Designation: D5464 – 16

Standard Test Method for pH Measurement of Water of Low Conductivity[1]

This standard is issued under the fixed designation D5464; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is applicable to determine the pH of water samples with a conductivity of 2 to 100 µS/cm over the pH range of 3 to 11 and is frequently used in power generation low conductivity samples. pH measurements of water of low conductivity are problematic. Specifically, this test method avoids contamination of the sample with atmospheric gases and prevents volatile components of the sample from escaping. This test method provides for pH electrodes and apparatus that address additional considerations discussed in Annex A2. This test method also minimizes problems associated with the sample's pH temperature coefficient when the operator uses this test method to calibrate an on-line pH monitor or controller (see Appendix X1).

1.2 This test method covers the measurement of pH in water of low conductivity with a lower limit of 2.0 µS/cm, utilizing a static grab-sample procedure where it is not practicable to take a real-time flowing sample.

NOTE 1—Test Method D5128 for on-line measurement is preferred over this method whenever possible. Test Method D5128 is not subject to the limited conductivity range, temperature interferences, potential KCl contamination, and time limitations found with this method.

1.3 For on-line measurements in water with conductivity of 100 µS/cm and higher, see Test Method D6569.

1.4 For laboratory measurements in water with conductivity of 100 µS/cm and higher, see Test Method D1293.

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

1.6 *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:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1293 Test Methods for pH of 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
D4453 Practice for Handling of High Purity Water Samples
D5128 Test Method for On-Line pH Measurement of Water of Low Conductivity
D6569 Test Method for On-Line Measurement of pH

3. Terminology

3.1 *Definitions of Terms*—For definitions of terms used in this test method, refer to Terminology D1129.

3.2 *Definitions:*

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *liquid-junction potential, n*—a dc potential that appears at the point of contact between the reference electrode's salt bridge (also known as reference junction or diaphragm) and the sample solution.

3.3.1.1 *Discussion*—Ideally, this potential is near zero and is stable. However, in low-conductivity water this potential may change from its value in buffer solution 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

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[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 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] 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.

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

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*—References to water that is used for reagent preparation, rinsing or dilution shall be understood to mean water that conforms to the quantitative specifications of Type II reagent water of Specification D1193.

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. 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 D1293 for the preparation of reference buffer solutions if desired.

4.4 *Buffer A*—Commercially available 7.0 pH buffer.

4.5 *Buffer B*—Commercially available 4.0 pH buffer.

4.6 *Buffer C*—Commercially available 9.0 or 10.0 pH buffer.

5. Summary of Test Method

5.1 The pH meter and associated electrodes are first standardized with two calibration pH buffer solutions.

5.2 A grab sample of high purity water is taken by means of rinsing and filling two narrow mouth bottles at the sample point. Once each container is filled to the top with a representative sample excluding any air, the containers are capped and the samples are transported quickly to a laboratory for analysis.

5.3 pH measurement of the sample is made with high purity water pH calibration apparatus comprised of pH and reference electrodes, and automatic temperature compensator (if used). The first container is used to rinse the sensors and begin temperature equilibration and the second container is used for measurement.

5.4 A trace amount of KCl electrolyte enters calibration buffer solutions and samples via the controlled leakage rate of the reference electrode liquid junction (diaphragm) to stabilize the liquid junction potential. Excessive KCl introduction from the electrode liquid junction into low ionic strength samples will increase solution conductivity, and may alter solution pH, and should be avoided.

5.5 Temperature must be measured and both Solution Temperature Coefficient (STC) and Nernst electrode effects compensated, either manually to the measured value or automatically by the pH meter. See Appendix X1 for a discussion of temperature effects.

6. Significance and Use

6.1 pH measurement of low conductivity water is frequently applied to power plant water and condensed steam samples for corrosion and scale prevention. It is sometimes used in pure water treatment systems between multiple pass membranes to optimize performance.

6.2 High purity water is highly unbuffered and small amounts of contamination can change the pH significantly. Specifically, high purity water rapidly absorbs CO_2 gas from the atmosphere, which lowers the pH of the sample. The sample container and accompanying pH measurement technique minimize exposure of the high purity water sample to the atmosphere.

6.3 The high purity water sample may contain volatile trace components that will dissipate from the sample if exposed to the atmosphere. The sample container 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 close to the temperature of the sample stream and appropriate compensation should be applied.

6.5 When the preferred Test Method D5128, which requires a real-time, flowing sample, cannot be utilized for practical reasons such as physical plant layout, unacceptable loss of water, location of on-line equipment sample points, or availability of dedicated test equipment, this method offers a viable alternative. The most significant difference between the two test methods is that Test Method D5128 obtains a real-time pH measurement from a flowing sample and this method obtains a time delayed pH measurement from a static grab sample.

