



Designation: D 5464 – 93 (Reapproved 2001)

Standard Test Methods for pH Measurement of Water of Low Conductivity¹

This standard is issued under the fixed designation D 5464; 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 These test methods are applicable to determine the pH of water samples with a conductivity lower than 100 $\mu\text{S}/\text{cm}$ (see Annex A1 and Table A1.1 and Table A1.2) over the pH range of 3 to 11 (see Fig. 1). pH measurements of water of low conductivity are problematical (see Annex A2). Specifically, these test methods avoid contamination of the sample with atmospheric gases (see Section 7) and prevent volatile components of the sample from escaping. These test methods provide for pH electrodes and apparatus that address the considerations discussed in Annex A2. These test methods also minimize problems associated with the sample's pH temperature coefficient when the operator uses these test methods to calibrate an on-line pH monitor or controller (see Appendix X1). Two test methods are given as follows:

Test Method	Sections
Test Method A—Precise pH Measurement of Low Conductivity Water Utilizing the Real-Time Flowing Sample Procedure	5 to 12
Test Method B—pH Measurement of Low Conductivity Water Utilizing the Static Grab Sample Procedure	13 to 20

1.2 Test Method A covers the precise measurement of pH in water of low conductivity utilizing a real-time, short duration, flowing sample procedure.

1.3 Test Method B covers the measurement of pH in water of low conductivity with a lower limit of 2.0 $\mu\text{S}/\text{cm}$, utilizing a static grab-sample procedure where it is not practicable to take a real-time flowing sample.

NOTE 1—Test Method A is preferred over Test Method B whenever possible. Test Method A is not subject to the limited conductivity range, temperature interferences, potential KCl contamination, and time limitations found with Test Method B.

1.4 The values stated in SI units are to be regarded as standard.

1.5 *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.*

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, Surveillance of Water, and Flow Measurement of Water.

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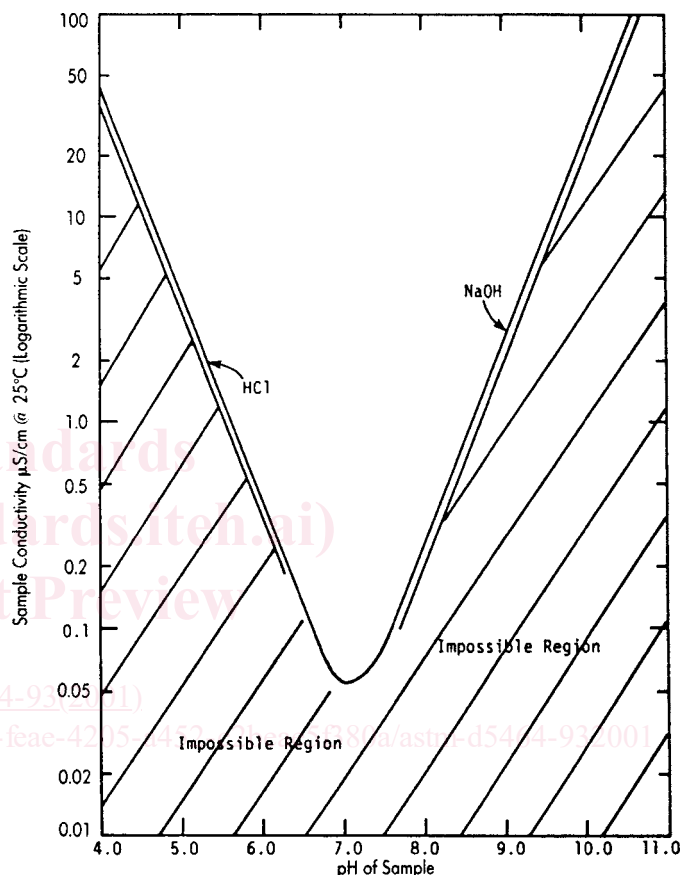


FIG. 1 Restrictions Imposed by the Conductivity-pH Relationship

2. Referenced Documents

2.1 ASTM Standards:

- D 1067 Test Methods for Acidity or Alkalinity of Water²
- D 1129 Terminology Relating to Water²
- D 1193 Specification for Reagent Water²
- D 1293 Test Methods for pH of Water²
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water²
- D 4453 Practice for Handling Ultra-Pure Water Samples²
- D 5128 Test Method for On-Line pH Measurement of Water of Low Conductivity²

² Annual Book of ASTM Standards, Vol 11.01.

