Designation: D 5015 – 02

Standard Test Method for pH of Atmospheric Wet Deposition Samples by Electrometric Determination[1]

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 Water[2]
D 1193 Specification for Reagent Water[2]
D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water[2]
D 5012 Guide for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition[3]
D 5111 Guide for Choosing Locations and Sampling Methods to Monitor Atmospheric Deposition at Non-Urban Locations[3]
E 1 Specification for ASTM Thermometers[4]
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 and D 1356. 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:

$$\mathrm{pH}\,(X) = \mathrm{pH}\,(S_1) + \frac{E_X - E_{S_1}}{E_{S_2} - E_{S_1}}\,[\mathrm{pH}\,(S_2) - \mathrm{pH}\,(S_1)] \tag{1}$$

where:

pH(X) = pH of an unknown sample,
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)**.[6] Special emphasis must be placed on minimizing the effect of the residual liquid junction potential bias.

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[1] This test method is under the jurisdiction of ASTM Committee D22 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.

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.

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.

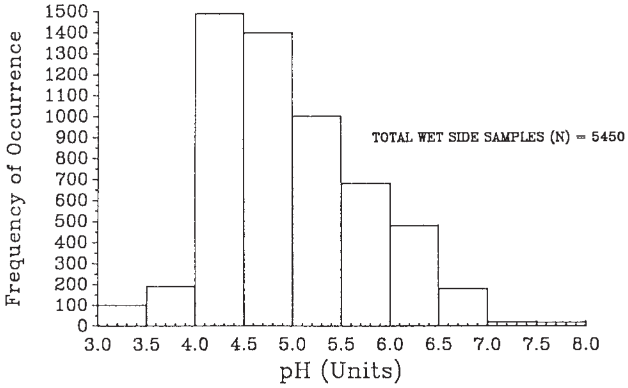

FIG. 1 Frequency Distribution of Measured Laboratory pH of Atmospheric Wet Deposition From the 1984 National Atmospheric Deposition Program (NADP)/National Trends Network (NTN)

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 Specification E 1) to verify that all standards and samples are maintained at temperatures within ±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)[7] where such specifications are available.

8.2 *Purity of Water*—Use water conforming to Specification D 1193, Type I. Point of use 0.2 µm filters are recommended for all faucets supplying ASTM Type I 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 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* (5.0×10^{-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 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 ($CHCl_3$) may be used to stabilize the organic acid component of the measured pH and

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

NIST Standard Sample Designation	Buffer Salt[A]	pH at 25°C
186-If	potassium dihydrogen phosphate, 0.025 *M*	6.865
186-IIf	disodium hydrogen phosphate, 0.025 *M*	6.865
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.

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[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.

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 D 5012.

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.

NOTE 3—**Caution:** 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 4—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 deposition to be analyzed. The difference between the measured pH of the QCS and the certified value constitutes the bias of the pH measurement system. All measured values of the pH of subsequent wet deposition samples should be corrected for this bias by subtracting this difference from the measured value. The source of bias is attributable to residual liquid junction potential (EMF) differences between high-ionic strength calibration buffers and low-ionic strength wet deposition samples. This residual junction potential difference has been shown to be constant, for any given electrode, over the pH range of 4 to 7 **(2).** Once the magnitude of the difference has been established using a low ionic strength QCS, subsequent wet deposition measurements can be corrected for this bias. If the bias exceeds 0.3 pH unit, the electrodes are probably not suitable for wet deposition measurements and should be replaced. Individual laboratory quality control practices should establish the limits of acceptable bias and establish the conditions under which the correction for bias need not be applied. It is recommended that the data obtained from the QCS checks be plotted on a control chart for routine assessments of bias and precision.

12.2.1 QCS measurements should be made after every ten samples or after completion of a batch of samples consisting of less than ten. If the measured pH of the QCS has changed by more than 0.03 pH units, reanalyze all samples since the last QCS check.

13. Procedure

13.1 Bring all buffers, solutions, and samples to the same temperature (7.5).

13.2 Calibrate the electrode assembly with two reference buffer solutions as described in 11.5-11.7.

13.3 After the electrode(s) and meter are calibrated, determine the bias by analyzing a QCS sample. Refer to 12.2 and 14.1.