6.6 pH measurements of low conductivity water are always subject to interferences (7.1 – 7.5) and Test Method D5128 is more effective in eliminating these interferences especially with regard to contamination. This static grab sample method 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.

7. Interferences

7.1 High purity, low conductivity samples are especially sensitive to contamination from atmospheric gases, from sample containers, from sample handling techniques and from excessive electrolyte (KCl) contamination from reference electrode or sample preparation such as a KCl "dosing" technique. Refer to Practice D4453 and *ASTM STP 823* (**2**) for discussions of sample handling and avoidance of sample contamination.

7.2 High purity water will rapidly absorb CO_2 from the atmosphere and this will lower the pH of the sample at a rate depending on the buffer capacity of the sample, the surface area of the sample exposed to air, movement of the sample, and the concentration of CO_2 at the surface of the sample which may increase if the operator exhales over the container during sampling or measurement. See Appendix X3, Table X3.1, and Fig. X3.1.

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[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 *Annual 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.

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 since temperature compensation is not perfect.

7.4 If pH is to be referenced to 25°C as required by most specifications, temperature compensation must be provided for both the Nernst response of the electrode output (provided in most pH meters) and solution ionization effects (provided only with some on-line pH meters or by calculation with lab meters). For a discussion of temperature effects on pH measurements of high purity water see Appendix X1.

7.5 The reference junction potential can vary with ionic strength of the sample and provide an undetectable zero offset between the high ionic strength of the buffer solution and the low ionic strength of the sample. A flowing junction reference electrode (one which requires periodic refilling with electrolyte solution or that has internal electrolyte pressurization or both) minimizes this effect.

8. Apparatus

8.1 *pH Meter,* capable of reading to 0.01 pH. The meter should preferably have automatic temperature compensation for the Nernst response of pH electrodes which provides the conversion of the electrode millivolt signal to the pH value at the measured temperature. Some on-line meters also provide an input for a solution temperature coefficient for ionization effects of the particular sample. This allows direct readout of pH referenced to 25°C. Otherwise a calculation is required.

8.2 *Sample Containers*—Two clean, narrow-mouth 250 to 500 mL bottles with cap are required. The mouth diameter should be the minimum necessary to allow insertion of the electrode(s), and temperature compensator or thermometer. A 3-hole stopper may be used to hold these sensors. The container and cap minimize exposure to atmospheric gases.

8.3 *Combination pH Electrode*—A probe incorporating the measuring, reference and temperature compensator functions in a single unit is recommended for its ease of insertion into a very narrow mouth sample container. Each function should conform to the characteristics in 8.4 – 8.6. Where this is not available, individual electrodes and compensator (8.4 – 8.6) may be used with a 3-hole stopper to hold them and seal the container during measurement.

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 D1293. 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 refillable flowing junction with a positive electrolyte leakage rate not to exceed 10 µL/h. A sealed reference electrode is suitable only if it is internally pressurized to force an electrolyte flow outward. Prepare and maintain the reference electrode according to the manufacturer's instructions.

8.6 *Temperature Compensator*—See paragraph 10.4 in Test Methods D1293. The automatic temperature compensator must fit into the sample container to measure the temperature of the water within the container.

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

8.8 Equipment for this test method should be dedicated for high purity water use only.

9. Sampling and Sample Handling

9.1 The sample containers should be rinsed three times before use, with sample or reagent water.

9.2 Static grab samples are taken via clean tubing attached to the sample take-off point. The other end of the tubing is inserted to the bottom of the sample container. The sample flows through the tube, into the bottom of the container, and then over the top to trough or sink drain. After a 5-min flush of the container with the sample water, the tubing is removed and the cap immediately installed, excluding any air. This seals the container and isolates the sample from the atmosphere. The second container is filled and capped in the same way. In the lab, the first container is used to rinse the electrodes and temperature device and the second container is used for measurement.

10. Calibration

10.1 Turn on the pH meter and allow it to warm up according to the manufacturer's instructions. If an on-line meter is used that has a solution temperature coefficient setting, be sure it is turned off or is set to 0 pH/°C for calibration in buffer solutions. Conventional Nernst temperature compensation should be active at all times and requires no setting.

10.2 Remove the electrode(s) and temperature compensator (if used) from storage. Check the reference electrode for proper electrolyte level as recommended by the manufacturer.