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 *liquid junction potential*—a dc potential which appears at the point of contact between the reference electrode's salt bridge and the sample solution. Ideally this potential is near zero, and is stable. However, in low conductivity water it becomes larger by an unknown amount, and is a zero offset (1).³

4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁴ 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.

4.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

4.3 *Commercial Buffer Solutions*—Commercially available prepared buffers traceable to NIST standards should be adequate to perform the calibration procedures in 10.1-10.4. These commercial buffer solutions usually have pH values near 4.01, 6.86, and 10.01 pH at 25°C. The exact pH of the buffer will change with temperature and this pH versus temperature data will be provided by the purveyor of the specific buffer. Refer to Test Methods D 1293, Method A for the preparation of reference buffer solutions if desired.

4.4 *Buffer A*—Commercially available 7.00 pH buffer.

4.5 *Buffer B*—Commercially available 4.00 pH buffer.

4.6 *Buffer C*—Commercially available 10.00 pH buffer.

TEST METHOD A—PRECISE pH MEASUREMENT OF LOW CONDUCTIVITY WATER UTILIZING THE REAL-TIME FLOWING SAMPLE PROCEDURE

5. Summary of Test Method

5.1 The pH meter and associated electrodes are first standardized with two calibration pH buffers. The pH and reference electrodes and the automatic temperature compensator (if used) must be removed from the sample chamber (see Fig. 2) to proceed with this calibration. The complete calibration procedure is given in Section 10 of this test method.

5.2 A real-time flowing grab sample is taken by means of a flow-through sample chamber with the inlet located at the bottom and the outlet located at the top of the chamber. The

