



Designation: D5015 – 15 (Reapproved 2022)

# Standard Test Method for pH of Atmospheric Wet Deposition Samples by Electrometric Determination<sup>1</sup>

This standard is issued under the fixed designation D5015; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method is applicable to the determination of pH in atmospheric wet deposition samples by electrometric measurement using either a pH half cell with a reference probe or a combination electrode as the sensor.

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

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

1.4 **Warning**—Mercury has been designated by many regulatory agencies as a hazardous material that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury-containing products. See the applicable product Safety Data Sheet (SDS) for additional information. Users should be aware that selling mercury or mercury-containing products into your state or country may be prohibited by law.

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>

[D1129 Terminology Relating to Water](#)

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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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.

[D1193 Specification for Reagent Water](#)

[D1356 Terminology Relating to Sampling and Analysis of Atmospheres](#)

[D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)

[D5012 Practice for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition](#)

[D5111 Guide for Choosing Locations and Sampling Methods to Monitor Atmospheric Deposition at Non-Urban Locations](#)

[E1 Specification for ASTM Liquid-in-Glass Thermometers](#)

[E2251 Specification for Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids](#)

[IEEE/ASTM SI-10 American National Standard for Metric Practice](#)

## 3. Terminology

3.1 *Definitions*:

3.1.1 *pH*—the negative logarithm to the base ten of the conventional hydrogen ion activity.

3.1.2 For definitions of other terms used in this test method, refer to Terminologies [D1129](#) and [D1356](#). For an explanation of the metric system including units, symbols, and conversion factors, see [IEEE/ASTM SI-10](#).

## 4. Summary of Test Method

4.1 The pH meter and the associated electrodes are calibrated with two reference buffer solutions that bracket the anticipated sample pH. The pH of the wet deposition sample is determined from this calibration and a quality control standard. The quality control standard is necessary in this application to evaluate the bias due to residual liquid junction potentials and to correct for this bias.

4.2 The pH of a solution is related to the EMF (millivolts) of a pH electrode system according to the operational definition for a two-point calibration:

$$\text{pH}(X) = \text{pH}(S_1) + \frac{E_x - E_{S_1}}{E_{S_2} - E_{S_1}} [\text{pH}(S_2) - \text{pH}(S_1)] \quad (1)$$

where:

$\text{pH}(X)$  = pH of an unknown sample,

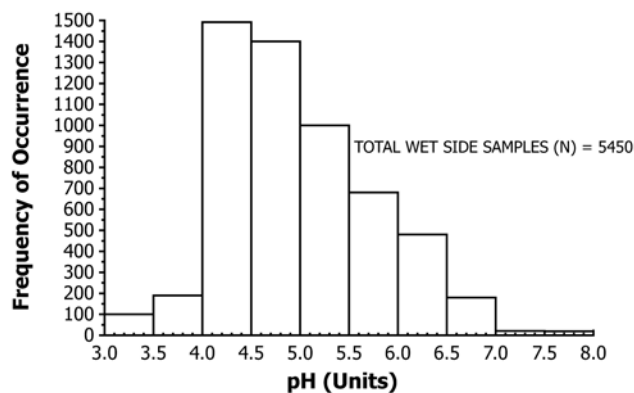


FIG. 1 Frequency Distribution of Measured Laboratory pH of Atmospheric Wet Deposition From the 1984 National Atmospheric Deposition Program (NADP)/National Trends Network (NTN)

- $pH(S_1)$  = pH of a Standard Solution 1,
- $pH(S_2)$  = pH of a Standard Solution 2,
- $E_X$  = EMF (mV) measured in an unknown sample,
- $E_{S_1}$  = EMF (mV) measured in Standard Solution 1, and
- $E_{S_2}$  = EMF (mV) measured in Standard Solution 2.

## 5. Significance and Use

5.1 The accurate measurement of pH in atmospheric wet deposition is an essential and critically important component in the monitoring of atmospheric wet deposition for trends in the acidity and overall air quality. Atmospheric wet deposition is, in general, a low ionic strength, unbuffered solution. Special precautions, as detailed in this test method, are necessary to ensure accurate pH measurements (1).<sup>3</sup> Special emphasis must be placed on minimizing the effect of the residual liquid junction potential bias.

