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**Designation: D5128 − 14 (Reapproved 2022)**

## **Standard Test Method for On-Line pH Measurement of Water of Low Conductivity1**

This standard is issued under the fixed designation D5128; 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  $(\varepsilon)$  indicates an editorial change since the last revision or reapproval.

## **1. Scope**

1.1 This test method covers the precise on-line determination of pH in water samples of conductivity lower than 100 µS ⁄cm (see Table 1 and Table 2) over the pH range of 3 to 11 (see Fig. 1), under field operating conditions. pH measurements of water of low conductivity are problematic for conventional pH electrodes, methods, and related measurement apparatus.

1.2 This test method includes the procedures and equipment required for the continuous pH measurement of low conductivity water sample streams including the requirements for the control of sample stream pressure, flow rate, and temperature. For off-line pH measurements in low conductivity samples, refer to Test Method D5464.

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

1.4 *This standard does not purport to address all of the*  $\frac{3.2.1.1 \text{ Discussion}}{3.2.1.1 \text{ Discussion}}$ *safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*<br>  $\frac{8}{\text{calibration}}$  remains s http1.5 This international standard was developed in accor-9c46-4c93-be47-5c72bab8d7a7/astm-d5128-142022 *dance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## **2. Referenced Documents**

2.1 *ASTM Standards:*<sup>2</sup> D1129 [Terminology Relating to Water](https://doi.org/10.1520/D1129)

#### D1193 [Specification for Reagent Water](https://doi.org/10.1520/D1193)

D1293 [Test Methods for pH of Water](https://doi.org/10.1520/D1293)

- D2777 [Practice for Determination of Precision and Bias of](https://doi.org/10.1520/D2777) [Applicable Test Methods of Committee D19 on Water](https://doi.org/10.1520/D2777)
- D3864 [Guide for On-Line Monitoring Systems for Water](https://doi.org/10.1520/D3864) [Analysis](https://doi.org/10.1520/D3864)

D4453 [Practice for Handling of High Purity Water Samples](https://doi.org/10.1520/D4453) D5464 [Test Method for pH Measurement of Water of Low](https://doi.org/10.1520/D5464) **[Conductivity](https://doi.org/10.1520/D5464)** 

#### **3. Terminology**

3.1 *Definitions—*For definitions of other terms used in this test method, refer to Terminology D1129 and Practice D3864.

**inductivity samples,**<br> **it also standard:**<br> **3.2.1** *liquid junction potential***.** *n***—a dc potential** 

3.2.1 *liquid junction potential, n—*a dc potential that appears at the point of contact between the reference electrode's salt bridge (sometimes called diaphragm) and the sample solution.

3.2.1.1 *Discussion—*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. As long as it remains stable its effect can be minimized by "grab sample" calibration **(3)**. <sup>3</sup>

3.2.2 *streaming potential, n—*the static electrical charge that is induced by the movement of a low ionic strength solution having a high electrical resistivity or low electrical conductivity (such as pure water), across relatively non-conductive surfaces such as the pH electrode or other non-conductive wetted materials found in flowing sample streams.

#### **4. Summary of Test Method**

4.1 pH is measured by electrodes contained in an all stainless steel flow cell. The pH measurement half-cell is constructed of a glass membrane suitable for continuous service in low conductivity water. The reference half-cell is constructed in such a manner that the salt bridge uses either a flowing liquid electrolyte, or a pressurized gel electrolyte that resists significant dilution for periods up to several months of continuous operation.

<sup>&</sup>lt;sup>1</sup> This test method is under the jurisdiction of ASTM Committee [D19](http://www.astm.org/COMMIT/COMMITTEE/D19.htm) on Water and is the direct responsibility of Subcommittee [D19.03](http://www.astm.org/COMMIT/SUBCOMMIT/D1903.htm) on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

Current edition approved Nov. 1, 2022. Published December 2022. Originally approved in 1990. Last previous edition approved in 2014 as D5128 – 14. DOI: 10.1520/D5128-14R22.

<sup>&</sup>lt;sup>2</sup> 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.