10.3 Calibrate the electrode(s) and pH meter at two points according to manufacturer's instructions. Also, refer to Section 12 of Test Methods D1293 for guidelines on the calibration 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 the electrode(s) and glassware with reagent water three times between immersion in each buffer solution.

10.4 Obtain calibration precision of the pH electrode(s) 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 electrode(s).

NOTE 2—The pH electrodes in use may pass the above calibration procedures (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(s) and the pH meter based on experience. 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(s) and the temperature compensator or temperature reading device and the sample container three times with sample or reagent water after calibration and before measurement.

11. Procedure

11.1 Before starting the procedure, make certain the two sample containers are clean and empty. See Section 9.

NOTE 3—If on-line pH sensors are to be calibrated by this test method (refer to Test Method D5128), steps should be taken to prevent the disturbance of the on-line pressure and flow rate while the grab sample is being taken. Appropriate pressure and flow regulation equipment should be installed at the grab sample point upstream of the on-line sensor. See D3370. Appendix Appendix X2 provides guidance on grab sample calibration of on-line instrumentation.

11.2 Open the sample valve and pull sample without interrupting the sample flow-rate or pressure of the on-line pH sensor assembly if used (see on-line pH sensor manufacturer's instructions for its optimum flowrate). The grab sample flowrate should be at least 200 mL/min.

11.3 With the sample flowing, rinse the outside surfaces of the sample tubing for at least 15 seconds by holding it with the open discharge end upward like a fountain, allowing the sample to flow over the outside tubing surfaces for more than the length that will be later immersed in the sample container, allowing the flow to drain into the sampling trough or sink.

11.4 Run the end of the sample tubing to the bottom of the sample container letting the sample overflow into the sink.

11.5 Thoroughly flush the sample container with sample water for at least 5 min at a flow rate of at least 200 mL/min.

11.6 Remove the sample tubing and immediately cap the container. Repeat for the second container and close sample valve.

11.7 Transport the sample containers to the laboratory without delay and immediately immerse the sensors (which have already been calibrated and rinsed thoroughly) in the first container for 1 min to acclimate them to the sample composition and temperature.

11.8 Move the sensors to the second container. Take the pH and temperature measurements within 3 min in order to minimize KCl contamination from the reference electrode and change in the temperature of the grab sample.

11.9 Report the pH value with 0.01 pH resolution and the temperature with 0.1°C resolution.

11.10 If the pH must be referenced to 25°C and the sample is not already at 25.0 ± 0.5°C, determine the applicable solution temperature coefficient and calculate the pH at 25.0°C in accordance with Appendix X1 and report it with resolution of 0.01 pH.

11.11 To use this pH measurement to calibrate an on-line pH sensor, call the value from 11.9 or 11.10 R_1 and refer to the procedure addendum in Appendix X2.

NOTE 4—If no further samples are to be taken, the calibrated pH electrode(s) may be kept stored in the sample container containing the last pure water sample until the next calibration or sample requirement. For long term storage of the pH electrode(s), replace them in their respective soaker bottles and appropriate storage solutions (see manufacturer's instructions).

12. Quality Control

12.1 Two-point instrument calibration must be performed according to the manufacturer's instructions within 12 h of making measurements.

12.2 With power plant samples containing predominately ammonia and negligible carbon dioxide, an accurate correlation with specific conductivity can be made. See Fig. X3.1. Under these conditions, periodically verify pH readings corrected to 25°C by solution temperature compensation with the conductivity also referenced to 25°C. Some two-channel conductivity instrumentation includes an option for the calculation of pH based on specific and cation conductivity and will make a correction for the presence of minor amounts of carbon dioxide and other contaminants. If available, use this calculated value to verify the measured pH readings under normal plant operating conditions.

13. Precision and Bias

13.1 Neither precision nor bias data can be obtained for this test method from a collaborative study designed in accordance with the requirements of Practice D2777 since this test method relies on the capture of a flowing sample, and the sample must remain captive until after the measurement is taken due to its high vulnerability to contamination. This inability to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice D2777.

14. Keywords

14.1 automatic temperature compensator; controlled leakage rate; flowing liquid junction; high purity water; liquid junction potential; low conductivity water; pH glass electrode; pH temperature coefficient; reference electrode; solution temperature coefficient

ANNEXES

(Mandatory Information)

A1. DISCUSSION OF THE CONDUCTIVITY RANGE FOR THIS TEST METHOD

A1.1 The scope of this test method provides the user with a guideline conductivity range (<100 µS/cm) for what is considered low conductivity or pure water. This conductivity range is not a specific cut-off or limit, but is intended to provide the user with an indication of when to apply this test method for reliable pH measurements. Tables A1.1 and A1.2 illustrate the high pH sensitivity of low ionic strength water samples containing low concentrations of contaminants. The sources of these contaminants can include the atmosphere (see Table X3.1), the pH measurement apparatus, and improper procedures.