5.2 This test method is applicable only to the measurement of pH in atmospheric wet deposition. Its use in other applications may result in inaccuracies.

5.3 Fig. 1 provides a frequency distribution of precipitation pH values measured in conjunction with a national monitoring program within the United States. These data are an indication of the range of pH values common to atmospheric wet deposition.

## 6. Interferences

6.1 The pH meter and the associated electrodes reliably measure pH in nearly all aqueous solutions and in general are not subject to solution interferences from color, turbidity, oxidants, or reductants.

6.2 The pH of an aqueous solution is affected by the temperature. The electromotive force (EMF) between the glass and the reference electrode is a function of temperature as well as pH. Temperature effects can be approximately compensated for automatically or manually depending on the pH meter selected.

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

6.3 Organic materials dispersed in water appear to poison the glass electrode, particularly when analyzing low ionic strength solutions. Difficulty encountered when standardizing the electrode(s), erratic readings, or slow response times may be an indication of contamination of the glass bulb or the liquid junction of the reference electrode. To remove these coatings, refer to the manual accompanying the probe for the manufacturer’s recommendations.

6.4 When analyzing samples that have low ionic strengths, such as wet deposition, an effect known as “residual junction potential” can lead to errors as large as 0.3 pH units. This error occurs when the junction potential of the sample differs greatly from that of the standard. These conditions are frequently met in wet deposition analyses when the electrodes are calibrated with high ionic strength standard reference buffers. In many cases, this error has been reduced by using a reference electrode with a ceramic junction (2, 3).

6.5 To speed electrode equilibration, the sample should be agitated prior to measurement. Care must be taken, however, to avoid introducing a source of error known as “residual streaming potential” that can result in a significant difference between the stirred and unstirred pH of the sample (4). The magnitude of the streaming potential is dependent on the electrodes and on the stirring rate. Differences in pH for stirred and unstirred wet deposition samples when the electrode assembly has been calibrated only with quiescent reference standards average 0.05 pH units at a stirring rate of four revolutions per second.

6.5.1 Eliminate the errors associated with residual streaming potentials by agitating all calibration standards and wet deposition samples thoroughly to speed electrode equilibration and then allowing each aliquot to become quiescent before taking a pH reading.

6.5.2 If magnetic stirring is used, take care not to contaminate the sample when inserting the stirring bar. Maintain an air space between the surface of the stirring motor and the sample container to prevent heating the wet deposition sample.

6.6 Laboratories used for the measurements of pH should be free from gaseous and particulate contaminants that may affect the true solution pH. Fumes from mineral acids such as hydrochloric acid, sulfuric acid, and nitric acid should be kept isolated from areas where pH measurements are made as well as alkaline fumes from solutions such as ammonia.

## 7. Apparatus and Equipment

7.1 *Laboratory pH Meter*—The meter may have either an analog or digital display with a readability of at least 0.01 pH units. A meter that has separate calibration and slope adjustment features and is electrically shielded to avoid interferences from stray currents or static charge is necessary. It may be powered by battery or 110 VAC; if battery powered, the meter must have a battery check feature. A temperature compensator control for measurements at temperatures other than 25 °C is desirable.

7.2 *Sensing Electrode*—Select a general purpose glass electrode that meets the performance criteria described in 12.2. This electrode type is characterized by a quick response, and

has a useful range from 2 to 11 pH units. This electrode should be used exclusively for atmospheric wet deposition measurements.

**7.3 Reference Electrode**—The reference electrode recommended for wet deposition analysis is one equipped with a ceramic junction with controlled leakage of the internal electrolyte fill solution. The ceramic construction minimizes differences in potential between high ionic strength buffers and low ionic strength samples thus reducing errors from residual junction potential (1). This electrode should be used exclusively for atmospheric wet deposition measurements.

**7.4 Combination Electrode**—The combination electrode combines the indicating and reference elements in a single unit. A ceramic reference junction is recommended (see 7.3). Since sample volume requirements are a consideration when analyzing wet deposition samples, combination electrodes are more convenient than separate glass and reference electrodes. This electrode should be used exclusively for atmospheric wet deposition measurements and must meet the criteria stated in 12.2.