<sup>&</sup>lt;sup>3</sup> The boldface numbers given in parentheses refer to a list of references at the end of this standard.

#### **TABLE 1 Calculated Conductivity and pH Values at 25 °C of Low Concentrations of NaOH in Pure Water** *<sup>A</sup>*

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, ma/L	Sample Conductivity, $\mu$ S/cm	Sample pH	$\Delta$ pH Error from Addi- tional 1 mg/L NaOH Contaminate
0.001	0.055	7.05	$\triangle$ 2.35
0.010	0.082	7.45	$\Delta$ 1.95
0.100	0.625	8.40	$\triangle$ 1.03
1.0	6.229	9.40	$\Delta$ 0.30
8.0	49.830	10.30	$\Delta$ 0.05

*<sup>A</sup>* Data courtesy of Ref **(1)**. *<sup>B</sup>* This data developed from algorithms originally published in Ref **(2)**.<br><sup>*B* The boldface numbers in parentheses refer to a list of references at the end of</sup>

this standard.

#### **TABLE 2 Calculated Conductivity and pH Values at 25 °C of Low Concentrations of HCl in Pure Water** *<sup>A</sup>*

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 **interaction** to contaminants, the last column lists errors that would 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.<br>
Sample or equipment handling errors.<br>
Sample Sample



*<sup>A</sup>* Data courtesy of Ref **(1)**. This data developed from algorithms originally published in Ref **(2)**.

4.2 This test method describes the apparatus and procedures to be used for the continuous on-line pH measurement of low conductivity water sample streams. The requirements for conditioning sample pressure and flow rate are defined, and arrangements for this associated equipment are illustrated.

4.3 The apparatus and procedures described in this test method are intended to be used with process-grade, pH analyzer/transmitter instruments.

#### **5. Significance and Use**

5.1 Continuous pH measurements in low conductivity samples are sometimes required in pure water treatment using multiple pass reverse osmosis processes. Membrane rejection efficiency for several contaminants depends on pH measurement and control between passes where the conductivity is low.

5.2 Continuous pH measurement is used to monitor power plant cycle chemistry where small amounts of ammonia or amines or both are added to minimize corrosion by high temperature pure water and steam.



**FIG. 1 Restrictions Imposed by the Conductivity pH Relationship**

5.3 Conventional pH measurements are made in solutions that contain relatively large amounts of acid, base, or dissolved  $\frac{\text{ASA 0.30}}{5128-1}$  salts. Under these conditions, pH determinations may be made  $\frac{8.0}{\text{A Data}}$  courtesy of Bef (1). This data developed from algorithms originally  $\alpha$  quickly and precisely. Continuous on-line pH measurements in water samples of low conductivity are more difficult **(4, 5)**. These low ionic strength solutions are susceptible to contamination from the atmosphere, sample stream hardware, and the pH electrodes. Variations in the constituent concentration of low conductivity waters cause liquid junction potential shifts (see [3.2.1\)](#page-0-0) resulting in pH measurement errors. Special precautions are required.

#### **6. Interferences**

6.1 Sample systems for high purity, low conductivity waters are especially sensitive to contamination from atmospheric gases (especially carbon dioxide, see Appendix X1 and Table 3), and to accumulation of power plant corrosion particles in sample lines that can absorb or desorb contaminants. Excessive KCl electrolyte leakage from the pH reference half-cell can also affect the sample. Refer to Practice [D4453](#page-0-0) and Refs **(6)** and **(7)**.

6.2 Streaming potentials that are developed by flowing, low conductivity water across non-conductive surfaces are dynamic in nature and will add to the potential (millivolt) generated by the pH sensor. This resultant pH error appears as a noisy, flow-sensitive and drifting pH signal. These effects are minimized by using a conductive flow cell, low sample flowrates

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*<sup>A</sup>* Data extracted from Ref **(8)**.

and, in some cases, a symmetrical combination measurement/ reference electrode **(9)**.