TABLE A1.1 Calculated Conductivity and pH Values at 25°C of Low Concentrations of NaOH in Pure Water [A, B]

NOTE 1—This table tabulates the theoretical conductivity and pH values of low levels of NaOH in pure water as calculated from available thermodynamic data.

NOTE 2—To illustrate the high sensitivity of the sample pH at these low concentrations to contaminants, the last column lists errors that would result if the sample were contaminated with an additional 1 mg/L through sample or equipment handling errors.

Sample Concentration, mg/L	Sample Conductivity, µS/cm	Sample pH	ΔpH Error from Additional 1 mg/L NaOH Contaminate
0.001	0.055	7.05	Δ2.35
0.010	0.082	7.45	Δ1.95
0.100	0.625	8.40	Δ1.03
1.0	6.229	9.40	Δ0.30
8.0	49.830	10.30	Δ0.05

[A] Data courtesy of R. C. Hunt, "Calculated pH and Conductivity Values," Sensor Development, Inc., June 1986.

[B] This data was developed from algorithms originally published in *Ultrapure Water* as: Hunt, Robert C., "A Review of pH and Conductivity Measurement Techniques in High Purity Water, with Bibliography," *Ultrapure Water*, Vol 4, 1987, p. 26.

TABLE A1.2 Calculated Conductivity and pH Values at 25°C of Low Concentrations of HCl in Pure Water [A, B]

NOTE 1—This table tabulates the theoretical conductivity and pH values of low levels of HCl in pure water as calculated from available thermodynamic data.

NOTE 2—To illustrate the high sensitivity of the sample pH at these low concentrations to contaminants, the last column lists errors that would result if the sample were contaminated with an additional 1 mg/L through sample or equipment handling errors.

Sample Concentration, mg/L	Sample Conductivity, µS/cm	Sample pH	ΔpH Error from Additional 1 mg/L HCl Contaminate
0.001	0.060	6.94	Δ2.38
0.010	0.134	6.51	Δ1.95
0.100	1.166	5.56	Δ1.03
1.0	11.645	4.56	Δ0.30
8.0	93.163	3.66	Δ0.05

[A] Data courtesy of R. C. Hunt, "Calculated pH and Conductivity Values," Sensor Development, Inc., June 1986.

[B] This data was developed from algorithms originally published in *Ultrapure Water* as: Hunt, Robert C., "A Review of pH and Conductivity Measurement Techniques in High Purity Water, with Bibliography," *Ultrapure Water*, Vol 4, 1987, p. 26.

A2. CONSIDERATIONS FOR THE REQUIREMENT OF SPECIALIZED pH MEASUREMENT APPARATUS

A2.1 pH electrodes are available in many different configurations containing a wide variety of membrane and liquid junction designs as well as a variety of internal electrolyte formulations. Selection of the appropriate pH electrode features required for pH measurement of low conductivity water is not necessarily obvious.

A2.1.1 The temperature coefficient of the electrodes will affect the accuracy and repeatability of the measurement. Electrodes which quickly equilibrate to each other and the sample temperature must be selected for this service. Refer to X1.2 in Test Method D1293.

A2.1.2 Continuous exposure of the pH electrode to low ionic strength solutions may result in the degradation of the glass membrane portion of some pH electrodes (**3**). Electrodes suitable for continuous service in low conductivity water should be included in the pH electrode selection.

A2.1.3 The development of changes in liquid junction potentials (**1**) with time and eventual degradation of the reference half-cell caused by diffusion of low ionic strength sample water into the high ionic strength electrolyte of the half cell must be avoided in order to effect an accurate and stable pH measurement.

A2.2 All sorts of laboratory glassware and plasticware containers have been used to grab and contain low conductivity water samples for pH measurement. A sample container used for this service should be dedicated for use with only low conductivity water samples to avoid carry-over contamination. Further, such a container should be designed such that it seals the sample from atmospheric gas contaminants (see Table X3.1) while preventing volatile sample constituents from escaping for the duration of each sample measurement. The sample container should contain the pH electrodes and temperature compensator in such a manner that the sample is minimally exposed to the atmosphere. This container should permit a short duration grab sample to be taken in such a manner that the sample temperature is not altered.

APPENDIXES

(Nonmandatory Information)

X1. TEMPERATURE EFFECTS IN PURE WATER

X1.1 There are two types of temperature effects that are of main concern during the pH measurement of low conductivity waters: Standard Nernst equation temperature factor and Solution Temperature Coefficient (STC) effect of low conductivity water where it is typically required to report the pH referenced to 25°C.

