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Standard Test Methods for pH of Water¹

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This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the determination of pH by electrometric measurement using the glass electrode as the sensor. Two test methods are given as follows:

Test Method A—Precise Laboratory Measurement	Sections 8 to 15
Test Method B—Routine or Continuous Measurement	16 to 24

1.2 Test Method A covers the precise measurement of pH in water utilizing at least two of seven standard reference buffer solutions for instrument standardization.

1.3 Test Method B covers the routine measurement of pH in water and is especially useful for continuous monitoring. Two buffers are used to standardize the instrument under controlled parameters, but the conditions are somewhat less restrictive than those in Test Method A. For on-line measurement, also see Test Method D6569 which provides more detail.

1.4 Both test methods are based on the pH scale established by NIST (formerly NBS) Standard Reference Materials.²

1.5 Neither test method is considered to be adequate for measurement of pH in water whose conductivity is less than about 5 $\mu\text{S}/\text{cm}$. Refer to Test Methods D5128 and D5464.

1.6 Precision and bias data were obtained using buffer solutions only. It is the user's responsibility to assure the validity of these test methods for untested types of water.

1.7

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

1.8 *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:*³

D1066 Practice for Sampling Steam

D1067 Test Methods for Acidity or Alkalinity of Water

D1129 Terminology Relating to Water⁴ ~~D1192~~

D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits

D1193 Specification for Reagent Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D3370 Practices for Sampling Water from Closed Conduits

D5128 Test Method for On-Line pH Measurement of Water of Low Conductivity

D5464 Test Method for pH Measurement of Water of Low Conductivity

D6569 Test Method for On-Line Measurement of pH

E70 Test Method for pH of Aqueous Solutions With the Glass Electrode

¹ These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.03 on Sampling of 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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² "Standard Reference Materials: Standardization of pH Measurements" Wu and Koch, NBS Special Publications No. 260-53, 1988.

³ 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.

⁴ Withdrawn.

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *pH, n*—the negative logarithm of the hydrogen ion activity in an aqueous solution or the logarithm of the reciprocal of the hydrogen ion activity.

3.2.1.1 *Discussion*—the pH of an aqueous solution is derived from E , the electromotive force (emf) of the cell



(where the double vertical line represents a liquid junction) when the electrodes are immersed in the solution in the diagrammed position, and E_s is the electromotive force obtained when the electrodes are immersed in a reference buffer solution.

With the assigned pH of the reference buffer designated as pH_s , and E and E_s expressed in volts is the following:⁵

$$\text{pH} = \text{pH}_s + \frac{(E - E_s)F}{2.3026 RT}$$

where:

F = Faraday, Faraday constant,

R = gas constant, and

T = absolute temperature, t (°C) + 273.15.

The reciprocal of $F/2.3026 RT$ is known as the slope of the electrode, and is the expected difference in observed voltage for two measurements one pH unit apart. Values of the slope at various temperatures are given in Table 1.

4. Summary of Test Method

4.1 The pH meter and associated electrodes are standardized against at least two reference buffer solutions that closely bracket the anticipated sample pH. The sample measurement is made under strictly controlled conditions and prescribed techniques.

5. Significance and Use

5.1 The pH of water is a critical parameter affecting the solubility of trace minerals, the ability of the water to form scale or to cause metallic corrosion, and the suitability of the water to sustain living organisms. It is a defined scale, based on a system of buffer solutions² with assigned values. In pure water at 25°C, pH 7.0 is the neutral point, but this varies with temperature and the ionic strength of the sample.⁶ Pure water in equilibrium with air has a pH of about 5.5, and most natural uncontaminated waters range between pH 6 and pH 9.

6. Purity of Reagents

6.1 Reagent grade chemicals shall be used in all tests, except as specifically noted for preparation of reference buffer solutions. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical

<https://standards.iteh.ai/catalog/standards/sist/618e6aeb-f19e-41b9-bcc5-09b4a4b61b27/astm-d1293-12>

⁵ Bates, R. G., *Determination of pH: Theory and Practice*, 2nd Ed., J. Wiley and Sons, New York, 1973, p. 29.

⁶ The relative acidity or alkalinity measured by pH should not be confused with total alkalinity or total acidity (for example, Test Methods D1067). Thus, 0.1 M HCl and 0.1 M acetic acid have the same total acidity, but the HCl solution will be more acidic (approximately pH 1 versus pH 3.).