6.3 Reference electrode liquid junction potentials are significant in low conductivity waters and shift the potential of the pH reference half-cell, resulting in both short and long-term pH measurement errors. The instability of liquid junction potentials depends on reference half-cell design, electrical conductivity of the sample water, time, and sampling conditions such as flow rate and pressure. Generally, reference electrodes with refillable liquid electrolyte flowing junctions provide more stable junction potential than non-refillable, sealed reference electrodes. Exposure of the pH electrodes to pH calibration in units of pH in power plants buffer solutions, that have a higher ionic strength than the pure water sample stream, causes significant change in the liquid<br>
iunction potential of sealed reference electrodes from what it is junction potential of sealed reference electrodes from what it is in a low conductivity sample, resulting in pH measurement  $6.4.3$  Further dis<br>errors that appear immediately after calibration in buffer measurements is pre errors that appear immediately after calibration in buffer solutions.

6.3.1 Liquid junction potentials must be stable to make a reliable calibration of the system. Sealed reference electrodes<sup>8</sup> must be that have been exposed to the much higher ionic strength of  $\epsilon$  discussion of the flow sensitivity is presented in Annex. buffer solutions require considerable rinse time to establish a stable liquid junction potential in high purity water. To determine the pH electrode's suitability in low conductivity water, a comparative low conductivity water sample calibration, or on-line calibration with low conductivity standards similar to the samples being addressed should be performed, as described in 9.5.

6.3.2 The severity of the error resulting from a liquid junction potential shift when the ionic strength of the sample changes, for example, measuring 1.0 mg/L ammonia  $(pH = 9.38$  and conductivity = 6.58 S/cm) followed by measuring  $0.1 \text{ mg/L}$  ammonia ( $pH = 8.65$  and conductivity =  $1.24$  S/cm) is not known and is a deficiency in the state-of-the-art. Table 4 and Fig. X1.1 provide a correlation between pH and specific conductivity of dilute ammonia.

6.4 Temperature compensation of pH in low conductivity water is more significant and more involved than in conventional measurements.

6.4.1 All pH measurements must compensate for the changing output of the electrode with temperature. This effect is represented by a changing slope with units of millivolts per pH. This slope is proportional to absolute temperature according to the Nernst equation.

#### **TABLE 4 pH versus Specific Conductivity At 25 °C***<sup>A</sup>*

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



*<sup>A</sup>* Data courtesy of Ref **(1)**. This data developed from algorithms originally published in Ref **(2)**.

6.4.2 In addition, pH measurements in low conductivity water in the power industry must compensate for the change of the dissociation of water and ammonia or amines with temperature to report pH at  $25^{\circ}$ C. This is typically set into the instrument by the user with a solution temperature coefficient in units of pH per °C. Most process pH instrumentation for use in power plants has a setting for solution temperature compensation which the user must enter to activate this compensation. Laboratory instrumentation typically does not have this capability **(5, 9, 10, 11, 12, 13)**.

6.4.3 Further discussion of the temperature effects on pH measurements is presented in Annex A1.

6.5 The flow rate to the pH electrodes and related apparatus must be controlled in order to obtain repeatable results. A discussion of the flow sensitivity is presented in Annex A2.

#### **7. Apparatus**

7.1 A complete high purity water pH sensor assembly is required. The pH flow cell and connecting tubing should be constructed of stainless steel and be earth grounded. The sensor assembly design shall provide shielding to prevent noise pick-up and shall minimize air entrapment and corrosion particle accumulation. Sample discharge shall be near the top of the flow cell to purge any air bubbles rapidly and shall go downward to an open drain to prevent any back pressure on the electrode(s).

7.1.1 A single probe combination measuring and reference electrode with integral temperature compensator enables use of a very small volume flow cell which creates a high sample flow velocity that prevents power plant sample corrosion particles from accumulating.

7.1.2 Where separate measuring, reference and temperature compensator probes are used, a larger volume flow cell is necessary and the design should enable convenient periodic cleanout of accumulated corrosion particles.

7.2 Electrodes should have half-cells that quickly equilibrate to each other and the sample temperature. Refer to Ref **(6)**.

<span id="page-3-0"></span>7.3 Electrodes should be suitable for continuous service in low conductivity water **(14)**.