X1.2 The standard Nernst compensation is normally provided by the automatic temperature compensation (ATC) feature of most pH meters and the temperature sensor provided with the pH electrodes or sensor assembly. It corrects for the changing output signal (mV/pH) of glass measuring electrodes with temperature and provides the pH value at the measured temperature..

X1.2.1 pH meters with manual temperature compensation can accomplish the same result as long as the operator accurately measures the sample temperature and enters that temperature into the pH meter.

X1.3 The STC effect is the rate at which a particular water sample changes its pH with changes in temperature due to partial ionization effects. This rate varies with the amounts and types of trace constituents that are found in a particular sample of high purity water. Small amounts of alkaline contaminants such as ammonia or amines in power plant samples can cause samples to have temperature coefficients near –0.03 pH unit/°C.

X1.4 The technician must determine the appropriate solution temperature coefficient (STC) for the sample composition to make the correction. For example, the technician can measure the pH in the laboratory at 20°C and then calculate what the pH would be at 25°C by applying the STC. The compensation calculation is $pH_{25} = pH_T + (25 - T) \times STC$. For this example, with a STC of –0.03 pH/°C, a pH of 9.00 measured at 20°C without solution temperature compensation would have a pH at 25°C of $9.00 + (25 - 20) \times (-0.03) = 8.85$.

X1.4.1 The technician may attempt to empirically derive the STC by measuring the pH of a known solution at two or more different temperatures. The technician must observe and record the pH of the high purity water at various temperatures over a period of time during which the water chemistry is constant and representative. This technique is vulnerable to errors caused by contamination during the temperature changes. However, for water chemistries that remain fairly constant, it may be possible to empirically derive a STC correction factor which can then be used to reference all pH readings of that particular water stream to 25°C.

X1.4.2 Table X1.1 and Table X1.2 list pH values and temperature corrections for normalizing pH measurements to 25°C as calculated by NUS Corporation. These calculated values are applicable for the following solutions:

X1.4.2.1 Pure water;

X1.4.2.2 Matrix No. 1: 4.84 mg/L sulfate (prepared from sulfuric acid), which represents an acidic solution at pH 4.0 at 25°C;

TABLE X1.1 pH as a Function of Temperature for Different Matrixes [A, B]

Temperature, °C	Matrix No. 1 pH	Matrix No. 2 pH	Matrix No. 3 pH	Matrix No. 4 pH
0	4.004	9.924	10.491	10.388
1	4.004	9.882	10.451	10.345
2	4.004	9.840	10.411	10.303
3	4.004	9.800	10.372	10.261
4	4.004	9.759	10.333	10.219
5	4.004	9.719	10.294	10.178
6	4.004	9.680	10.256	10.138
7	4.004	9.640	10.218	10.098
8	4.004	9.602	10.181	10.058
9	4.004	9.563	10.144	10.019
10	4.004	9.525	10.108	9.981
11	4.004	9.488	10.072	9.943
12	4.004	9.451	10.036	9.905
13	4.004	9.414	10.001	9.868
14	4.005	9.378	9.966	9.831
15	4.005	9.342	9.932	9.795
16	4.005	9.307	9.898	9.759
17	4.005	9.272	9.864	9.723
18	4.005	9.237	9.831	9.688
19	4.005	9.203	9.798	9.654
20	4.005	9.169	9.765	9.619
21	4.005	9.135	9.732	9.583
22	4.006	9.102	9.700	9.552
23	4.006	9.069	9.669	9.519
24	4.006	9.036	9.637	9.486
25	4.006	9.002	9.604	9.451
26	4.006	8.972	9.576	9.421
27	4.006	8.940	9.545	9.390
28	4.007	8.909	9.515	9.358
29	4.007	8.878	9.485	9.327
30	4.007	8.847	9.456	9.296
31	4.007	8.817	9.426	9.266
32	4.007	8.787	9.397	9.236
33	4.008	8.757	9.369	9.206
34	4.008	8.728	9.340	9.177
35	4.008	8.699	9.312	9.148
36	4.008	8.670	9.284	9.119
37	4.009	8.641	9.257	9.091
38	4.009	8.613	9.229	9.063
39	4.009	8.585	9.202	9.035
40	4.010	8.557	9.175	9.007
41	4.010	8.529	9.149	8.980
42	4.010	8.502	9.122	8.953
43	4.010	8.475	9.096	8.925
44	4.011	8.448	9.070	8.900
45	4.011	8.422	9.044	8.874
46	4.011	8.396	9.019	8.848
47	4.012	8.370	8.994	8.823
48	4.012	8.344	8.969	8.757
49	4.012	8.318	8.944	8.772
50	4.013	8.293	8.919	8.748

[A] See X1.4.
Matrix No. 1: 4.84 mg/L $SO_4^{=}$ (from sulfuric acid),
2: 0.272 mg/L NH_3 + 20 µg/L N_2H_4,
3: 1.832 mg/L NH_3 + 10.0 mg/L morpholine + 50 µg/L N_2H_4, and
4: 3.0 mg/L PO_4 at 2.7 Na^+:$PO_4^{=}$ + 0.30 mg/L NH_3.

