [D19.03](#) on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

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² "Standard Reference Materials: Standardization of pH Measurements" Wu and Koch, NBS Special Publications No. 260-53, 1988.

2. Referenced Documents

2.1 *ASTM Standards:*³

- [D1066 Practice for Sampling Steam](#)
- [D1067 Test Methods for Acidity or Alkalinity of Water](#)
- [D1129 Terminology Relating to Water](#)
- [D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits \(Withdrawn 2003\)](#)⁴
- [D1193 Specification for Reagent Water](#)
- [D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)
- [D3370 Practices for Sampling Water from Closed Conduits](#)
- [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](#)
- [E70 Test Method for pH of Aqueous Solutions With the Glass Electrode](#)

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology [D1129](#).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *pH, n*—the negative logarithm of the hydrogen ion activity in an aqueous solution or the logarithm of the reciprocal of the hydrogen ion activity.

3.2.1.1 *Discussion*—the pH of an aqueous solution is derived from E , the electromotive force (emf) of the cell



(where the double vertical line represents a liquid junction) when the electrodes are immersed in the solution in the diagrammed position, and E_s is the electromotive force obtained when the electrodes are immersed in a reference buffer solution.

With the assigned pH of the reference buffer designated as

³ 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.

⁴ The last approved version of this historical standard is referenced on www.astm.org.

TABLE 1 Slope Factor at Various Temperatures

Temperature, °C	Slope, millivolts
0	54.20
5	55.19
10	56.18
15	57.17
20	58.17
25	59.16
30	60.15
35	61.14
40	62.13
45	63.13
50	64.12
55	65.11
60	66.10
65	67.09
70	68.09
75	69.08
80	70.07
85	71.06
90	72.05
95	73.05

pH_s, and E and E_s expressed in volts is the following:⁵

$$\text{pH} = \text{pH}_s + \frac{(E - E_s)F}{2.3026 RT}$$

where:

- F = Faraday constant,
- R = gas constant, and
- T = absolute temperature, $t(^{\circ}\text{C}) + 273.15$.

The reciprocal of $F/2.3026 RT$ is known as the slope of the electrode, and is the expected difference in observed voltage for two measurements one pH unit apart. Values of the slope at various temperatures are given in [Table 1](#).

4. Summary of Test Method

4.1 The pH meter and associated electrodes are standardized against at least two reference buffer solutions that closely bracket the anticipated sample pH. The sample measurement is made under strictly controlled conditions and prescribed techniques.

5. Significance and Use

5.1 The pH of water is a critical parameter affecting the solubility of trace minerals, the ability of the water to form scale or to cause metallic corrosion, and the suitability of the water to sustain living organisms. It is a defined scale, based on a system of buffer solutions² with assigned values. In pure water at 25°C, pH 7.0 is the neutral point, but this varies with temperature and the ionic strength of the sample.⁶ Pure water in equilibrium with air has a pH of about 5.5, and most natural uncontaminated waters range between pH 6 and pH 9.

⁵ Bates, R. G., *Determination of pH: Theory and Practice*, 2nd Ed., J. Wiley and Sons, New York, 1973, p. 29.

⁶ The relative acidity or alkalinity measured by pH should not be confused with total alkalinity or total acidity (for example, Test Methods [D1067](#)). Thus, 0.1 M HCl and 0.1 M acetic acid have the same total acidity, but the HCl solution will be more acidic (approximately pH 1 versus pH 3.).

6. Purity of Reagents

6.1 Reagent grade chemicals shall be used in all tests, except as specifically noted for preparation of reference buffer solutions. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁷ 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification [D1193](#), Type I.

7. Sampling

7.1 Collect samples in accordance with Practice [D1066](#), or Practices [D3370](#), whichever is applicable.

TEST METHOD A—PRECISE LABORATORY MEASUREMENT OF pH

8. Scope

8.1 This test method covers the precise measurement of pH in water under strictly controlled laboratory conditions.

9. Interferences

9.1 The glass electrode reliably measures pH in nearly all aqueous solutions and in general is not subject to solution interference from color, turbidity, colloidal matter, oxidants, or reductants.

9.2 The reference electrode may be subject to interferences and should be chosen to conform to all requirements of Sections [10](#) and [12](#). Refer also to Appendix [X1.3](#).

9.3 The true pH of an aqueous solution or extract is affected by the temperature. The electromotive force between the glass and the reference electrode is a function of temperature as well as pH. The temperature effect can be compensated automatically in many instruments or can be manually compensated in most other instruments. The temperature compensation corrects for the effect of changes in electrode slope with temperature but does not correct for temperature effects on the chemical system being monitored. It does not adjust the measured pH to a common temperature; therefore, the temperature should be reported for each pH measurement. Temperature effects are discussed further in Appendix [X1.2](#).

