



## Standard Test Method for pH Measurement of Water of Low Conductivity<sup>1</sup>

This standard is issued under the fixed designation D 5464; 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.

### 1. Scope

1.1 This test method is applicable to determine the pH of water samples with a conductivity of 2 to 100  $\mu\text{S}/\text{cm}$  over the pH range of 3 to 11. pH measurements of water of low conductivity are problematic. Specifically, this test method avoids contamination of the sample with atmospheric gases and prevents volatile components of the sample from escaping. This test method provides for pH electrodes and apparatus that address additional considerations discussed in **Annex A2**. This test method also minimizes problems associated with the sample's pH temperature coefficient when the operator uses this test method to calibrate an on-line pH monitor or controller (see **Appendix X1**).

1.2 This test method covers the measurement of pH in water of low conductivity with a lower limit of 2.0  $\mu\text{S}/\text{cm}$ , utilizing a static grab-sample procedure where it is not practicable to take a real-time flowing sample.

NOTE 1—Test Method **D 5128** for on-line measurement is preferred over this method whenever possible. Test Method **D 5128** is not subject to the limited conductivity range, temperature interferences, potential KCl contamination, and time limitations found with this method.

1.3 For on-line measurements in water with conductivity of 100  $\mu\text{S}/\text{cm}$  and higher, see Test Method **D 6569**.

1.4 For laboratory measurements in water with conductivity of 100  $\mu\text{S}/\text{cm}$  and higher, see Test Method **D 1193**.

1.5 The values stated in SI units are to be regarded as standard.

1.6 *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:<sup>2</sup>

**D 1129** Terminology Relating to Water

**D 1193** Specification for Reagent Water

**D 1293** Test Methods for pH of Water

**D 2777** Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

**D 4453** Practice for Handling of Ultra-Pure Water Samples

**D 5128** Test Method for On-Line pH Measurement of Water of Low Conductivity

**D 6569** Test Method for On-Line Measurement of pH

### 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 **liquid junction potential**—a dc potential which appears at the point of contact between the reference electrode's salt bridge (also known as reference junction or diaphragm) and the sample solution. Ideally this potential is near zero, and is stable. However, in low conductivity water it may change from its value in buffer solution by an unknown amount, and is a zero offset (**1**).<sup>3</sup>

### 4. Reagents

4.1 **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>4</sup> Other grades may be used,

<sup>1</sup> 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

<sup>4</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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type III of Specification [D 1193](#).

4.3 *Commercial Buffer Solutions*—Commercially available prepared buffers traceable to NIST standards should be adequate to perform the calibration procedures in [10.1-10.4](#). The exact pH of the buffer will change with temperature and this pH versus temperature data will be provided by the purveyor of the specific buffer. Refer to Test Methods [D 1293](#) for the preparation of reference buffer solutions if desired.

4.4 *Buffer A*—Commercially available 7.0 pH buffer.

4.5 *Buffer B*—Commercially available 4.0 pH buffer.

4.6 *Buffer C*—Commercially available 9.0 or 10.0 pH buffer.

## 5. Summary of Test Method

5.1 The pH meter and associated electrodes are first standardized with two calibration pH buffer solutions.

5.2 A grab sample of high purity water is taken by means of rinsing and filling two narrow mouth bottles at the sample point. Once each container is filled to the top with a representative sample excluding any air, the container is capped and the samples are transported quickly to a laboratory for analysis.

5.3 pH measurement of the sample is made with high purity water pH calibration apparatus comprised of pH and reference electrodes, and automatic temperature compensator (if used). The first container is used to rinse the sensors and begin temperature equilibration and the second container is used for measurement.

5.4 A trace amount of KCl electrolyte enters calibration buffer solutions and samples via the controlled leakage rate of the reference electrode liquid junction (diaphragm) to stabilize the liquid junction potential. Excessive KCl introduction from the electrode liquid junction into low ionic strength samples will increase solution conductivity, and may alter solution pH, and should be avoided.

5.5 Temperature must be measured and both Solution Temperature Coefficient (STC) and Nernstian electrode effects compensated, either manually to the measured value or automatically by the pH meter. See [Appendix X1](#) for a discussion of temperature effects.

