

**ASTM-D1293**

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# Standard Test Methods for pH of Water<sup>1</sup>

This standard is issued under the fixed designation D 1293; 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 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:

|                                                 | Sections |
|-------------------------------------------------|----------|
| Test Method A—Precise Laboratory Measurement    | 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.

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

1.5 Neither test method is considered to be adequate for measurement of pH in water whose conductivity is less than about 5 μS/cm. Refer to Test Methods D 5128 and D 5464.

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 *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:

- D 1066 Practice for Sampling Steam<sup>3</sup>
- D 1067 Test Methods for Acidity or Alkalinity of Water<sup>3</sup>
- D 1129 Terminology Relating to Water<sup>3</sup>
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits<sup>3</sup>

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-19 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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<sup>2</sup> “Standard Reference Materials: Standardization of pH Measurements” Wu and Koch, NBS Special Publications No. 260-53, 1988.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

D 1193 Specification for Reagent Water<sup>3</sup>

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>3</sup>

D 3370 Practices for Sampling Water from Closed Conduits<sup>3</sup>

D 5128 Test Method for On-Line pH Measurement of Water of Low Conductivity<sup>3</sup>

D 5464 Test Methods for pH Measurement of Water of Low Conductivity<sup>3</sup>

E 70 Test Method for pH of Aqueous Solutions with the Glass Electrode<sup>4</sup>

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

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

glass electrode | solution || reference electrode

(where the double vertical line represents a liquid junction) when the electrodes are immersed in the solution in the diagrammed position, and *E<sub>s</sub>* 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 pH<sub>s</sub>, and *E* and *E<sub>s</sub>* expressed in volts is the following:<sup>5</sup>

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

where:

*F* = Faraday,

*R* = gas constant, and

*T* = absolute temperature, *t* (°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

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             |

against 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 solutions<sup>2</sup> 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.<sup>6</sup> 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.

## 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.<sup>7</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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I.

<sup>6</sup> The relative acidity or alkalinity measured by pH should not be confused with total alkalinity or total acidity (for example, Test Methods D 1067). 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.).

<sup>7</sup> *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.

## 7. Sampling

7.1 Collect samples in accordance with Practice D 1066, Specification D 1192, or Practices D 3370, 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 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 12.5. 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.