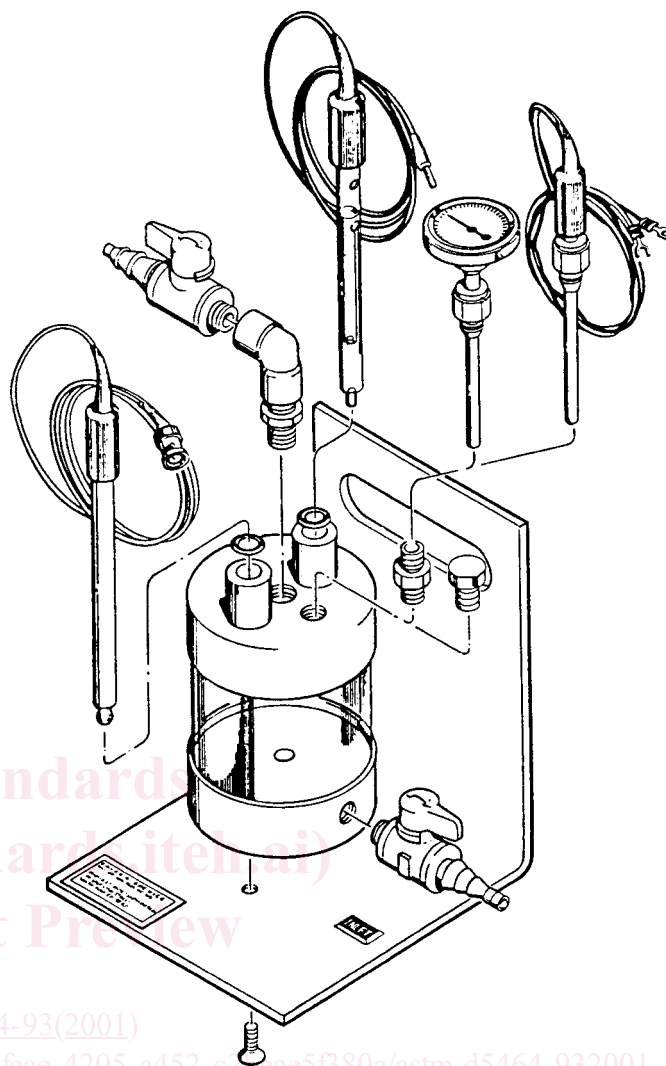


FIG. 2 Exploded View of Sample Chamber

sample chamber prevents the flowing sample from being exposed to the atmosphere. This sample chamber has the pH and reference electrode inserted into the top through gas tight fittings. The temperature compensator (if used) is inserted in a like manner (see Fig. 2 and Fig. 3). The pH of the flowing sample is measured only after the sample chamber has been flushed out with sample water and purged of all air.

5.3 pH measurement of the sample is made with a high purity water pH calibration kit⁵ comprised of a sample chamber, pH and reference electrodes, and automatic temperature compensator (if used). No other type of electrode(s) and pH calibration kit have yet been validated for use with this test method. The sample chamber should accommodate electrodes with an outside diameter of 12 mm ± 0.20 mm (0.472 in. ± 0.008 in.). This is the standard outside diameter size for most pH electrodes manufactured in the United States and Europe.

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

⁴ *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

⁵ Commercially available from Broadley-James Corporation, HPW pH Cal-Kit Series, Santa Ana, CA; Leeds & Northrup, 7082-90/7773 Series, North Wales, PA.; or equivalent.

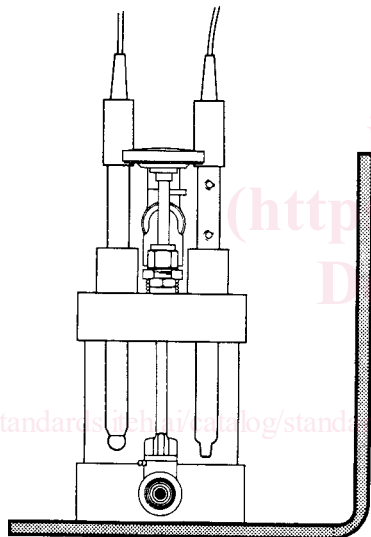
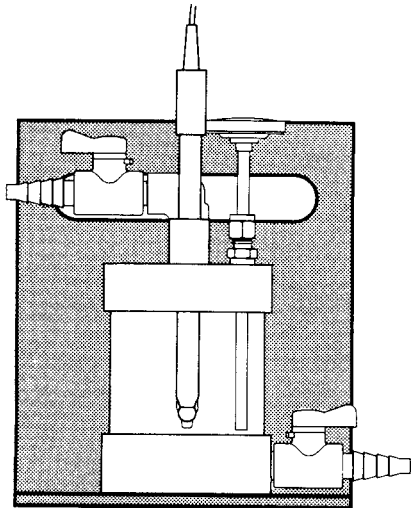


FIG. 3 High Purity Water pH Calibration Sample Chamber

5.4 A trace amount of KCl electrolyte is introduced to calibration buffers and to samples via the controlled leakage rate of the reference electrode liquid junction which stabilizes the liquid junction potential. Excessive KCl introduction from the electrode liquid junction into low ionic strength samples should be avoided. The use of proper apparatus which includes a sample chamber that prevents intrusion of atmospheric gases and a reference electrode with a positive electrolyte leakage rate not to exceed a rate of 10 $\mu\text{L/h}$, will prevent excessive KCl introduction to the sample. Higher rates of up to 50 $\mu\text{L/h}$ of electrolyte leakage can be used if the sample chamber design positions the reference electrode far enough down stream from the glass pH electrode to prevent these impurities from affecting the pH of the sample at the pH electrode site.

