Standard Test Methods for pH of Water[1]

This standard is issued under the fixed designation D 1293; 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.

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:

	Sections
Test Method A—Precise Laboratory Measurement	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.

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 µS/cm. Refer to Test Methods D 5128 and D 5464.

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 *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]

D 1066 Practice for Sampling Steam

D 1067 Test Methods for Acidity or Alkalinity of Water
D 1129 Terminology Relating to Water
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[4]
D 1193 Specification for Reagent Water
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water
D 3370 Practices for Sampling Water from Closed Conduits
D 5128 Test Method for On-Line pH Measurement of Water of Low Conductivity
D 5464 Test Methods for pH Measurement of Water of Low Conductivity
E 70 Test Method for pH of Aqueous Solutions with the Glass Electrode

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

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

glass electrode | solution ‖ reference electrode

(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]

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

where:
F = Faraday,
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

---

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

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 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 solutions[2] 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 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 D 1193, Type I.

7. Sampling

7.1 Collect samples in accordance with Practice D 1066, Specification D 1192, or Practices D 3370, 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.

---

[6] The relative acidity or alkalinity measured by pH should not be confused with total alkalinity or total acidity (for example, Test Methods D 1067). 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.).

[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.

TABLE 2 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	...	...

[A]For 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.

10.2 *Glass Electrode*—The pH response of the glass electrode shall conform to the requirements set forth in 12.1 through 12.5. 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 satisfacto-

rily as required in the standardizing procedure described in 12.1 through 12.5. A discussion of reference electrodes is given in Appendix X1.3.

10.4 *Temperature Compensator*—The thermocompensator is a temperature-sensitive resistance element immersed in the water sample with the electrodes. 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 pH values of the reference buffer solutions measured at several temperatures are listed in Table 2. Table 3 identifies each buffer salt by its National Institute of Standards and Technology (NIST) number and provides a recommended drying procedure prior to use. The current renewal of each NIST standard reference material should be used. 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 (Na$_2$B$_4$O$_7$·10H$_2$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)$_2$) 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

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

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

[A]The buffer salts listed can be purchased from the Standard Reference Materials Program, National Institute of Standards and Technology, Gaithersburg, MD 20899.

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.

11.1.4 *Phthalate Reference Buffer Solution (pH_s = 4.00 at 25°C)*—Dissolve 10.12 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) in water and dilute to 1 L.

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 ($KHC_4H_4O_6$) 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 ($KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$) 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 ($NaHCO_3$) and 2.640 g of sodium carbonate (Na_2CO_3) 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_s 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_s value of the buffer solution by not more than ± 0.02 pH unit.

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 Wash the electrodes and the sample container three times with water. Place the second reference buffer solution in the sample container, 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 12.2 to 12.5.

13. Procedure

13.1 Standardize the assembly with two reference buffer solutions as described in 12.2 to 12.5 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 and either a thermometer (for meters with manual temperature compensation) or an ATC probe (for meters with automatic temperature compensation).

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 D 5464 describe additional precautions that should be taken if the electrical conductivity of the sample is less than about 5 µS/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.

15.2 Statistical treatment of the data conforms to the recommendations of Practice D 2777. Further information, based on a different statistical interpretation, can be found in Test Method E 70.

15.3 *Precision*—The overall and single-operator precision of this test method varies with pH as shown in Fig. 1.

15.4 *Bias*—The pH values of the buffer solutions, as determined using a gaseous hydrogen electrode, are compared with values obtained using this test method in Table 4.

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

TEST METHOD B—ROUTINE OR CONTINUOUS MEASUREMENT OF pH

16. Scope

16.1 This test method is used for the routine measurement of pH in the laboratory and the measurement of pH under various process conditions.

17. Summary of Test Method

17.1 A direct standardization technique is employed in this test method for routine batch samples. Two buffers are used to standardize the instrument under controlled parameters, but the conditions are somewhat less restrictive than those in Test Method A. An indirect standardization procedure is used on flowing systems in which grab samples are removed periodically in order to compare a monitored pH value (of the system) with the reading of a laboratory pH meter.

18. Interferences

18.1 For information on interferences, see Section 9 and Appendix X1.4.

19. Apparatus

19.1 *Laboratory pH Meter*—See 10.1.

19.2 *Glass Electrode*—See 10.2.

19.3 *Reference Electrode*—See 10.3.

19.4 *Temperature Compensator*—See 10.4.

19.5 *Process pH Measurement Instrumentation*— Instruments that are used for process pH measurements are generally much more rugged than those which are used for very accurate measurements in the laboratory.