TABLE 1 Slope Factor at Various Temperatures

Temperature, °C	Slope, millivolts
0	54.20
5	55.19
10	56.18
15	57.17
20	58.17
25	59.16
30	60.15
35	61.14
40	62.13
45	63.13
50	64.12
55	65.11
60	66.10
65	67.09
70	68.09
75	69.08
80	70.07
85	71.06
90	72.05
95	73.05

Reagents of the American Chemical Society, where such specifications are available.⁷ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I.

7. Sampling

7.1 Collect samples in accordance with Practice D1066, ~~Specification D1192~~, or Practices D3370, whichever is applicable.

TEST METHOD A—PRECISE LABORATORY MEASUREMENT OF pH

8. Scope

8.1 This test method covers the precise measurement of pH in water under strictly controlled laboratory conditions.

9. Interferences

9.1 The glass electrode reliably measures pH in nearly all aqueous solutions and in general is not subject to solution interference from color, turbidity, colloidal matter, oxidants, or reductants.

9.2 The reference electrode may be subject to interferences and should be chosen to conform to all requirements of Sections 10 and 12. Refer also to Appendix X1.3.

9.3 The true pH of an aqueous solution or extract is affected by the temperature. The electromotive force between the glass and the reference electrode is a function of temperature as well as pH. The temperature effect can be compensated automatically in many instruments or can be manually compensated in most other instruments. The temperature compensation corrects for the effect of changes in electrode slope with temperature but does not correct for temperature effects on the chemical system being monitored. It does not adjust the measured pH to a common temperature; therefore, the temperature should be reported for each pH measurement. Temperature effects are discussed further in Appendix X1.2.

9.4 The pH response of the glass electrode/reference electrode pair is imperfect at both ends of the pH scale. The indicated pH value of highly alkaline solutions may be too low, by as much as 1 pH, depending on electrode composition and sample conditions. See X1.5.1. The indicated pH value of strong aqueous solutions of salts and strong acids having a pH less than 1, will often be higher than the true pH value. Interferences can be minimized by the selection of the proper glass and reference electrodes for measurements in highly alkaline or acidic solutions.

9.5 A few substances sometimes dispersed in water appear to poison the glass electrode. A discussion of this subject is given in Appendix X1.4.

10. Apparatus

10.1 *Laboratory pH Meter*—Almost all commercially available meters are of the digital type and will have either manual or automatic calibration, and either manual or automatic temperature (slope) correction. All four types are permissible. However, readability to 0.01 pH is essential (Section 14), and the ability to read in millivolts is useful in troubleshooting.

10.2 *Glass Electrode*—The pH response of the glass electrode shall conform to the requirements set forth in 12.1 through 12.5 and 12.6. The glass electrode lead wire shall be shielded. New glass electrodes and those that have been stored dry shall be conditioned and maintained as recommended by the manufacturer.

10.3 *Reference Electrode*—This may be used as separate “half cell,” or it may be purchased integral with the glass pH electrode body, as a combination electrode. The internal reference element may be calomel (mercury/mercurous chloride), silver/silver chloride, or an iodide-iodine redox couple. For best performance, the reference element should be the same type in both the reference electrode and inside the pH electrode. For all three types, the junction between the reference filling solution and the sample may be either a flowing or nonflowing junction. The flowing liquid junction-type unit ensures that a fresh liquid junction is formed for each measurement and shall be used for Test Method A determinations. If a saturated calomel electrode is used, some potassium chloride crystals shall be contained in the saturated potassium chloride solution. If the reference electrode is of the flowing junction type, the design of the electrode shall permit a fresh liquid junction to be formed between the reference electrode solution and the buffer standard or tested water for each measurement and shall allow traces of solution to be washed from the outer surfaces of the electrodes. To ensure the desired slow outward flow of reference electrode solution, the solution pressure inside the liquid junction should be kept somewhat in excess of that outside the junction. In nonpressurized applications, this requirement can be met by maintaining the inside solution level higher than the outside water level. If the reference electrode is of the nonflowing junction type, these outward flow and pressurization considerations do not apply. The reference electrode and junction shall perform satisfactorily as required in the standardizing procedure described in 12.1 through 12.5 and 12.6. A discussion of reference electrodes is given in Appendix X1.3.