5.5 Temperature must be measured and both Solution Temperature Coefficient (STC) and Nernstian effects compensated for, either manually or automatically. The sample chamber, pH electrode pair, and temperature device must be exposed to the

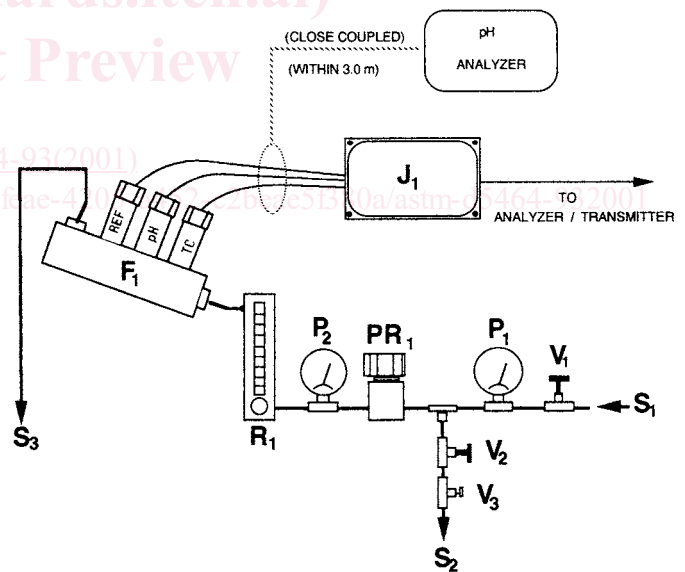
flowing sample long enough to permit temperature equilibration before any measurements are taken.

5.6 The flow rate of the sample through the chamber must be controlled and held constant in order to obtain repeatable results. Each manufacturer of sample chamber must specify a constant flowrate that is optimum for their particular apparatus. To meet this specified constant flowrate, either the grab sample outlet should be controlled with a tamper resistant valve (see Fig. 4 and Fig. 5) or the sample chamber itself should be equipped with an optional rotameter (see Fig. 6). The flowrate should be held constant in the 100 to 300 mL/min range with a constant flowrate of 200 ± 25 mL/min being typically optimal.

6. Significance and Use

6.1 The pH determination of water is a relatively reliable indication of its acidic or alkaline tendency. It is not a measure of the quantity of acidity or alkalinity in a water sample (refer to Test Methods D 1067 and Appendix X1). A pH value less than 7.0 at 25°C shows a tendency toward acidity while a value greater than 7.0 shows a tendency toward alkalinity.

6.2 High purity water is highly unbuffered and the slightest amount of contamination can change the pH significantly. Specifically, high purity water rapidly absorbs CO₂ gas from the atmosphere, which lowers the pH of the sample. The



S₁ SAMPLE INLET, 6.35 mm (1/4 in.) STAINLESS STEEL TUBE FITTING	PR₁ SECONDARY PRESSURE REGULATOR, 0 - 172.4 kPa (gage) (0 - 25 psig)
V₁ HIGH PRESSURE SAMPLE INLET SHUT - OFF VALVE	R₁ ROTAMETER, WITH CONTROL VALVE, 0 - 600 mL/min
P₁ SAMPLE INLET PRESSURE GAUGE 0 - 689.4 kPa (gage) (0 - 100 psig)	P₂ FLOW-CELL PRESSURE GAUGE, 0 - 172.4 kPa (gage) (0 - 25 psig)
V₂ GRAB SAMPLE VALVE / ON-OFF	F₁ HIGH PURITY WATER pH SENSOR
V₃ TAMPER RESISTANT FLOW RATE VALVE, MAX. 200 mL/min AT SPECIFIED SYSTEM PRESSURE	S₃ SAMPLE OUTLET, TO DRAIN, 6.35 mm (1/4 in.), STAINLESS STEEL TUBE FITTING
S₂ GRAB SAMPLE OUTLET	J₁ JUNCTION BOX WITH INTERFACE MODULE