**7.5 Temperature Control**—Use either a constant temperature water bath, a temperature compensator, or a thermometer (see Specifications E1 or E2251) to verify that all standards and samples are maintained at temperatures within  $\pm 1$  °C of one another. If a thermometer is used, select one capable of being read to the nearest 1 °C and covering the range from 0 to 40 °C.

**7.6 Stirring Device (Optional)**—Electric or water-driven. If an electric stirrer is selected, leave an air gap or place an insulating pad between the stirrer surface and the solution container to minimize heating of the sample. Use a fluorocarbon-coated stirring bar.

**7.7 Storage of Electrodes**—When not in use, soak the electrodes in a solution that is 0.1 mol/L of potassium chloride and 0.1 mmol/L of hydrochloric acid. Do not store the electrodes in buffers, concentrated acids, concentrated potassium chloride, basic solutions, or distilled water. Some manufacturers recommend dry storage for specific types of electrodes. If the electrode is of this specific type, store dry. Use these electrodes exclusively for atmospheric wet deposition measurements.

## 8. Reagents and Materials

**8.1 Purity of Reagents**—Use reagent or higher grade chemicals for all solutions. All reagents shall conform minimally to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS)<sup>4</sup> where such specifications are available.

**8.2 Purity of Water**—Use water conforming to Specification D1193, Type I. Point of use 0.2  $\mu$ m filters are recommended for all faucets supplying ASTM Type I water to prevent the

<sup>4</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.

**TABLE 1 National Institute of Standards and Technology (NIST) Salts for Reference Buffer Solutions**

NIST Standard Sample Designation	Buffer Salt <sup>a</sup>	pH at 25 °C
186-lf	potassium dihydrogen phosphate, 0.025 M	6.865
186-lif	disodium hydrogen phosphate, 0.025 M	6.865
185g	potassium hydrogen phthalate	4.003

<sup>a</sup> These buffer salts can be purchased from the Office of Standard Reference Materials, National Institute of Standards and Technology, Gaithersburg, MD 20899.

introduction of bacteria or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

**8.3 Buffer Solutions**—Either NIST buffers or commercially available buffer solutions traceable to NIST buffers must be used for standardization. These buffer solutions usually have pH values near 3, 4, 6, and 7, the exact pH and use temperature being provided by the supplier of the specific buffer. Table 1 identifies each buffer salt by its National Institute of Standards and Technology (NIST) number. Store the reference buffer solutions in polyethylene or chemical-resistant glass bottles and replace after one year or sooner if a visible change such as the development of colloidal or particulate materials is observed. Follow the directions on the Certificate of Analysis for preparing solutions of known pH (5).

**8.4 Quality Control Sample (QCS)**—Quality control samples of verified pH in an atmospheric wet deposition matrix are to be used. Internally formulated quality control samples (see 8.4.1) may be prepared by dilutions of strong acids with water. The pH of such samples must be verified by comparison with a NIST traceable low-ionic strength solution of known pH.

**8.4.1 Dilute Nitric Acid** ( $5.0 \times 10^{-5}$  mol/L HNO<sub>3</sub>)—Add 1.0 mL of concentrated nitric acid (HNO<sub>3</sub>, sp gr 1.42) to 0.5 L water, dilute to 1 L and mix well. Dilute 3.2 mL of this stock solution to 1 L with water. The resulting solution has a pH of  $4.30 \pm 0.10$  at 25 °C. Store at room temperature in a high-density polyethylene or polypropylene container. Various factors may affect the stability of this solution. Verify the pH of this solution with a NIST traceable standard at monthly intervals.

## 9. Safety Hazards

**9.1** The reference buffer solutions, sample types, and most reagents used in this test method pose no hazard to the analyst as used in this test method. Use a fume hood, protective clothing, and safety glasses when handling concentrated nitric acid.

**9.2** Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this test method (6).

## 10. Sample Collection, Preservation, and Storage

**10.1** Collect samples in high-density polyethylene (HDPE) containers that have been thoroughly rinsed with water. Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample.



Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection containers after cleaning to prevent contamination from airborne contaminants; air dry collection containers in a laminar flow clean air work station and wrap in polyethylene bags prior to use. If a laminar flow work station is not available, pour out any residual rinse water and bag or cap the containers immediately. Do not dry the container's interior by any method other than air drying in a laminar flow clean air work station.