## 7.4 Changes in liquid junction potential **(3)** 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 maintain an accurate and stable pH measurement. To achieve this, a liquid-electrolyte, flowing-junction reference system is preferred. A sealed reference half-cell (requiring no electrolyte replenishment) that is pressurized or otherwise constructed in such a manner that the salt bridge, while making diffusion contact to the sample, resists significant dilution for periods up to several months of continuous operation in low conductivity water measurements may also be used.

7.5 A sample stream conditioning manifold with capabilities similar to Fig. 2 shall be used immediately upstream of the pH sensor. The manifold provides proper sample stream pressure and flow rate control after primary sample cooling and pressure regulation. This manifold shall also provide a grab sample outlet for verification or calibration of the pH sensor. This manifold shall operate such that when a grab sample is being taken for calibration purposes, neither the sample flow rate nor pressure shall vary at the on-line pH sensor location.

#### **8. Reagents**

**Reagents**<br>
8.1 *Commercial Buffer Solutions*—Commercially available PH sensor flow prepared buffers traceable to National Institute of Standards prepared buffers traceable to National Institute of Standards<br>and Technology (NIST) standards should be adequate for the **19.3.1** When using a seal calibration procedures in  $9.2 - 9.5$ . These commercial buffer solutions usually have pH values near  $4, 7, 9$ , and  $10$  pH at  $25^{\circ}$ C. The exact pH of the buffer will change with temperature to remove all trace 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 Method A in Test  $\frac{9.3.2}{6}$ <br>Mathod D1202 for the preparation of reference buffer colutions Method D1293 for the preparation of reference buffer solutions if desired. if desired. Care's iteh.ai/catalog/standards/sist/ccbe9c10-9c4 (flow cell for a minimum of 15 min before using measurements.

8.2 *Buffer A—*Commercially available 7 pH buffer.



- 8.3 *Buffer B—*Commercially available 4 pH buffer.
- 8.4 *Buffer C—*Commercially available 9 pH buffer.
- 8.5 *Buffer D—*Commercially available 10 pH buffer.

8.6 *Purity of Water—*Reference to water shall mean water that meets or exceeds the quantitative specifications for Type II reagent water of Specification D1193, Section 1.1, unless otherwise specified.

#### **9. Calibration**

9.1 Perform initial and subsequent start-ups of the on-line pH sensor in accordance with manufacturer's instructions.

9.2 Perform a two point calibration of the pH measurement and reference electrodes after removing them from the on-line pH sensor flow chamber. Refer to Method B in Test Method [D1293](#page-0-0) for guidelines on the standardization of a pH meter and electrode assembly. Be certain to include the temperature compensator with the pH instrument in the automatic temperature compensation (ATC) mode. Use a quiescent sample of both buffer solutions and laboratory containers dedicated for this service only. For proper pH calibration buffers, see 8.1 – 8.5. Thoroughly rinse electrodes and glassware with reagent water between each buffer calibration.

9.3 Thoroughly rinse electrodes with reagent water or low ionic strength sample water and reinsert them into the on-line pH sensor flow cell in accordance with the manufacturer's instructions.

9.3.1 When using a sealed reference electrode, permit the pure water sample stream to flush the sensor flow cell for a minimum of 3 to 4 h at manufacturer's recommended flow rate to remove all traces of the high ionic strength pH buffer solutions before using measurements.

9.3.2 When using a reference electrode with refillable liquid electrolyte, allow the pure water sample stream to flush the

9.4 Connect the pH electrodes and automatic temperature compensator to the pH instrument in accordance with the manufacturer's instructions.

9.5 The technique for subsequent or routine calibrations of the on-line pH sensor depends on the type of reference electrode being used.

9.5.1 When using a sealed reference electrode, perform comparative-sample calibration in accordance with Test Method D5464 in lieu of conventional direct buffer calibration of this on-line high purity pH sensor. Test Method [D5464](#page-0-0) has the advantage of using a liquid electrolyte reference electrode with minimal change in junction potential between high ionic strength buffer solutions and high purity samples.