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.

10.4 *Temperature Compensator*—The thermocompensator is a temperature-sensitive resistance element immersed in the water sample with the electrodes. The thermocompensator may be incorporated into the pH electrode or may be a separate probe. The thermocompensator automatically corrects for the change in slope of the glass electrode (with change of temperature) but does not correct for actual changes in sample pH with temperature. The automatic thermocompensator is not required if the water temperature is essentially constant and the analyst chooses to use the manual temperature compensation feature of the pH meter.

11. Reagents

11.1 *Reference Buffer Solutions* —The approximate pH values of the reference buffer solutions measured at several temperatures are listed in Table 2-. If traceability to NIST standard reference materials (SRMs) is required, follow exactly the NIST certificate drying, preparation, and storage instructions for the given renewal of the respective SRM buffer, and obtain the certified value from the certificate for that SRM renewal at the applicable temperature. The current renewal of each NIST SRM should be used. Buffer solution compositions and preparations given in Sections 11.1.1 through 11.1.7 are for use with non-NIST materials. For NIST SRMs, follow the instructions included with the SRM.

Table 3 identifies each buffer salt by its National Institute of Standards and Technology (NIST) number and provides a recommended Dry the buffer salt before use. The drying procedure prior to use. The will be according to the current renewal of each the NIST standard certificate. Recommended drying procedures for non-NIST reference material should be used. materials are also provided, in the last column of the table. Keep the five reference buffer solutions with pH less than 9.5 in bottles of chemically resistant glass. Keep the calcium hydroxide solutions in a plastic bottle that is nonporous to air (that is, polypropylene or high density polyethylene). Keep all the reference buffer solutions well-stoppered and replace if a visible change is observed.

11.1.1 *Borax Reference Buffer Solution* ($pH_s = 9.18$ at 25°C)—Dissolve 3.80 g of sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in water and dilute to 1 L. When using the NIST SRM, prepare in accordance with the current renewal of the certificate. For other reference materials, follow associated instructions or dissolve 3.80 g of sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in water and dilute to 1 L.

11.1.2 *Calcium Hydroxide Reference Buffer Solution* ($pH_s = 12.45$ at 25°C)—Prepare pure calcium hydroxide (Ca(OH)_2) When using the NIST SRM, prepare in accordance with the current renewal of the certificate. For other reference materials, follow associated instructions or prepare pure calcium hydroxide (Ca(OH)_2) from well-washed calcium carbonate (CaCO_3) of low-alkali grade by slowly heating the carbonate in a platinum dish at 1000°C and calcining for at least 45 min at that temperature. After cooling in a dessicator, add the calcined product slowly to water with stirring, heat the resultant suspension to boiling, cool, and filter through a funnel having a fritted-glass disk of medium porosity. Collect the solid from the filter, dry it in an oven at 110°C , and crush it to a uniform and fine granular state. Prepare a saturated calcium hydroxide solution by vigorously shaking a considerable excess (about 3 g/L) of the fine granular product in water at 25°C in a stoppered plastic bottle (that is, polypropylene or high density polyethylene) that is essentially nonporous to gases. Allow the gross excess of solid to settle and filter the solution with suction through a fritted-glass funnel of medium porosity. The filtrate is the reference buffer solution. Contamination of the solution with atmospheric carbon dioxide renders it turbid and indicates need for replacement.

11.1.3 *Phosphate Reference Buffer Solution* ($pH_s = 6.86$ at 25°C)—Dissolve 3.39 g of potassium dihydrogen phosphate (KH_2PO_4) and 3.53 g of anhydrous disodium hydrogen phosphate (Na_2HPO_4) in water and dilute to 1 L. When using the NIST SRM, prepare in accordance with the current renewal of the certificate. For other reference materials, follow associated instructions or dissolve 3.39 g of potassium dihydrogen phosphate (KH_2PO_4) and 3.53 g of anhydrous disodium hydrogen phosphate (Na_2HPO_4) in water and dilute to 1 L.