[B] Values calculated by John Riddle, NUS Corporation, Pittsburgh, PA.

TABLE X1.2 Temperature Corrections of pH Measurements for Different Matrixes [A, B]

Temperature, ° C	Pure Water Temperature Correction	Matrix No. 1 Temperature Correction	Matrix No. 2 Temperature Correction	Matrix No. 3 Temperature Correction	Matrix No. 4 Temperature Correction
0	−0.477	−0.002	−0.923	−0.887	−0.937
1	−0.455	−0.002	−0.881	−0.847	−0.894
2	−0.433	−0.002	−0.838	−0.807	−0.851
3	−0.412	−0.002	−0.798	−0.767	−0.809
4	−0.390	−0.002	−0.757	−0.728	−0.768
5	−0.369	−0.002	−0.717	−0.690	−0.727
6	−0.349	−0.002	−0.678	−0.652	−0.686
7	−0.328	−0.002	−0.639	−0.614	−0.647
8	−0.308	−0.002	−0.600	−0.577	−0.607
9	−0.288	−0.002	−0.561	−0.540	−0.568
10	−0.269	−0.002	−0.524	−0.504	−0.530
11	−0.249	−0.002	−0.486	−0.468	−0.491
12	−0.230	−0.002	−0.449	−0.432	−0.454
13	−0.211	−0.002	−0.412	−0.397	−0.417
14	−0.193	−0.002	−0.376	−0.362	−0.380
15	−0.174	−0.001	−0.340	−0.327	−0.343
16	−0.156	−0.001	−0.305	−0.293	−0.308
17	−0.138	−0.001	−0.270	−0.260	−0.272
18	−0.120	−0.001	−0.235	−0.226	−0.237
19	−0.102	−0.001	−0.201	−0.193	−0.202
20	−0.085	−0.001	−0.167	−0.160	−0.168
21	−0.068	−0.001	−0.133	−0.128	−0.132
22	−0.051	−0.001	−0.100	−0.096	−0.100
23	−0.034	−0.000	−0.067	−0.064	−0.057
24	−0.017	−0.000	−0.034	−0.033	−0.034
25	0.000	0.000	0.000	0.000	0.000
26	0.015	0.000	0.030	0.029	0.030
27	0.031	0.000	0.062	0.059	0.062
28	0.047	0.001	0.093	0.089	0.093
29	0.063	0.001	0.124	0.119	0.124
30	0.078	0.001	0.154	0.149	0.155
31	0.094	0.001	0.185	0.178	0.185
32	0.109	0.001	0.215	0.207	0.215
33	0.124	0.002	0.245	0.236	0.245
34	0.139	0.002	0.274	0.264	0.274
35	0.153	0.002	0.303	0.292	0.304
36	0.168	0.002	0.332	0.320	0.332
37	0.182	0.003	0.361	0.348	0.361
38	0.196	0.003	0.389	0.375	0.389
39	0.210	0.003	0.417	0.402	0.417
40	0.224	0.004	0.445	0.429	0.444
41	0.238	0.004	0.472	0.456	0.471
42	0.252	0.004	0.500	0.482	0.498
43	0.265	0.004	0.527	0.508	0.525
44	0.278	0.005	0.553	0.534	0.551
45	0.292	0.005	0.580	0.560	0.577
46	0.305	0.005	0.606	0.585	0.603
47	0.318	0.006	0.632	0.611	0.629
48	0.330	0.006	0.658	0.636	0.654
49	0.343	0.006	0.684	0.661	0.679
50	0.356	0.007	0.709	0.685	0.704

[A] See X1.4.
Matrix No. 1: 4.84 mg/L $SO_4^{=}$ (from sulfuric acid),
2: 0.272 mg/L NH_3 + 20 µg/L N_2H_4,
3: 1.832 mg/L NH_3 + 10.0 mg/L morpholine + 50 µg/L N_2H_4, and
4: 3.0 mg/L PO_4 at 2.7 Na^+:$PO_4^{=}$ + 0.30 mg/L NH_3.