13.4 *Sample Analysis*:

13.4.1 Rinse the electrode(s) with three aliquots of water or with a flowing stream from a wash bottle. Dispense two aliquots of atmospheric wet deposition sample into separate, clean plastic sample cups. Insert the electrode(s) into one aliquot for 30 s to condition the electrode(s).

13.4.2 Remove the electrode(s) from the first aliquot and insert directly into the second, once again allowing the system time to stabilize. Samples may be stirred or agitated to speed equilibration time but must be quiescent while measurements are being made. The time necessary for the system response to stabilize depends on the pH of the sample. The pH electrode response time is typically 3 to 5 min for samples with a $pH < 6$. For samples with $pH > 6$, a stable response is typically generated in 5 to 7 min **(9).** Record the pH measurements when readings differ by no more than ± 0.01 pH units within a 30-s period. Record the pH and the temperature of the sample. Correct for the bias (12.2 and 14.1.1) and report the corrected value as the pH of the wet deposition sample. Maintain a record of the bias correction calculation in order to monitor continually electrode performance.

14. Calculation

14.1 Most pH meters are calibrated in pH units and the measured pH of the sample is obtained directly by reading the meter scale. If EMF (millivolt) measurements are made, record the millivolt readings, and convert to pH using the equation in 3.1.1. Record pH measurements to the nearest hundredth of a pH unit and sample temperature to the nearest degree. Subtract the bias as determined in 14.1.1 and report this corrected value as the pH of the wet deposition sample.

14.1.1 As an example of the bias correction, after calibration of the system with buffers, (Section 11), a QCS sample with a certified pH value of 3.59 is used in accordance with Section 12. For illustrative purposes, suppose the reading of the pH meter is 3.68 for this QCS. Then, the bias is as follows:

$$\text{pH reading} - \text{pH certified} = \text{bias} \tag{2}$$

$$3.68 - 3.59 = +0.09$$

Subsequently, a rainwater sample is read from the display of the pH meter as 4.21. This value is corrected by subtracting the bias, that is:

$$\text{pH reading} - \text{bias} = \text{corrected value of pH} \tag{3}$$

$$4.21 - (+0.09) = 4.12$$

The value 4.12 is reported as the pH of the rainwater sample. Be mindful of the signs (+ or −) of the bias.

15. Precision and Bias [8]

15.1 Precision and bias for this test method were calculated using Practice D 2777 based on the results of an interlaboratory test involving three simulated atmospheric wet deposition samples and eight laboratories. The precision data are summarized in Table 2. Bias data are summarized in Table 3.

TABLE 2 Precision of pH Measurements from Simulated Atmospheric Wet Deposition Samples[A]

Sample Number	$\bar{x}$	S_T[B]	S_O[C]
1	4.89	0.05	0.02
2	4.33	0.03	0.01
3	4.42	0.03	0.01

[A] where:

$\bar{x}$ = mean values for eight laboratories,
S_T = standard deviation between laboratories, and
S_O = standard deviation within laboratories (pooled).

[B] Overall precision in pH units.

[C] Single-operator precision in pH units.

TABLE 3 Bias of pH Measurements from Simulated Atmospheric Wet Deposition Samples

Sample Number	Amount Added pH (std. dev.)	Amount Found pH (std. dev.)	Bias (Found − Added)	Significant Bias[A]
1	4.84 (0.04)[B]	4.89 (0.05)	+0.05	yes
2	4.31 (0.04)[C]	4.33 (0.03)	+0.02	yes
3	4.41 (0.04)[D]	4.42 (0.03)	+0.01	no

[A] 95 % confidence level.

[B] Mean and standard deviation of ten determinations by three analysts in formulating laboratory; calculated pH from ion balance calculations was 4.87.

[C] Mean and standard deviation of ten determinations by three analysts in formulating laboratory; calculated pH from ion balance calculations was 4.29.

[D] Calculated pH from a dilution of Sample Number 2 (160 mL sample + 40 mL deionized water).

16. Keywords

16.1 atmospheric deposition; hydrogen ion; low ionic strength solutions; pH; precipitation; wet deposition

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[8] Data supporting the results from the interlaboratory test are on file at ASTM Headquarters. Request RR:D-22-1018.

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