19.5.1 *Electrode Chamber*—For process pH measurements; the electrodes and thermocompensator are mounted in an electrode chamber or cell.

19.5.1.1 *Flow-Through Chamber* completely encloses the electrodes and the sample is piped to and from the chamber in a flow-through configuration. Commercially available chambers generally can tolerate temperatures as high as 100°C over a pH range from 0 to 14, and pressures up to 1034 kPa (approximately 150 psi).

---

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D19–1111.
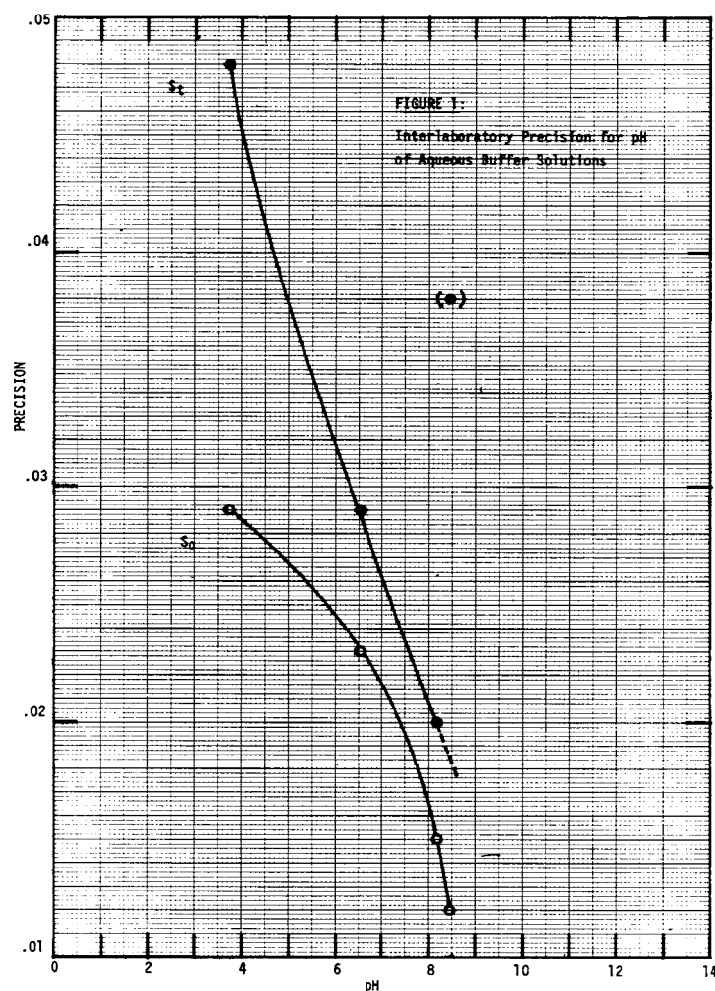
FIG. 1 Interlaboratory Precision for pH of Aqueous Buffer Solutions

TABLE 4 Determination of Bias

pH Expected	pH Found	Bias, $\pm$ %[A]	Statistically Significant (95 % Confidence Level)
3.714	3.73	+0.48	No
6.517	6.53	+0.20	Yes
8.147	8.19	+0.53	Yes
8.470	8.45	−0.24	Yes

[A]Since pH is a logarithmic function, this value may be misleading. It may be more useful to calculate bias as the difference between the values for pH Expected and pH Found.

19.5.1.2 *Immersion Type Chamber*, suitable for measurement in open streams or tanks, shields but does not completely enclose the electrodes. Immersion-style chambers are available for use at depths to 30 m (100 ft).

19.5.2 *Signal Transmission*—The glass electrode is usually a high-impedance device from which only an extremely small current can be drawn. Shielded cable must be used to connect the electrode to the pH analyzer. The signal can frequently be transmitted up to 300 m (approximately 1000 ft) with no loss in accuracy if the manufacturer's recommendations are followed carefully. However, long runs are vulnerable to electrical noise pickup and high impedance signal leakage. The signal is usually amplified for distances greater than 5 m (approximately 16 feet).

19.5.3 *pH Signal Retransmission*—The electrical output signal of on-line pH instrumentation shall be electrically isolated from the electrode measuring circuit to prevent ground loop problems when measuring pH in a grounded sample and connecting the output signal to a computer, control system, data acquisition system, or other grounded equipment.