FIG. 4 Schematic for In-Line pH Sensor System with Grab Sample Outlet

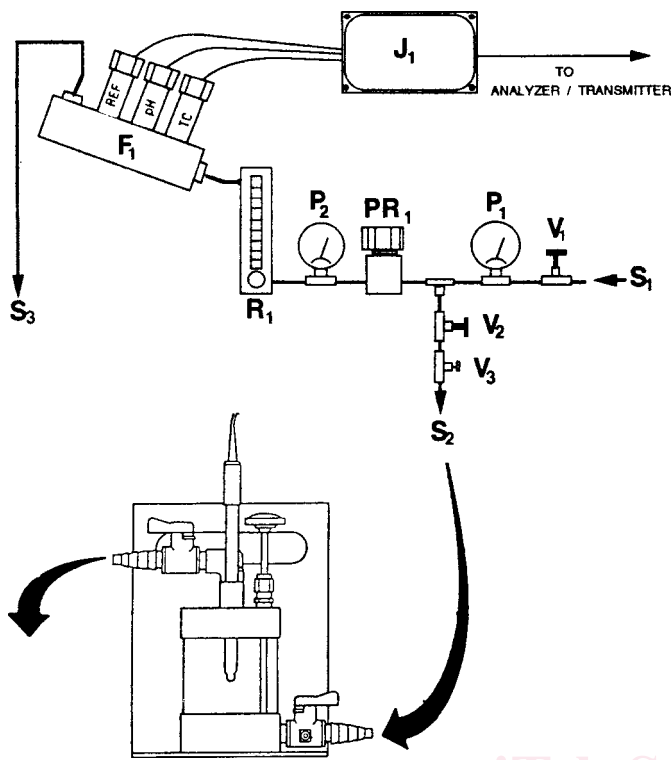


FIG. 5 Sample Chamber Flow Scheme

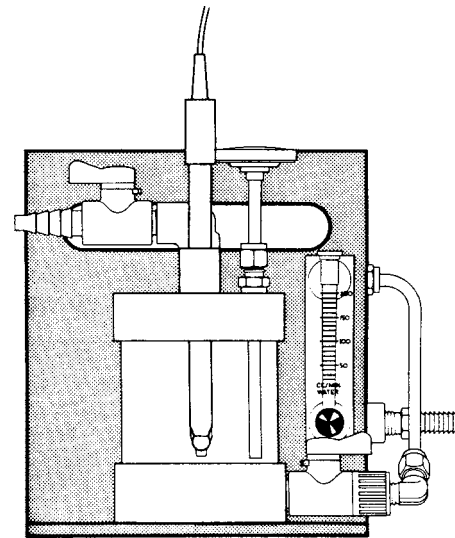


FIG. 6 Sample Chamber with Integral Rotameter

sample chamber and accompanying pH measurement technique avoid exposure of the high purity water sample to the atmosphere.

6.3 The high purity water sample may contain volatile trace components that will rapidly dissipate from the sample if exposed to the atmosphere. The sample chamber used in this test method will prevent these losses.

6.4 High purity water has a significant solution temperature coefficient. For greatest accuracy the sample to be measured should be at the same temperature as the sample stream. By taking a flowing grab sample at the sample line, the operator will use the sample water itself to bring the sample chamber and the measurement electrodes to the sample-line temperature.

7. Interferences

7.1 High purity, low conductivity samples are especially sensitive to contamination from atmospheric gases, from sample containers, and from sample handling techniques and excessive KCl contamination from reference electrode or sample preparation such as a KCl “dosing” technique. Refer to Practice D 4453 and ASTM STP 823 (2) for discussions of sample handling and avoidance of sample contamination.

7.2 Specifically, high purity water will rapidly absorb CO₂ from the atmosphere and this will lower the pH of the sample. See Appendix X4, Table X4.1, and Fig. X4.1.

7.3 The temperature stability of the sample and how closely the sample’s temperature matches the sample stream’s temperature will have a direct effect on accuracy of the pH determination. For a discussion of temperature effects on pH measurements of high purity water see Appendix X1.