9.4 The pH response of the glass electrode/reference electrode pair is imperfect at both ends of the pH scale. The indicated pH value of highly alkaline solutions may be too low, by as much as 1 pH, depending on electrode composition and sample conditions. See [X1.5.1](#). The indicated pH value of strong aqueous solutions of salts and strong acids having a pH

⁷ *Reagent Chemicals, American Chemical Society Specifications*, 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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

TABLE 2 Approximate pH_s of Reference Buffer Solutions^A

Temperature, °C	Tetroxalate Solution	Tartrate Solution	Phthalate Solution	Phosphate Solution	Borax Solution	Sodium Bicarbonate Sodium Carbonate	Calcium Hydroxide Solution
0	1.67	...	4.00	6.98	9.46	10.32	13.42
5	1.67	...	4.00	6.95	9.39	10.25	13.21
10	1.67	...	4.00	6.92	9.33	10.18	13.00
15	1.67	...	4.00	6.90	9.28	10.12	12.81
20	1.68	...	4.00	6.88	9.23	10.06	12.63
25	1.68	3.56	4.00	6.86	9.18	10.01	12.45
30	1.68	3.55	4.01	6.85	9.14	9.97	12.29
35	1.69	3.55	4.02	6.84	9.11	9.93	12.13
40	1.69	3.55	4.03	6.84	9.07	9.89	11.98
45	1.70	3.55	4.04	6.83	9.04	9.86	11.84
50	1.71	3.55	4.06	6.83	9.02	9.83	11.71
55	1.72	3.55	4.07	6.83	8.99	...	11.57
60	1.72	3.56	4.09	6.84	8.96	...	11.45
70	1.74	3.58	4.12	6.85	8.92
80	1.77	3.61	4.16	6.86	8.89
90	1.79	3.65	4.19	6.88	8.85
95	1.81	3.67	4.21	6.89	8.83

^AFor a discussion of the manner in which these pH values were assigned, see Bates, R. G., "Revised Standard Values for pH Measurements from 0 to 95°C," *Journal of Research*, NBS, Vol 66A, 1962, p. 179. The reference values were obtained without a liquid junction, which has an uncertainty of ±0.005. Liquid junction electrode values may have an uncertainty of ±0.012, with uncertainty ± 0.03 for the tetroxalate and the Ca(OH)₂. More recent values have been published in *pH Measurement* by Helmuth Galster, VCH Publishers, Inc., New York, 1991.

less than 1, will often be higher than the true pH value. Interferences can be minimized by the selection of the proper glass and reference electrodes for measurements in highly alkaline or acidic solutions.

9.5 A few substances sometimes dispersed in water appear to poison the glass electrode. A discussion of this subject is given in Appendix X1.4.

10. Apparatus

10.1 *Laboratory pH Meter*—Almost all commercially available meters are of the digital type and will have either manual or automatic calibration, and either manual or automatic temperature (slope) correction. All four types are permissible. However, readability to 0.01 pH is essential (Section 14), and the ability to read in millivolts is useful in troubleshooting.

10.2 *Glass Electrode*—The pH response of the glass electrode shall conform to the requirements set forth in 12.1 through 12.6. The glass electrode lead wire shall be shielded. New glass electrodes and those that have been stored dry shall be conditioned and maintained as recommended by the manufacturer.

10.3 *Reference Electrode*—This may be used as separate "half cell," or it may be purchased integral with the glass pH electrode body, as a combination electrode. The internal reference element may be calomel (mercury/mercurous chloride), silver/silver chloride, or an iodide-iodine redox couple. For best performance, the reference element should be the same type in both the reference electrode and inside the pH electrode. For all three types, the junction between the reference filling solution and the sample may be either a flowing or nonflowing junction. The flowing liquid junction-type unit ensures that a fresh liquid junction is formed for each measurement and shall be used for Test Method A determinations. If a saturated calomel electrode is used, some potassium

chloride crystals shall be contained in the saturated potassium chloride solution. If the reference electrode is of the flowing junction type, the design of the electrode shall permit a fresh liquid junction to be formed between the reference electrode solution and the buffer standard or tested water for each measurement and shall allow traces of solution to be washed from the outer surfaces of the electrodes. To ensure the desired slow outward flow of reference electrode solution, the solution pressure inside the liquid junction should be kept somewhat in excess of that outside the junction. In nonpressurized applications, this requirement can be met by maintaining the inside solution level higher than the outside water level. If the reference electrode is of the nonflowing junction type, these outward flow and pressurization considerations do not apply. The reference electrode and junction shall perform satisfactorily as required in the standardizing procedure described in 12.1 through 12.6. A discussion of reference electrodes is given in Appendix X1.3.

10.4 *Temperature Compensator*—The thermocompensator is a temperature-sensitive resistance element immersed in the water sample with the electrodes. The thermocompensator may be incorporated into the pH electrode or may be a separate probe. The thermocompensator automatically corrects for the change in slope of the glass electrode (with change of temperature) but does not correct for actual changes in sample pH with temperature. The automatic thermocompensator is not required if the water temperature is essentially constant and the analyst chooses to use the manual temperature compensation feature of the pH meter.

11. Reagents

11.1 *Reference Buffer Solutions* —The approximate pH values of the reference buffer solutions measured at several temperatures are listed in Table 2. If traceability to NIST