20. Reagents

20.1 *Commercial Buffer Solutions*—Commercially available prepared buffer should be adequate for the standardization in Test Method B. These commercial buffer solutions usually have pH values near 4, 7, and 10, the exact pH and use temperature being provided by the purveyor of the specific buffer. The pH 10 buffer is especially susceptible to contamination from atmospheric carbon dioxide, and frequently used or partially filled bottles are particularly vulnerable to this error.

20.2 For more information on reagents, see Section 11.

21. Standardization of Assembly

21.1 Turn on the analyzer, allow it to warm up thoroughly in accordance with the manufacturer's instructions. Wash the electrodes, the thermocompensator, 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 reference electrode junction is used. If manual temperature compensation is to be used, note the temperature of the water sample and adjust the temperature dial of the meter to correspond.

21.2 *Direct Standardization*:

21.2.1 Select two reference buffer solutions that have pH_s values that bracket the anticipated pH of the water sample. Warm or cool the reference solution to within 2°C of the temperature of the water sample.

21.2.2 Fill the sample container with the first reference buffer solution and immerse the electrodes. Set the known pH_s of the reference buffer solution according to the instrument manufacturer's instructions. Repeat with successive portions of the reference buffer solution until two successive instrument readings are obtained which differ from the pH_s value of the buffer solution by no more than 0.02 pH unit.

21.2.3 Wash the electrodes and sample container three times with water. Place the second reference buffer solution in the sample container, and measure the pH. Adjust the slope control only until the reading corresponds to the temperature corrected value of the second reference buffer solution. Use additional portions of the second reference buffer solution, as before, until two successive readings differ by not more than 0.02 pH unit.

21.2.4 If only an occasional pH determination is made, standardize the assembly each time it is used. In a long series of measurements, supplement initial and final standardizations by interim checks at regular intervals. 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 performance. For continuous on-line measurements, the frequency of calibration shall be determined by experience since it is highly application dependent.

21.3 *Indirect Standardization*:

21.3.1 This procedure is to be employed when it is not convenient or practical to remove the electrodes from the flowing stream or container on which the pH is being determined. Use of a laboratory pH meter or an additional analyzer is required.

21.3.2 Standardize the laboratory pH meter or additional process analyzer as outlined in 21.2.

21.3.3 Collect a grab sample of the water from the immediate vicinity of the electrodes or from the discharge of a flow-through chamber. Measure the pH of this grab sample immediately, using the standardized laboratory pH meter.

21.3.4 Adjust the standardization control on the process analyzer until the reading corresponds to the pH of the grab sample. Repeat the grab sampling, analyzing, and adjusting procedure until two successive readings are obtained that differ by no more than 0.05 pH unit or within an acceptable accuracy.

NOTE 3—Indirect standardization as described above cannot be employed when the pH of the water being tested fluctuates by more than 0.05 pH unit. The standardization shall be accomplished in the shortest possible time if the pH is fluctuating. It is absolutely essential that the grab sample be representative of the water in contact with the electrodes of the analyzer being standardized. The integrity of the grab sample shall be maintained until its pH has been measured by the standardized meter, and its temperature shall remain constant. An alternate procedure giving greater flexibility is available using commercially-available process analyzers which provide a *hold* function. This function is manually activated at the time a grab sample is taken. It holds the pH value on the display, and allows time for the grab sample to be measured and its value to be used for calibration. After this standardization, the *hold* feature is deactivated.

21.3.5 Indirect standardization is a one-point calibration and does not establish the proper response of the electrodes over a pH range.

22. Procedure, Batch Samples

22.1 Standardize the assembly as described in 21.2 and wash the electrodes with three changes of water or by means of a flowing stream from a wash bottle.

22.2 Place the water sample in a clean glass beaker provided with a thermometer and a stirring bar. 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.

22.3 Insert the electrodes and determine a preliminary pH value (the reading may drift). Measure successive portions of the water sample until readings on two successive portions differ by no more than 0.05 pH unit. Two portions will usually be sufficient if the water is well-buffered.

22.4 Record the pH and temperature of the sample.

NOTE 4—*Continuous Determination of pH*—Make the selection of the electrodes and the electrode chamber to suit the physical and chemical characteristics of the process water. Locate a submersion style electrode chamber so that fresh representative sampling is provided continuously across the electrodes. Agitation may be required to improve homogeneity. Process pH measurements generally employ automatic temperature compensation. The pH value is usually displayed continuously and can be noted at any specific time. Also, record the successive pH values frequently to provide a permanent record. If the temperature of the sample fluctuates significantly with time, the temperature should also be recorded to interpret the pH values correctly.