8. Apparatus

8.1 *Laboratory pH Meter*—See 10.1 in Test Methods D 1293; or use an equivalent portable pH meter.

8.2 *Sample Chamber*— A high purity water pH calibration chamber⁵ is required (refer to Fig. 3). The chamber enables the operator to measure the pH of a real-time flowing sample of water without exposing the sample to atmospheric gases. The chamber is connected to the sample line via a vinyl tube. Vinyl tubing shall be a laboratory grade which will not affect analyses made on solutions or gases which are put through it. The sample flows into the chamber through the bottom port and out of the chamber through the top port. The chamber has o-ring sealed access ports for the insertion of a pH electrode and a reference electrode. Additionally, the chamber has a 316 stainless steel gland fitting for an automatic temperature compensator or a direct-reading temperature measurement device. The chamber is portable, with an integral stand and carrying handle (see Fig. 2 and Fig. 3).

8.3 *Rotameter (optional)*—The flow rate of the sample chamber must be controlled and stabilized in order to obtain repeatable results (see Fig. 6). Some chambers are available with an integral rotameter.

8.4 *pH Glass Electrode*—The pH response of the glass electrode shall conform to the requirements set forth in 12.1 through 12.5 of Test Methods D 1293. New glass electrodes and those that have been stored dry shall be conditioned and maintained as recommended by the manufacturer.

8.5 *Reference Electrode*—Double junction design, having a flowing junction with a positive electrolyte leakage rate not to exceed a rate of 10 $\mu\text{L/h}$ (see 5.4). Prepare and maintain the reference electrode according to the manufacturer's instructions. When using a sample chamber designed for high electrolyte leakage rates, a reference electrode with a maximum rate of 50 $\mu\text{L/h}$ may be used.

8.6 *Temperature Compensator*—See paragraph 10.4 in Test Methods D 1293. The automatic temperature compensator must adapt for use with the sample chamber to measure the temperature of the water within the chamber.

8.7 *Temperature Indicator*—A direct temperature indicating device must be used to measure sample water temperature within the sample chamber if an automatic temperature compensator is not used.

9. Sampling and Sample Handling

9.1 Equipment as described in apparatus Section 8 should be dedicated for high purity water use only.

9.2 The sample chamber should be rinsed three times before use, twice with sample or tap water and once with reagent water. The electrodes, temperature compensator, or temperature reading device, or all of these, should be rinsed three times, using the same procedure as with the sample chamber, after each calibration in pH buffer solutions and before they are inserted into the sample chamber.

9.3 Real-time samples are taken via vinyl tubing attached to the sample take-off point (see Fig. 5) on the sample line. The other end of the tubing is attached to the bottom port of the sample chamber. The sample flows through the vinyl tube, into the bottom of the chamber, and then out the top of the chamber to an atmospheric discharge trough. The pH measurement is made in a continuous flowing sample, which is completely sealed from the atmosphere.

10. Calibration

10.1 Turn on the pH meter and allow it to warm up according to the manufacturer's instructions.

10.2 Remove the pH and reference electrode and temperature compensator (if used) from the sample chamber. After removal, check the reference electrode for proper electrolyte level as recommended by the manufacturer.

10.3 *Two point*—calibrate the electrode pair and pH meter according to manufacturer's instructions. Also, refer to Section 12 of Test Methods D 1293 for guidelines on the standardization of a pH meter and electrode assembly. Use a quiescent sample of Buffer A and Buffer B if the sample point of interest is below 7.0 pH. Use a quiescent sample of Buffer A and Buffer C if the sample point of interest is above 7.0 pH. Use laboratory glassware dedicated for this service only. Thoroughly

rinse electrode pair and glassware with water three times between each buffer calibration.

10.4 Obtain calibration precision of the pH electrode pair and the pH meter by repeating the two-point calibration described in 10.3, making any necessary readjustments to the pH meter. If the electrode slope (efficiency) is less than 94 % or greater than 101 %, refer to manufacturer's instructions for repair or replacement of electrodes. Thoroughly rinse electrode pair and glassware with water three times between each buffer calibration.