TABLE 2 Approximate pH_s of Reference Buffer Solutions^A

Temperature, °C	Tetroxalate Solution	Tartrate Solution	Phthalate Solution	Phosphate Solution	Borax Solution	Sodium Bicarbonate Sodium Carbonate	Calcium Hydroxide Solution
0	1.67	...	4.00	6.98	9.46	10.32	13.42
5	1.67	...	4.00	6.95	9.39	10.25	13.21
10	1.67	...	4.00	6.92	9.33	10.18	13.00
15	1.67	...	4.00	6.90	9.28	10.12	12.81
20	1.68	...	4.00	6.88	9.23	10.06	12.63
25	1.68	3.56	4.00	6.86	9.18	10.01	12.45
30	1.68	3.55	4.01	6.85	9.14	9.97	12.29
35	1.69	3.55	4.02	6.84	9.11	9.93	12.13
40	1.69	3.55	4.03	6.84	9.07	9.89	11.98
45	1.70	3.55	4.04	6.83	9.04	9.86	11.84
50	1.71	3.55	4.06	6.83	9.02	9.83	11.71
55	1.72	3.55	4.07	6.83	8.99	...	11.57
60	1.72	3.56	4.09	6.84	8.96	...	11.45
70	1.74	3.58	4.12	6.85	8.92
80	1.77	3.61	4.16	6.86	8.89
90	1.79	3.65	4.19	6.88	8.85
95	1.81	3.67	4.21	6.89	8.83

^AFor a discussion of the manner in which these pH values were assigned, see Bates, R. G., "Revised Standard Values for pH Measurements from 0 to 95°C ," *Journal of Research*, NBS, Vol 66A, 1962, p. 179. The reference values were obtained without a liquid junction, which has an uncertainty of ± 0.005 . Liquid junction electrode values may have an uncertainty of ± 0.012 , with uncertainty ± 0.03 for the tetroxalate and the Ca(OH)_2 . More recent values have been published in *pH Measurement* by Helmuth Galster, VCH Publishers, Inc., New York, 1991.

TABLE 3 National Institute of Standards and Technology (NIST) Materials for Reference Buffer Solutions

NIST Standard Reference Material Designation	Buffer Salt ^A	NIST SRM Drying Procedure	Drying Procedure ^B
187	Borax (sodium tetraborate decahydrate)		Drying not necessary (this salt should not be oven-dried)
187	Borax (sodium tetraborate decahydrate)	see NIST material certificate	Drying not necessary (this salt should not be oven-dried)
186	disodium hydrogen phosphate		2 h in oven at 130°
186	disodium hydrogen phosphate	see NIST material certificate	2 h in oven at 130°
186	potassium dihydrogen phosphate		2 h in oven at 130°C
186	potassium dihydrogen phosphate	see NIST material certificate	2 h in oven at 130°C
185	potassium hydrogen phthalate		2 h in oven at 110°C
185	potassium hydrogen phthalate	see NIST material certificate	2 h in oven at 110°C
188	potassium hydrogen tartrate		drying not necessary
188	potassium hydrogen tartrate	see NIST material certificate	drying not necessary
189	potassium tetroxalate dihydrate		should not be dried
189	potassium tetroxalate dihydrate	see NIST material certificate	should not be dried
191	sodium bicarbonate		should not be dried
191	sodium bicarbonate	see NIST material certificate	should not be dried
192	sodium carbonate		2 h in oven at 275°C
192	sodium carbonate	see NIST material certificate	2 h in oven at 275°C
2193	calcium carbonate		see NIST material certificate
2193	calcium carbonate	see NIST material certificate	see NIST material certificate

^AThe buffer salts listed can be purchased from the Standard Reference Materials Program, National Institute of Standards and Technology, Gaithersburg, MD 20899.

^BThe drying procedures in this column do not apply to NIST SRM preparations, but these procedures may be used with materials from other sources where NIST traceability is not required.