## 6. Significance and Use

6.1 pH measurement of low conductivity water is frequently applied to power plant water and condensed steam samples for corrosion and scale prevention. It is sometimes used in pure water treatment systems between multiple pass membranes to optimize performance.

6.2 High purity water is highly unbuffered and small amounts of contamination can change the pH significantly. Specifically, high purity water rapidly absorbs CO<sub>2</sub> gas from the atmosphere, which lowers the pH of the sample. The sample container and accompanying pH measurement technique minimize exposure of the high purity water sample to the atmosphere.

6.3 The high purity water sample may contain volatile trace components that will dissipate from the sample if exposed to the atmosphere. The sample container used in this test method will prevent these losses.

6.4 High purity water has a significant solution temperature coefficient. For greatest accuracy the sample to be measured should be close to the temperature of the sample stream and appropriate compensation should be applied.

6.5 When the preferred Test Method [D 5128](#), which requires a real-time, flowing sample, cannot be utilized for practical reasons such as physical plant layout, unacceptable loss of water, location of on-line equipment sample points, or availability of dedicated test equipment, this method offers a viable alternative. The most significant difference between the two test methods is that Test Method [D 5128](#) obtains a real-time pH measurement from a flowing sample and this method obtains a time delayed pH measurement from a static grab sample.

6.6 pH measurements of low conductivity water are always subject to interferences ([7.1-7.5](#)) and Test Method [D 5128](#) is more effective in eliminating these interferences especially with regard to contamination. This static grab sample method is more prone to contamination and temperature-induced errors because of the time lag between the sampling in the plant and sample pH reading which is taken in the laboratory.

## 7. Interferences

7.1 High purity, low conductivity samples are especially sensitive to contamination from atmospheric gases, from sample containers, from sample handling techniques and from excessive electrolyte (KCl) contamination from reference electrode or sample preparation such as a KCl “dosing” technique. Refer to Practice [D 4453](#) and *ASTM STP 823 (2)* for discussions of sample handling and avoidance of sample contamination.

7.2 High purity water will rapidly absorb CO<sub>2</sub> from the atmosphere and this will lower the pH of the sample at a rate depending on the buffer capacity of the sample, the surface area of the sample exposed to air, movement of the sample, and the concentration of CO<sub>2</sub> at the surface of the sample which may increase if the operator exhales over the container during sampling or measurement. See [Appendix X3](#), [Table X3.1](#), and [Fig. X3.1](#).

7.3 The temperature stability of the sample and how closely the sample’s temperature matches the sample stream’s temperature will have a direct effect on accuracy of the pH determination since temperature compensation is not perfect.

7.4 If pH is to be referenced to 25°C as required by most specifications, temperature compensation must be provided for both the Nernstian response of the electrode output (provided in most pH meters) and solution ionization effects (provided only with some on-line pH meters or by calculation with lab meters). For a discussion of temperature effects on pH measurements of high purity water see [Appendix X1](#).

7.5 The reference junction potential can vary with ionic strength of the sample and provide an undetectable zero offset between the high ionic strength of the buffer solution and the low ionic strength of the sample. A flowing junction reference

electrode (one which requires periodic refilling with electrolyte solution or that has internal electrolyte pressurization or both) minimizes this effect.

## 8. Apparatus

8.1 *pH Meter*—See 10.1 in Test Methods [D 1293](#).

8.2 *Sample Containers*—Two clean, narrow-mouth 250 to 500 mL bottles with cap are required. The mouth diameter should be the minimum necessary to allow insertion of the electrode(s), and temperature compensator or thermometer. A 3-hole stopper may be used to hold these sensors. The container and cap minimize exposure to atmospheric gases.

8.3 *Combination pH Electrode*—A probe incorporating the measuring, reference and temperature compensator functions in a single unit is recommended for its ease of insertion into a very narrow mouth sample container. Each function should conform to the characteristics in [8.4-8.6](#). Where this is not available, individual electrodes and compensator ([8.4-8.6](#)) may be used with a 3-hole stopper to hold them and seal the container during measurement.

8.4 *pH Glass Electrode*—The pH response of the glass electrode shall conform to the requirements set forth in 12.1 through 12.5 of Test Methods [D 1293](#). New glass electrodes and those that have been stored dry shall be conditioned and maintained as recommended by the manufacturer.