NOTE 2—The pH electrodes in use may pass the above calibration procedures (see 10.1-10.4), but caution should be taken. pH electrodes that are not specifically designed for use in high purity water may develop problems with liquid junction potential during actual test measurements.

10.5 Determine the frequency of the two-point calibration of the electrode pair and the pH meter based on usage. Perform calibration at least daily when pure water sample testing is performed daily. For less frequent pure water sample testing, perform calibration procedures just prior to a consecutive series of sample tests.

10.6 Thoroughly rinse the electrode pair, the temperature compensator, or the temperature reading device, or all of these, and the sample chamber three times (twice with sample water or tap water and once with water), before inserting the probes into the sample chamber.

11. Procedure

11.1 Before starting the procedure, make certain the sample chamber is empty of water. If the chamber contains any water from the last calibration or storage, empty it. This "old" water will only contaminate the highly sensitive high purity water which will flow into the chamber.

11.2 The sample chamber is designed for a constant optimum flow rate of 200 ± 25 mL/min. Either preset a tamper-resistant valve at the grab sample outlet point (see V_3 and S_2 in Fig. 4) or equip the sample chamber with the optional rotameter (see Fig. 6). Do not allow by either means, the flow rate of sample through the sample chamber to exceed 225 mL/min. The flow rate should be held constant.

11.3 Make sure the bottom valve of the sample chamber is closed and the top valve is opened.

11.4 Connect the sample chamber to the sample outlet S_2 with vinyl tubing (see Fig. 5).

NOTE 3—If on-line pH sensors are to be calibrated by this test method (refer to Test Method D 5128), steps must be taken to prevent the disturbance of the on-line pressure and flow rate while the grab sample is being taken. The equipment set-up shown in Fig. 4 will control and stabilize this on-line pressure and flow rate by means of rotameter R_1 and secondary pressure regulator PR_1 even when a sample is taken at grab sample point S_2 (see Appendix X2).

11.5 Open valve V_2 and pull sample without interrupting the sample flow-rate or pressure of the on-line pH sensor assembly (see on-line pH sensor manufacturer's instructions for optimum settings of pressure regulator, rotameter, and valves). The optimum flow-rate through the high purity water sample chamber is a constant 200 ± 25 mL/min. (This flow rate will automatically be obtained after the on-off valve V_2 is opened

and the tamper resistant flow-rate valve V_3 is set as instructed by on-line pH sensor manufacturer.)

11.5.1 If the chamber with the optional integral rotameter is being used, then adjust the rotameter for a constant flow rate of 200 ± 25 mL/min.

11.5.2 Starting with an empty chamber, thoroughly flush the high purity water sample chamber with sample water for at least 15 min at a flow rate of 200 ± 25 mL/min.

11.6 Observe the temperature of the water as indicated on the chamber thermometer and record it for future reference. If the portable pH meter being used has manual temperature compensation, adjust the Temp. Comp. control to the temperature of the sample water in the chamber.

11.7 After the 15 to 30 min sample water flush is complete, allow the water to continue flowing through the chamber. The pH electrode pair will have reached equilibrium by now and the pH meter will be indicating the pH of the sample water. Call this reading R_1 and list the temperature of the sample along with the pH value.

11.8 To use this pH measurement to calibrate an on-line pH sensor, refer to the procedure presented in [Appendix X2](#).

11.9 Close sample valve V_2 followed by the sample chamber's lower inlet valve and finally the upper outlet valve.

NOTE 4—If no further samples are to be taken, the calibrated pH electrode pair may be kept stored in the sample chamber containing a trace amount of the last pure water sample not in contact with either electrode (with inlet and outlet valves shut tight) until the next calibration or sample requirement. For long-term storage of the pH electrode pair, replace them in their respective soaker bottles and appropriate storage solutions (refer to manufacturer's instructions).