NOTE 1—If the comparative sample temperature is not maintained at 25 °C and is not compensated for solution temperature effects, its temperature must be recorded and the proper temperature correction applied. See Annex A1 for a discussion of temperature effects on pH measurements.

9.5.2 When using a reference electrode with refillable liquid electrolyte, for subsequent or routine calibrations use direct two-buffer calibration as in 9.2 and 9.3.

**FIG. 2 Schematic Sample System** Nore 2—Periodic confirmation of the calibration of the temperature

probe in the on-line pH sensor should be verified at least at one point in accordance with the manufacturer's instructions.

9.6 An alternative method of calibration may be considered which provides for the regular measurement of certifiable standards. This test method employs the use of a precision metering or syringe pump to inject a known standard solution of acid or base into a flowing deionized water stream meeting Type I water of Specification [D1193.](#page-0-0) From the ratio of flowrates and the concentration of the standard solution, very dilute, known concentrations can be obtained and used for calibration or verification **(15)**.

## **10. Procedure**

10.1 Install a sample system manifold as shown in [Fig. 2,](#page-3-0) using the components indicated in the equipment schedule. Wetted materials should consist of stainless steel, glass, PTFE, and ceramic. Use of dissimilar metals should be avoided to prevent galvanic corrosion of these metals. Galvanic corrosion could develop EMF potentials in the sample stream that could result in pH measurement errors. A discussion of contaminants in sample systems is presented in A3.1.

NOTE 3—PTFE is not suitable for radioactive samples and suitable materials should be substituted for all PTFE components in the radiation areas.

10.2 Flush all wetted components of the sample system 10.2 Flush all wetted components of the sample system<br>
manifold according to manufacturer's recommendations with<br>
with a periodically, d water or low ionic strength sample water for 3 to 4 h, especially if on-line pH sensor assembly has been exposed to pH<br>calibration buffers or other high ionic strength solutions. calibration buffers or other high ionic strength solutions.

10.3 Maintain sample stream flow rates at a fixed rate accurate correlation cording to the manufacturer's recommendation. It is impor-<br>See Fig. X1.1. Under according to the manufacturer's recommendation. It is important to maintain both the sample stream flow rate and pressure at recommended levels to prevent pH signal drift and noise resulting from electrode sensitivities to variations in these two two-chan parameters and to achieve repeatability of the pH electrode<sup>c</sup> for the calculation of pH of power plant samples base output signal. Determination of the sample line flow rate for a given installation will depend on variables such as total length of sample line and its effect on representative sampling and lag times, size, and age of existing sample lines, and upstream sample pressure and temperature conditioning. A discussion on sample stream flow rates is presented in Annex A2.

10.4 Maintain sample stream temperature at  $25 \pm 1$  °C or confirm that the appropriate solution temperature compensation setting has been entered into the measuring instrument. For more information, refer to [6.4.](#page-2-0) A discussion of sample stream temperature conditioning is presented in A3.2.3.

10.5 Install the on-line sensor in accordance with the manufacturer's instructions.

10.6 Connect the pH signal output of the high purity water pH sensor to the pH signal input of the on-line pH analyzer/ transmitter in accordance with the manufacturer's instructions.

10.7 After completion of the calibration procedures in [9.2](#page-3-0) to [9.5,](#page-3-0) record data continuously or manually until the run is completed.

## **11. Precision and Bias**

11.1 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 is a continuous determination. This inability of D2777 procedures to obtain precision and bias data for continuous determinations is recognized and stated in the scope of Practice [D2777.](#page-0-0)

## **12. Quality Control**

12.1 Two-point instrument calibration in two pH standard buffer solutions near the anticipated measuring range must be performed according to the manufacturer's instructions periodically, depending on the stability of the electrodes and the pH control specification.

12.2 With power plant samples containing predominately ammonia or amines or both, and negligible carbon dioxide, an accurate correlation with specific conductivity can be made. See Fig. X1.1. 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 of power plant samples 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 **(16, 17)**.