[B] Values calculated by John Riddle, NUS Corporation, Pittsburgh, PA.

X1.4.2.3 Matrix No. 2: 0.272 mg/L ammonia and 20 µg/L hydrazine, which represents average conditions for steam cycle all-volatile chemistry control (pH 9.0 at 25°C);

X1.4.2.4 Matrix No. 3: 1.832 mg/L ammonia, 10 mg/L morpholine, and 50µ g/L hydrazine, which represents conditions for all-volatile chemistry control at high pH with amines (pH 9.6 at 25°C);

X1.4.2.5 Matrix No. 4: 3 mg/L phosphate with a sodium-to-phosphate molar ratio of 2.7 with 0.3 mg/L ammonia, which represents average conditions for phosphate chemistry control.

X1.4.3 The results of the calculated pH values for these solutions and temperature corrections are given in Table X1.1 and Table X1.2. Observe that the temperature corrections for the basic solutions are essentially the same, and approximately twice the correction for pure water.

X1.4.4 Solutions other than the ones identified in X1.4.2.1 – X1.4.2.5 require specific information on the matrix. Generally, acidic solutions require no temperature correction for pH, a pure water solution changes about –0.016 pH unit per °C, and a basic solution changes approximately –0.033 pH unit per °C.

X1.5 pH instrumentation with settings for the STC correction factor enables automatic temperature compensation for both effects noted in X1.1 (**4**).

X2. SUPPLEMENT FOR GRAB SAMPLE CALIBRATION (GSC) OF ON-LINE pH SENSORS

X2.1 The following is an addendum that details how to use this method to calibrate an on-line pH sensor.

X2.2 In Section 11, after the second grab sample has been taken at the point of interest, immediately record the pH of the flowing sample stream as indicated by the on-line pH instrumentation. Designate this reading R_2.

X2.3 Transport the grab sample containers to the laboratory without delay. This grab sample must be kept close to the temperature of the flowing stream for measurement in the lab.

X2.4 In the lab, make the pH measurement as described and record the pH reading as R_1.

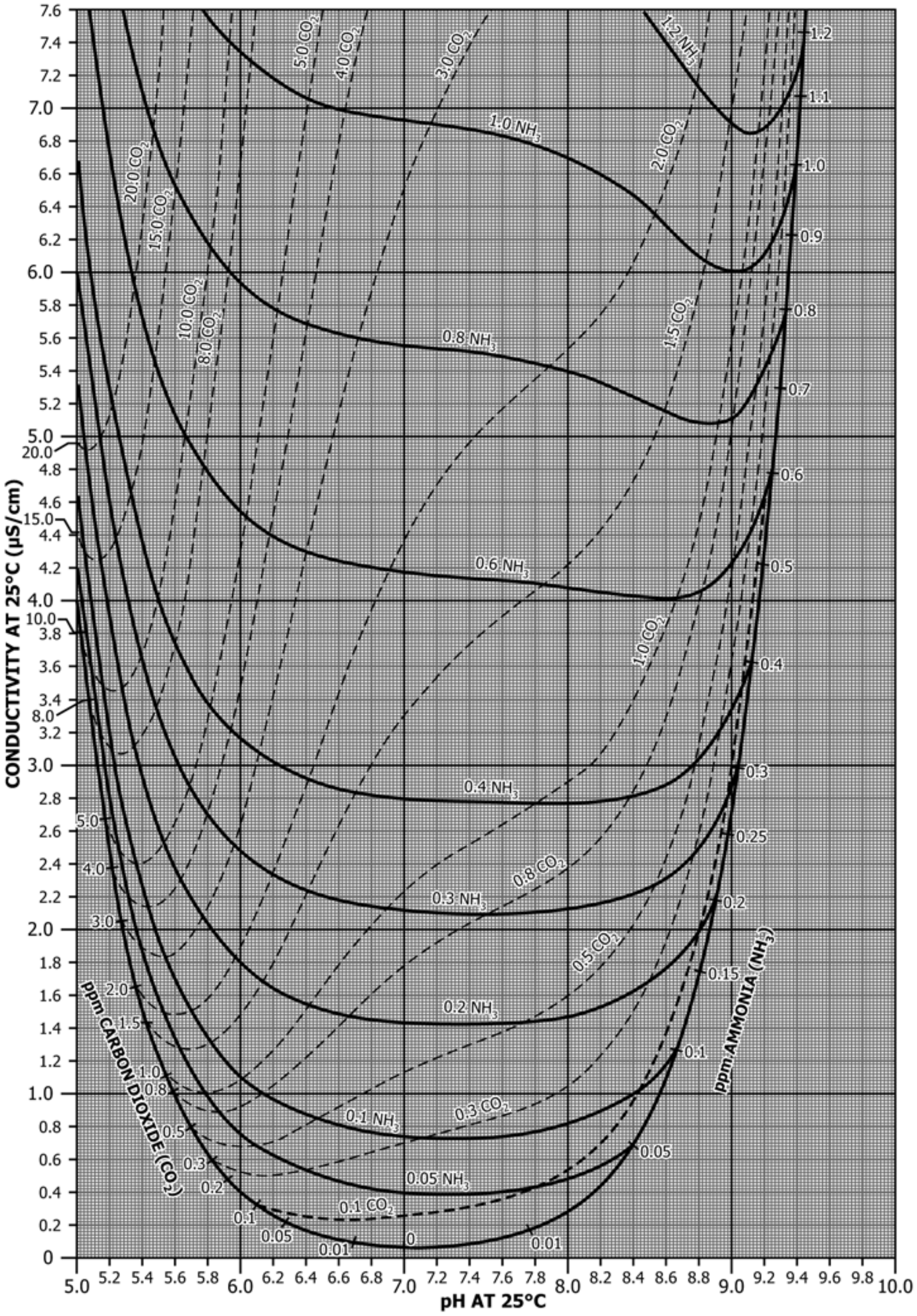
X2.5 Now compare lab pH meter reading, R_1, with the on-line pH instrumentation reading, R_2. If the two readings differ by more than 0.1 pH unit, adjust the standardization (that is, zero or offset) control of the on-line pH instrument by adding the difference between the first two readings, R_1 and R_2. Some microprocessor based on-line pH instruments provide this differential calibration automatically. In that case follow the instrument instruction manual for this calibration.