23. Report

23.1 Report the temperature of measurement to the nearest 1°C.

23.2 Report the pH to the nearest 0.1 pH unit.

24. Precision and Bias [8]

24.1 Because of the wide variability in measurement conditions and the changeable character of the pH of many process waters, the precision of this test method is probably less than that of Test Method A; however, a precision of 0.1 pH unit should be attainable under controlled conditions.

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

25. Keywords

25.1 hydrogen ion concentration; pH; pH buffer solution

APPENDIX

(Nonmandatory Information)

X1. MISCELLANEOUS NOTES ON GLASS ELECTRODE MEASUREMENTS AND EQUIPMENT

X1.1 Meaning of the Term pH

X1.1.1 The term pH historically has referred to the hydrogen ion activity of a solution and has been expressed as the logarithm to the base 10 of the reciprocal (negative logarithm) of the activity of hydrogen ions at a given temperature, as follows:

$$pH = \log l/(H^+) = -\log(H^+)$$

where:
(H^+) = activity of hydrogen ions.

X1.1.2 Although this expression is helpful in giving theoretical meaning to the term pH and can be used as an approximate definition, it may not be rigorously related to empirical pH measurements. The definition given in 3.2.1 has gained wide acceptance.

X1.2 Temperature Effects

X1.2.1 The effects of temperature on electrometric pH measurements arise chiefly from two sources: (*1*) temperature effects that are common to all electrometric measurements and (*2*) variations of sample pH with temperature. The first category includes the effect of temperature on the factor $F/2.3026\ RT$ that occurs in the definition of pH (see 3.2). Values of this factor for various temperatures are given in Table 1. When electrodes are moved from a solution at one temperature to a solution at another, time is required for internal reference elements to reach the new temperature and, if saturated solutions are involved (for example, calomel or silver chloride electrodes), for the elements to come to a new equilibrium. During this period, some drifting may be observed. The extent of the problem will depend on the nature of the reference elements and their location within the electrodes.

X1.2.2 Secondly, because of changes in activity coefficients and equilibrium constants with temperature, the pH of a sample will change with temperature. These changes are independent of the method of measurement. In general, the rate of change of pH with temperature is not constant, and it may be positive or negative. The data in Table 2, showing changes in pH_s of buffer solutions with temperature, are typical examples. Process samples with known temperature coefficients may take advantage of solution temperature compensation available on some process analyzers to provide readout of pH referenced to 25°C.

X1.3 Reference Electrodes

X1.3.1 In making pH measurements with the glass electrode, the reference electrode used to complete the cell assembly functions simply as a source of reproducible potential. The absolute value of the reference electrode potential is of no consequence owing to the way the measurements are made. Saturated calomel, silver/silver chloride, and iodide-iodine redox references are all widely used and have proven themselves to be satisfactory reference electrodes at normal room temperatures. The calomel is the least satisfactory at elevated temperatures, and the iodide-iodine is the least affected by changing temperatures. Depending on the environmental conditions, other electrodes may serve satisfactorily as reference electrodes.

X1.3.2 If a saturated calomel electrode is used under significantly changeable temperature conditions, care must be taken to see that sufficient solid potassium chloride is present at all the temperatures to ensure solution saturation throughout, both in the free solution in the electrode tube and in the solution permeating the electrode element. The electrode must be given 5 or 10 min to accommodate itself to a new temperature condition before a pH measurement is made. If the temperature falls appreciably, crystallization of potassium chloride may cause plugging of the liquid junction; one result may be high resistance and false or erratic potential at the junction. Any such accumulation of potassium chloride should therefore be removed by aqueous washing.

X1.3.3 Reference electrodes of the unsaturated type have been used preferentially in continuous mechanized pH monitoring where the temperature is likely to fluctuate. The selected potassium chloride concentration is frequently saturation at the lowest temperature of use (for example, approximately 3.3 *N* for 0°C). Such a reference electrode has the advantage of being free from the annoying effects caused by variable solubility, but take considerable care to prepare the required concentration and to maintain the prescribed value under plant operating conditions. Follow the instrument manufacturer's recommendations on choosing and maintaining reference electrodes.

X1.3.4 Reference electrodes are available with any number of means to establish the liquid junction. These include, but are not limited to, dependence on the porosity of wood, fibrous materials, glass-encased noble metal, ground-glass sleeves, ceramic frits, and nonflowing polymeric bodies. Most offsets and fluctuations in readings as a result of stirring are due to effects at the liquid junction of the reference electrode.[9] For laboratory use, cleanable junctions (usually of a sleeve type of construction or having renewable elements) will give more consistent performance in "dirty" samples.

