



Designation: D 5015 – 95

Standard Test Method for pH of Atmospheric Wet Deposition Samples by Electrometric Determination¹

This standard is issued under the fixed designation D 5015; 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 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 *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 1129 Terminology Relating to Water²
- D 1193 Specification for Reagent Water²
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water²
- D 5012 Guide for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition³
- D 5111 Guide for Choosing Locations and Sampling Methods to Monitor Atmospheric Deposition at Non-Urban Locations³
- E 1 Specification for ASTM Thermometers⁴
- E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)⁵

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 Terminology D 1129. For an explanation of the metric system including units, symbols, and conversion factors, see Practice E 380.

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:

- pH(X) = pH of an unknown sample,
- pH(S₁) = pH of a Standard Solution 1,
- pH(S₂) = pH of a Standard Solution 2,
- E_X = EMF (mV) measured in an unknown sample,
- E_{S₁} = EMF (mV) measured in Standard Solution 1, and
- E_{S₂} = 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).⁶ 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

¹ This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.06 on Atmospheric Deposition.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 11.03.

⁴ *Annual Book of ASTM Standards*, Vol 14.03.

⁵ *Annual Book of ASTM Standards*, Vol 14.02.

⁶ The boldface numbers in parentheses refer to the list of references at the end of this standard.

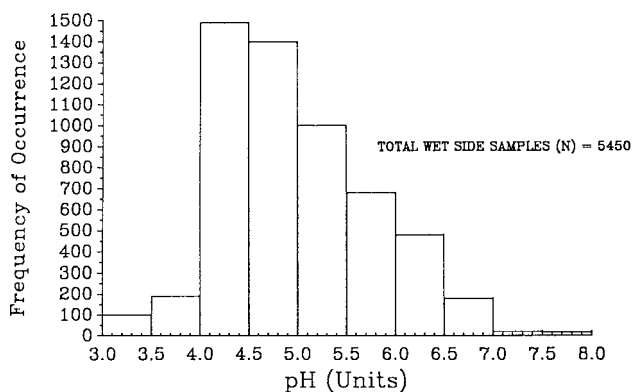


FIG. 1 Frequency Distribution of Measured Laboratory pH of Atmospheric Wet Deposition From the 1984 National Atmospheric Deposition Program (NADP)/National Trends Network (NTN)

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.

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 V ac line; 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). Table 1 lists three possibilities for suitable reference electrodes that have been found to be satisfactory. Other electrodes having similar characteristics are also suitable. 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

TABLE 1 Suitable pH Reference Electrodes for the Analysis of Wet Deposition Samples

Manufacturer	Model Number	Electrode Type
Beckman	39417	glass bodied with ceramic junction (calomel)
Corning	476109	glass bodied with ceramic junction (calomel)
Orion (Ross)	800500	glass bodied reference half cell with ceramic junction

deposition measurements and must meet the criteria stated in 12.2 .

TABLE 2 National Institute of Standards and Technology (NIST) Salts for Reference Buffer Solutions

NIST Standard Sample Designation	Buffer Salt ^A	pH at 25°C
186-Ie	potassium dihydrogen phosphate, 0.025 M	6.865
186-IIe	disodium hydrogen phosphate, 0.025 M	
185g	potassium hydrogen phthalate	4.003

^A These buffer salts can be purchased from the Office of Standard Reference Materials, National Institute of Standards and Technology, Gaithersburg, MD 20899.

7.5 Temperature Control—Use either a constant temperature water bath, a temperature compensator, or a thermometer (see Specification E 1) to verify that all standards and samples are maintained at temperatures within $\pm 1^\circ\text{C}$ 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)⁷ where such specifications are available.

8.2 Purity of Water—Use water conforming to Specification D 1193, Type II. Point of use 0.2 μm filters are recommended for all faucets supplying ASTM Type II water to prevent the 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 2 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)⁸—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 SRM 2694a or other NIST traceable low-ionic strength solutions of known pH.

8.4.1 Dilute Nitric Acid (5.0×10^{-5} mol/L HNO_3)—Add 1.0 mL of concentrated nitric acid (HNO_3 , 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 ± 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 5111 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

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.

⁸ Available from the National Institute of Standards and Technology as Standard Reference Material (SRM) 2694a, "Simulated Rainwater."