X3. EFFECTS OF CO_2 ON pH MEASUREMENTS OF HIGH PURITY WATER

X3.1 High purity water will rapidly absorb carbon dioxide when exposed to the atmosphere. Carbon dioxide levels in the atmosphere are greater than 300 ppm by volume and will reach a concentration near 1 mg/L in water if allowed to equilibrate at room temperature. Absolutely pure water by definition does not contain carbon dioxide. However, in practice CO_2 is present at low levels in most low conductivity water samples. High purity water sampling practices should be designed to minimize intrusion of carbon dioxide from the atmosphere. See Fig. X3.1 for the theoretical pH and conductivity values of ammonia solutions at various carbon dioxide levels. Also, see Table X3.1 for the theoretical pH shift caused by 0.2 mg/L CO_2 contamination of a high purity water sample. This information is provided to give the user an indication of the level of pH measurement error introduced by the presence of CO_2. The user should determine the actual effects of CO_2 contamination for specific operating conditions as they may differ from application to application.

X3.2 High purity water sampling practices should be designed to minimize intrusion of carbon dioxide from the atmosphere. See Fig. X3.1 for the theoretical pH and conductivity values of ammonia solutions at various carbon dioxide levels. Also, see Table X3.1 for the theoretical pH shift caused by 0.2 mg/L CO_2 contamination of a high purity water sample. This information is provided to give the user an indication of the level of pH measurement error introduced by the presence of CO_2.

X3.3 The user should determine the actual effects of CO_2 contamination for specific operating conditions as they may differ from application to application.



NOTE 1—Calculated by John Riddle, NUS Corporation, Pittsburgh, PA.

FIG. X3.1 pH and Conductivity of Ammonia Solutions at Various Carbon Dioxide Levels

TABLE X3.1 Calculated pH and Conductivity Values at 25°C of Water Solutions Containing only Ammonia and Carbon Dioxide [A]

Ammonia, mg/L	Carbon Dioxide, 0 mg/L		Carbon Dioxide, 0.2 mg/L		pH Shift Caused by 0.2 mg/L CO_2 Contamination of Sample
	µS/cm	pH	µS/cm	pH	
0	0.056	7.00	0.508	5.89	Δ1.11 pH
0.12	1.462	8.73	1.006	8.18	Δ0.55 pH
0.51	4.308	9.20	4.014	9.09	Δ0.11 pH
0.85	6.036	9.34	5.788	9.26	Δ0.08 pH
1.19	7.467	9.44	7.246	9.38	Δ0.06 pH

[A] Data extracted from CERL Laboratory Memorandum # RD/L/M 474 “Theoretical Calculation of the Electrical Conductivity of Power Station Waters,” W. G. Cummings and K. Torrance, CERL Laboratories, United Kingdom, Oct. 9, 1974.

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