8.5 *Reference Electrode*—Double junction design, having a flowing junction with a positive electrolyte leakage rate not to exceed 10  $\mu\text{L/h}$ . Prepare and maintain the reference electrode according to the manufacturer's instructions.

8.6 *Temperature Compensator*—See paragraph 10.4 in Test Methods [D 1293](#). The automatic temperature compensator must adapt for use with the sample container to measure the temperature of the water within the container.

8.7 *Temperature Indicator*—A direct temperature indicating device must be used to measure sample water temperature within the sample container if an automatic temperature compensator is not used.

## 9. Sampling and Sample Handling

9.1 Equipment described in Section [8](#) should be dedicated for high purity water use only.

9.2 The sample containers should be rinsed three times before use, with sample or reagent water. The electrode(s) and temperature device should be rinsed three times, using the same procedure as with the sample containers after each calibration in pH buffer solutions and before they are inserted into the first sample container.

9.3 Static grab samples are taken via vinyl tubing attached to the sample take-off point. The other end of the tubing is inserted to the bottom of the sample container. The sample flows through the vinyl tube, into the bottom of the container, and then over the top to trough or sink drain. After a 5-min flush of the container with the sample water, the tubing is removed and the cap immediately installed, excluding any air. This seals the container and isolates the sample from the atmosphere. The second container is filled and capped in the same way. In the lab, the first container is used to rinse the electrodes and temperature device and the second container is used for measurement.

## 10. Calibration

10.1 Turn on the pH meter and allow it to warm up according to the manufacturer's instructions.

10.2 Remove the electrode(s) and temperature compensator (if used) from storage. Check the reference electrode for proper electrolyte level as recommended by the manufacturer.

10.3 Calibrate the electrode(s) and pH meter at two points according to manufacturer's instructions. Also, refer to Section 12 of Test Methods [D 1293](#) for guidelines on the calibration of a pH meter and electrode assembly. Use a quiescent sample of Buffer A and Buffer B if the sample point of interest is below 7.0 pH. Use a quiescent sample of Buffer A and Buffer C if the sample point of interest is above 7.0 pH. Use laboratory glassware dedicated for this service only. Thoroughly rinse the electrode(s) and glassware with reagent water three times between immersion in each buffer solution.

10.4 Obtain calibration precision of the pH electrode(s) and the pH meter by repeating the two-point calibration described in [10.3](#), making any necessary readjustments to the pH meter. If the electrode slope (efficiency) is less than 94 % or greater than 101 %, refer to manufacturer's instructions for repair or replacement of electrode(s).

NOTE 2—The pH electrodes in use may pass the above calibration procedures ([10.1-10.4](#)), but caution should be taken. pH electrodes that are not specifically designed for use in high purity water may develop problems with liquid junction potential during actual test measurements.

10.5 Determine the frequency of the two-point calibration of the electrode(s) and the pH meter based on experience. Perform calibration at least daily when pure water sample testing is performed daily. For less frequent pure water sample testing, perform calibration procedures just prior to a consecutive series of sample tests.

10.6 Thoroughly rinse the electrode(s) and the temperature compensator or temperature reading device and the sample container three times with sample or reagent water after calibration and before measurement.

## 11. Procedure

11.1 Before starting the procedure, make certain the two sample containers are clean and empty.

NOTE 3—If on-line pH sensors are to be calibrated by this test method (refer to Test Method [D 5128](#)), steps must be taken to prevent the disturbance of the on-line pressure and flow rate while the grab sample is being taken. The pressure and flow control equipment shown in [Fig. 1](#) will control and stabilize this on-line pressure and flow rate by means of rotameter  $R_1$  and secondary pressure regulator  $PR_1$  even when a sample is taken at grab sample point  $S_2$  (see [Appendix X2](#)).

11.2 Open the sample valve  $V_2$  and pull sample without interrupting the sample flow-rate or pressure of the on-line pH sensor assembly (see on-line pH sensor manufacturer's instructions for its optimum flowrate). The grab sample flowrate should be at least 200 mL/min.

11.3 With the sample flowing, rinse the outside surfaces of the vinyl sample tubing for at least 15 seconds by holding it with the open discharge end upward like a fountain, allowing the sample to flow over the outside tubing surfaces for more than the length that will be later immersed in the sample container, allowing the flow to drain into the sampling trough or sink.