12. Precision and Bias

12.1 Since this test method takes a measurement on a flowing sample, a true precision and bias cannot be determined, as stated in Practice [D 2777](#).

12.2 For the results of a study comparing Test Methods A and B, see [Annex A3](#).

TEST METHOD B—pH MEASUREMENT OF LOW CONDUCTIVITY WATER UTILIZING THE STATIC GRAB SAMPLE PROCEDURE

13. Summary of Test Method

13.1 The pH meter and associated electrodes are first standardized with two calibration pH buffers. The pH and reference electrodes and the automatic temperature compensator (if used) must be removed from the sample chamber (see [Fig. 2](#)) to proceed with this calibration. The complete calibration procedure is given in Section 10 of Test Method A.

13.2 A grab sample of high purity water is taken by means of filling a sample chamber with the inlet located at the bottom and the outlet located at the top of the chamber. Both inlet and outlet ports are equipped with shut-off valves suitable for attaching the vinyl sample tubing. Once the chamber is filled with a representative sample, the valves can be shut off and the sample may be transported back to a laboratory for analysis. The sample chamber is equipped with o-ring sealed access ports for the pH electrode pair and a 316 stainless steel gland fitting for the temperature indicator or optional automatic

temperature compensator. A suitable stand with carrying handle is provided for portability of the sample chamber (see [Fig. 2](#) and [Fig. 3](#)).

13.3 pH measurement of the sample is made with a high purity water pH calibration kit⁵ comprised of a sample chamber, pH and reference electrodes, and automatic temperature compensator (if used). No other type of electrode(s) and pH calibration kit have yet been validated for use with this test method. The sample chamber should accommodate electrodes with an outside diameter of $12 \text{ mm} \pm 0.20 \text{ mm}$ ($0.472 \text{ in.} \pm 0.008 \text{ in.}$). This is the standard outside diameter size for most pH electrodes manufactured in the United States and Europe.

13.4 A trace amount of KCl electrolyte is introduced to calibration buffers and to samples via the controlled leakage rate of the reference electrode liquid junction to stabilize the liquid junction potential. Excessive KCl introduction from the electrode liquid junction into low ionic strength samples will increase solution conductivity, and alter solution pH, and should be avoided. The use of proper apparatus which includes a sealed sample chamber in conjunction with a reference electrode with a positive electrolyte leakage rate not to exceed a rate of $10 \mu\text{L/h}$, will prevent excessive KCl introduction to the sample.

13.5 Temperature must be measured and both Solution Temperature Coefficient (STC) and Nernstian effects compensated for, either manually or automatically on the pH meter. See [Appendix X1](#) for a discussion on temperature effects.

13.6 The chamber should not be filled at a rate of greater than 225 mL/min. Either the grab sample outlet should be controlled with a tamper resistant valve (as in [Fig. 4](#)) or the sample chamber should be equipped with an optional rotameter (as in [Fig. 6](#)).

14. Significance and Use

14.1 Although there are similarities between Test Methods A and B, there are also valid reasons for considering one test method versus the other. Whenever Test Method A, which requires a real-time, short duration, flowing sample, cannot be utilized for practical reasons such as physical plant layout, location of on-line equipment sample points, or availability of dedicated test equipment, Test Method B offers a viable alternative procedure.

14.1.1 The most significant difference between the two test methods is that Test Method A obtains a *real-time* pH measurement from a flowing sample and Test Method B obtains a *time delayed* pH measurement from a static grab sample.

14.2 pH measurements of low conductivity water are plagued with interferences (see [7.1-7.3](#)) and Test Method A is more effective in eliminating these interferences especially with regard to temperature effects. The static grab sample (Test Method B) is more prone to contamination and temperature-induced errors because of the time lag between the sampling in the plant and sample pH reading which is taken in the laboratory.

14.3 If the purpose of these pH measurements is to verify or calibrate, or both, an on-line pH sensor, refer to Test Method [D 5128](#) which requires a real-time, flowing sample technique