X1.4 Faulty Glass Electrode Response and Restorative Techniques

X1.4.1 *Detecting Faulty Electrodes*—The pH measuring assembly is standardized with two reference buffer solutions (see 12.2) to verify the response of the electrode combination at different pH values. Standardization also detects a faulty glass or reference electrode or an incorrect temperature compensator. The faulty electrode is indicated by a failure to obtain

[9] Brezinski, D. P., "Kinetic, Static and Stirring Errors of Liquid Junction Reference Electrodes," *The Analyst*, 1983, 108, 425.

a reasonably correct value for the pH of the second reference buffer solution after the meter has been standardized with the first. A cracked glass electrode will often yield pH readings that are essentially the same for both standards and should be discarded. Even though a normal glass electrode responds remarkably well to moderate pH changes, it is not necessarily fully responsive, and may miss the rigid requirements of 12.5, if, for example, the pH span is made as great as 5 pH units (phthalate to borax).

X1.4.2 *Imperfect pH Response*—The pH response of the glass electrode may be impaired by a few coating substances (certain oily materials or even some particulates). When the faulty condition is disclosed by the check with the two reference buffer solutions, the electrode can frequently be restored to normal by an appropriate cleaning procedure.

X1.4.3 *Stirring Errors*—If readings drift or are noisy only when the solution is stirred, there are two likely causes: (*1*) the sample is poorly buffered, and the pH is affected by air or CO_2 or (*2*) the reference junction is clogged or malfunctioning.

X1.4.4 *Glass Electrode Cleaning Techniques*—Where emulsions of free oil and water are to be measured for pH, it is absolutely necessary that the electrodes be cleaned thoroughly after each measurement. This may be done by washing with soap or detergent and water, followed by several rinses with water, after which the lower third of the electrodes should be immersed in HCl (1 + 9) to remove any film that may have been formed. Rinse the electrode thoroughly by washing it in several changes of water before returning it to service. Process pH analyzers used for continuous measurement may be provided with an ultrasonic cleaner to lessen or even eliminate the need for manual cleaning of electrodes.

X1.4.5 Thorough cleaning with a suitable solvent may be necessary after each measurement if the sample contains stickly soaps or suspended particles. If this fails, a chemical treatment designed to dissolve the particular deposited coating may prove successful. After the final rinsing of the electrode in the cleaning solvent, immerse the lower third of the electrodes in HCl (1 + 9) to remove a possible residual film. Wash the electrode thoroughly in several changes of water before subjecting it to the standardization procedure.

X1.4.6 Protein coatings may be removed by a 1 to 2 min soak of the bulb in a 30 % solution of a commercial hypochlorite bleach (approximately 1.5 % NaOCl). This should be followed by a rinse in 1 + 9 HCl:water and thorough washing with water.

X1.4.7 If an electrode has failed to respond to the treatment suggested in X1.4.3, try a more drastic measure as a last resort. This drastic treatment, which will limit the life of the electrode and should be used only as an alternative to discarding it, is immersing it in chromic acid cleaning solution for a period of several minutes (or longer if necessary). Chromic acid is particularly effective in cleaning foreign substances from the surface of the glass, but it also has a dehydrating effect on the glass. Consequently allow an electrode so treated, after thoroughly rinsing, to stand in water overnight before using it for measurements. Finally, if the electrode fails to respond to the chromic acid solution, it may be subjected to mild etching in ammonium bifluoride solution. Immerse the electrode for about 1 min in a 20 % solution of ammonium bifluoride (NH_4HF_2) in water, in a polyethylene cup. The bifluoride actually removes a portion of the bulb glass, and should be used only as a last resort (and then only infrequently). Follow the fluoride etch by thorough rinsing and conditioning as is recommended for a new electrode. The electrode manufacturer may have additional suggestions, specific to his own product.

X1.4.8 Techniques for cleaning flow cell electrodes include the use of ultrasonics, brushes, and high-velocity submerged jets.

X1.5 Special Measurements Techniques

X1.5.1 *Measurements on Alkaline Waters*—Although most modern pH glass formulations give good results in alkaline solutions, there can be an error if the solution is quite alkaline and contains high levels of sodium. This effect is greater at elevated temperatures. If in doubt, check with the electrode manufacturer.

X1.5.2 Carbon dioxide from the air tends to react with an alkaline water and to change its pH. Make all measurements with alkaline waters or buffer solutions as quickly as possible, with the water exposed to the air no longer than is absolutely necessary.