11.1.4 *Phthalate Reference Buffer Solution (pH_s = 4.00 at 25°C)*—Dissolve 10.12 g of potassium hydrogen phthalate (KHC₈H₄O₄) in water and dilute to 1 L.
—When using the NIST SRM, prepare in accordance with the current renewal of the certificate. For other reference materials, follow associated instructions or dissolve 10.12 g of potassium hydrogen phthalate (KHC₈H₄O₄) in water

11.1.5 *Tartrate Reference Buffer Solution (pH_s = 3.56 at 25°C)*—Shake vigorously an excess (about 75 g/L) of potassium hydrogen tartrate (KHC₄H₄O₆) with 100 to 300 mL of water at 25°C in a glass-stoppered bottle. Filter, if necessary, to remove suspended salt. Add a crystal of thymol (about 0.1 g) as a preservative.
—When using the NIST SRM, prepare in accordance with the current renewal of the certificate. For other reference materials, follow associated instructions or shake vigorously an excess (about 75 g/L) of potassium hydrogen tartrate (KHC₄H₄O₆) with 100 to 300 mL of water at 25°C in a glass-stoppered bottle. Filter, if necessary, to remove suspended salt. Add a crystal of thymol (about 0.1 g) as a preservative.

11.1.6 *Tetroxalate Reference Buffer Solution (pH_s = 1.68 at 25°C)*—Dissolve 12.61 g of potassium tetroxalate dihydrate (KHC₂O₄·H₂C₂O₄·2H₂O) in water and dilute to 1 L.
—When using the NIST SRM, prepare in accordance with the current renewal of the certificate. For other reference materials, follow associated instructions or dissolve 12.61 g of potassium tetroxalate dihydrate (KHC₂O₄·H₂C₂O₄·2H₂O) in water and dilute to 1 L.

11.1.7 *Sodium Bicarbonate—Sodium Carbonate Reference Buffer Solution (pH_s = 10.01 at 25°C)*—Dissolve 2.092 g of sodium bicarbonate (NaHCO₃) and 2.640 g of sodium carbonate (Na₂CO₃) in water and dilute to 1 L.
—When using the NIST SRM, prepare in accordance with the current renewal of the certificate. For other reference materials, follow associated instructions or dissolve 2.092 g of sodium bicarbonate (NaHCO₃) and 2.640 g of sodium carbonate (Na₂CO₃) in water and dilute to 1 L.

11.2 *Other Buffer Solutions*—A buffer solution other than that specified may be used as a working standard in the method providing that in each case such a solution is first checked against the corresponding reference buffer solution, using the procedures of the method, and is found to differ by not more than ± 0.02 pH unit.

11.3 *Commercial Buffer Solutions* —Commercially available prepared buffer solutions are not acceptable for the standardization in Test Method A.

12. Standardization of Assembly

12.1 Turn on the instrument, allow it to warm up thoroughly, and bring it to electrical balance in accordance with the manufacturer's instructions. Wash the glass and reference electrodes and the sample container with three changes of water or by means of flowing stream from a wash bottle. Form a fresh liquid junction if a sleeve-type reference junction is used. Note the temperature of the water to be tested. If temperature compensation is to be manual, adjust the temperature setting of the meter to correspond to the temperature of the water to be tested and allow time for all buffers, solutions, and electrodes to equilibrate thermally.

12.2 Select at least two reference buffer solutions, the pH_s values of which closely bracket the anticipated pH (refer to Table 2). Warm or cool the reference solutions as necessary to match within 2°C the temperature of the solution to be tested. Fill the sample container with the first reference buffer solution and immerse the electrodes. Stir the solution as described in 13.3.

12.3 Set the pH

12.3 Fill the sample container with the first reference buffer solution and immerse the electrodes. Stir the solution as described in 13.3.

12.4 Set the pH value of the reference buffer solution at the temperature of the buffer, as read from Table 2 or interpolated from the data therein, according to the manufacturer's instructions.

12.4 Empty the sample container and repeat, using successive portions of the reference buffer solution, until two successive readings are obtained without adjustment of the system. These readings should differ from the pH

12.5 Empty the sample container and repeat, using successive portions of the reference buffer solution, Repeat with successive portions of the reference buffer solution until two successive instrument readings are obtained which differ from the pH value of

~~the buffer solution by not more than ± 0.02 pH unit. value of the buffer solution by no more than ± 0.02 pH unit. Alternatively, follow the manufacturer's instructions for calibration with the first buffer.~~

NOTE 1—If the temperature of the electrode differs appreciably from that of the solution to be tested, use several portions of solution and immerse the electrodes deeply to assure that both the electrodes and the solution are at the desired temperature. To reduce the effects of thermal lag, keep the temperature of electrodes, reference buffer solutions, and the wash as close to that of the water sample as possible.