10.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. Guide **D5111** further discusses some of these issues. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

10.3 The dissolution of particulate materials and the presence of microbial activity will affect the stability of hydrogen ions (pH) in wet deposition samples (7,8). This instability generally results in a decrease in hydrogen ions (higher pH). Refrigeration of samples at 4 °C will minimize but will not prevent a change in the hydrogen ion content.

10.3.1 A biocide such as chloroform (CHCl<sub>3</sub>) may be used to stabilize the organic acid component of the measured pH and to prevent pH changes due to biological reactions on other sample constituents (8). Add the chloroform (0.5 mL per 250 mL sample) to a separate sample aliquot that will be used only for the measurement of pH.

NOTE 1—Filtration of samples through a deionized water-leached 0.45 µm membrane is effective at stabilizing pH values that are influenced by the dissolution of alkaline particulate matter (7). Monitoring of the filtration procedure is necessary to ensure that samples are not contaminated by the membrane or filtration apparatus.

NOTE 2—Additional guidelines for sample collection, preservation, and storage are contained in Guide **D5012**.

## 11. Calibration

11.1 Turn on the meter and allow it to stabilize according to manufacturer's instructions.

11.2 If necessary, add filling solution to the reference electrode before using. Maintain the filling solution level at least 1 in. above the level of the sample surface to ensure proper electrolyte flow rate.

11.3 Select two reference buffer solutions that bracket the anticipated pH of the wet deposition sample. The difference between the nominal pH values of the two buffers should not exceed three units. Buffers of nominal pH 7 and pH 4 are recommended for wet deposition samples.

11.4 Bring buffers, QCS solutions, and wet deposition samples to the same temperature, within 1 °C. Determine this temperature with a clean thermometer. (**Warning**—Do not contaminate the samples or buffers.)

11.5 *Calibration Function:*

11.5.1 Rinse the electrodes with three aliquots of water or with a flowing stream from a wash bottle. Dispense two aliquots of the buffer with the higher pH into separate, clean sample cups. Insert the electrode(s) into one aliquot for 30 s.

11.5.2 Remove the electrodes from the first aliquot and insert directly into the second. Samples may be stirred or agitated to speed equilibration time but must be quiescent while measurements are being made. Allow either two minutes for equilibration or allow sufficient time for the reading to remain steady within ±0.01 pH units for 30 s.

11.5.3 Adjust the calibration control until the reading corresponds to the temperature corrected value of the reference buffer solution.

11.6 *Slope Function:*

11.6.1 Rinse the electrodes with three aliquots of water or with a flowing stream from a wash bottle. Dispense two aliquots of the second reference buffer solution into separate, clean sample cups. Insert the electrodes into one aliquot for 30 s.

11.6.2 Remove the electrodes from the first aliquot and insert directly into the second. Allow the system to equilibrate as directed in 11.5.2.

11.6.3 Adjust the slope function until the reading corresponds to the temperature corrected value of the reference buffer solution. The slope function should be between 90 and 105 % of the theoretical Nernstian response.

NOTE 3—Possible causes for deviation from Nernstian response include: improper calibration; old or contaminated buffer solutions; insufficient rinsing of the electrodes between solutions; plugged reference junction; defective electrodes; and defective meter.

11.6.3.1 It may be necessary to replace the electrodes with a new pair if the non-Nernstian behavior persists even with accurately and freshly prepared buffer standards.

11.7 *Calibration Check:*

11.7.1 Remove the electrodes, rinse thoroughly, and place into the first reference buffer solution. If the pH does not read within ±0.01 units of the temperature corrected value, repeat the calibration procedure until the buffers agree.

## 12. Quality Control

12.1 It is recommended that electrodes used for the measurement of wet deposition samples should not be used for other sample types. Strongly acidic or basic solutions may cause electrode degradation and result in biased measurements and slow response, or both in precipitation samples. Similarly, samples characterized by high concentrations of organic matter may leave a residue on the glass sensing bulb, resulting in slow electrode response.

12.2 After the meter and electrodes have been calibrated, measure the pH of a quality control sample (QCS). This sample may be formulated in the laboratory (see 8.4.1), or obtained as a NIST traceable standard. Verify the pH value of internally formulated solutions by direct comparison with a NIST traceable standard before acceptance as QCS solutions. The QCS selected must be within the range of the calibration buffers and should approximate the pH of the samples of atmospheric wet