Designation: D5015 – 15 (Reapproved 2022)

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

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 (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 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:*[2]

D1129 Terminology Relating to Water

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:

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

where:

pH *(X)* = pH of an unknown sample,

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

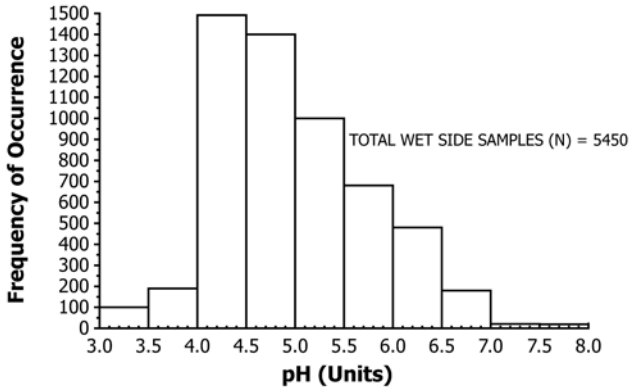

FIG. 1 Frequency Distribution of Measured Laboratory pH of Atmospheric Wet Deposition From the 1984 National Atmospheric Deposition Program (NADP)/National Trends Network (NTN)

$pH(S_1)$ = 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**).[3] 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.

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

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