~~12.5~~12.6 Wash the electrodes and the sample container three times with water. Place the second reference buffer solution in the sample container, stir and measure the pH. Set the temperature corrected value of the second reference buffer solution according to the meter manufacturer's instructions. Use additional portions of the second reference buffer solution, as before, until two successive readings differ by not more than ± 0.02 pH unit. The assembly shall be judged to be operating satisfactorily if the reading obtained for the second reference buffer solution agrees with its assigned pH_s value within 0.05 (or less) pH units.

~~12.6~~If only an occasional pH determination is made, standardize the assembly each time it is used. In a long series of measurements, supplemental interim checks at regular intervals are recommended. Inasmuch as commercially available pH assemblies exhibit different degrees of measurement stability, conduct these checks at intervals of 30 min, unless it is ascertained that less frequent checking is satisfactory to ensure the performance described in

12.7 Use additional portions of the second reference buffer solution, as before, until two successive readings differ by not more than ± 0.02 pH unit from pH_s . Alternatively, follow the manufacturer's instructions for calibration with the second buffer.

12.8 Interim Checks: The assembly shall be judged to be operating satisfactorily if the reading obtained for the second reference buffer solution agrees with its assigned pH_s value within ± 0.05 (or less) pH units.

12.9 If only an occasional pH determination is made, standardize the assembly each time it is used. In a long series of measurements, supplemental interim checks at regular intervals are recommended. Inasmuch as commercially available pH assemblies exhibit different degrees of measurement stability, conduct these checks at intervals of 30 min, unless it is ascertained that less frequent checking is satisfactory to ensure the performance described in 12.2 to ~~12.5~~12.6.

13. Procedure

13.1 Standardize the assembly with at least two reference buffer solutions as described in 12.2 to ~~12.5~~12.6 and then wash the electrodes with three changes of water or by means of a flowing stream from a wash bottle.

13.2 Place the water sample in a clean glass beaker provided with a stirring bar or stirrer and either a thermometer (for meters with manual temperature compensation) or an ATC probe (for meters with automatic temperature compensation) or use a pH electrode with integral temperature sensor.

13.3 Stir during the period of pH measurement at a rate that will prevent splashing and that will avoid loss or gain of acidic or basic gases by interchange with the atmosphere. When necessary, stir briskly enough to intermix the phases of a nonhomogeneous water sample. Stop the stirrer during periods of measurement if fluctuations in readings are observed. (See Appendix X1.3.4 and X1.4.3).

13.4 Insert the electrodes and determine a preliminary pH value (since this value may drift somewhat, it should be considered an estimated value). Measure successive portions of the water sample until readings on two successive portions differ by no more than ± 0.03 pH unit, and show drifts of less than ± 0.02 pH unit in 1 min. Two or three portions will usually be sufficient if the water is well buffered.

13.5 Record the pH and temperature of the sample.

13.6 Measure the pH of slightly buffered waters (that are in equilibrium with air) essentially as described in 13.1 to 13.5, but measure the pH of successive portions until the readings for two successive portions differ by no more than 0.1 pH unit. Six or more portions may be necessary.

NOTE 2—Take special precautions if the sample is not in equilibrium with the carbon dioxide of the atmosphere protecting the sample from exposure to the air during measurement. *Measurement of unbuffered or slightly buffered samples is more reliably made in flow-type cells as described in Note 4.* Test Methods D5464 describe additional precautions that should be taken if the electrical conductivity of the sample is less than about 5 $\mu\text{S}/\text{cm}$.

14. Report

14.1 Report the temperature of the measurement of the nearest 1°C.

14.2 Report the pH of the test solution to the nearest 0.01 pH unit when the pH measurement lies between 1.0 and 12.0.

14.3 Report the pH of the test solution to the nearest 0.1 pH unit when the pH measurement is less than 1.0 or greater than 12.0.

15. Precision and Bias ⁸

15.1 The information summarized in this section was derived from an interlaboratory study performed in 1973 on four buffer solutions having pH values of approximately 3.7, 6.5, 8.2, and 8.4. Eleven laboratories (fourteen operators, with one laboratory providing four operators) analyzed each solution in duplicate and replicated the analysis on another day for a total of 224 determinations. A variety of commercial meters was used in this study. It is assumed that all measurements were made at room temperature.

⁸ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1111.