## **13. Keywords**

13.1 high purity; low conductivity; on-line; pH; calculated pH

# **D5128 − 14 (2022)**

## **ANNEXES**

#### **(Mandatory Information)**

## <span id="page-5-0"></span>**A1. TEMPERATURE EFFECTS ON PH MEASUREMENTS OF LOW CONDUCTIVITY WATER (5, 9, 10, 11, 12, 13)**

A1.1 There are two types of temperature effects on pH measurement of low conductivity water **(10, 12)**.

A1.1.1 *Standard Nernst equation temperature compensation* accounts for the thermodynamic response of the glass pH electrode output slope in millivolts per pH which is proportional to absolute temperature. Nernst electrode temperature compensation converts the millivolt signal to pH units at the temperature of the sample. It does not compensate the pH of the sample to a reference temperature.

A1.1.1.1 Standard Nernstian compensation is provided by the automatic temperature compensation (ATC) feature of virtually all pH meters and the temperature element provided with the pH electrodes or sensor assembly.

A1.1.1.2 pH meters with manual temperature compensation can accomplish the same result as long as the operator measures the sample temperature and sets that temperature into the pH meter.

A1.1.2 *Solution Temperature Effect (STE)* is due to the temperature influence on the ionization of water and other<br>
materials present in the sample Ionic concentrations undergo materials present in the sample. Ionic concentrations undergo changes with temperature change. Small  $(mg/L)$  amounts of  $A1,1.2.4$  pH values for acidic or alkaline materials can have a substantial effect on this acidic or alkaline materials can have a substantial effect on this pH temperature influence. Compensation for this is typically pH temperature influence. Compensation for this is typically<br>accomplished by establishing a reference temperature and a<br>linear solution temperature coefficient (STC) that entrovinates the same, and appli linear solution temperature coefficient (STC) that approximates the influence. The reference temperature is usually 25 °C and the coefficient is nominally –0.03 pH/°C for very dilute alka-8-14( $\overrightarrow{A1.1.2}$ ) line solutions typical of power plant cycle chemistry samples. https://standard.ite/baby/catalog/standards/sistem.ai/catalog/standards/sistem.ai/catalog/standards/sistem.ai/catalog/standards/sist/catalog/standards/sist/catalog/standards/sist/catalog/standards/sistem.ai/catalog/standar referenced to 25 °C to eliminate variable sample temperature effects.

A1.1.2.1 To avoid solution temperature effect errors, it is necessary to develop a solution temperature coefficient (STC) that matches the specific sample pH across the operating temperature range. For example, once the STC is developed, the technician can measure the pH in the lab at 22 °C and then calculate what the referenced pH must be at 25 °C by applying the STC.

A1.1.2.2 The STC may be derived empirically by measuring the pH of a known solution under carefully controlled conditions at two or more temperatures covering the anticipated sample range as well as the reference temperature. From that, the best slope in pH/°C can be determined.

A1.1.2.3 Temperature data for normalizing pH measurements to 25 °C have been determined for the following:

*(1) Pure water*.

*(2) Matrix No. 1*—4.84 mg/L sulfate, that represents an acidic solution at pH 4.0 at 25 °C.

*(3) Matrix No. 2*—0.272 mg/L ammonia and 20 g/L hydrazine, that represents average conditions for steam cycle all-volatile reducing chemistry control (pH 9.0 at 25 °C).

*(4) Matrix No. 3*—1.832 mg/L ammonia, 10 mg/L morpholine, and 50 g/L hydrazine, that represents conditions for all-volatile reducing chemistry control at high pH with amines (pH 9.6 at 25  $^{\circ}$ C).

*(5) Matrix No. 4*—3 mg/L phosphate with a sodium-tophosphate molar ratio of 2.7 with 0.3 mg/L ammonia, that represents "average" conditions for phosphate chemistry control.

A1.1.2.4 pH values for these solutions and temperature corrections are given in Table A1.1 and Table A1.2. The temperature corrections for the basic solutions are essentially the same, and approximately twice the correction for pure water

A1.1.2.5 pH instrumentation with a setting and algorithm for the STC correction enables continuous on-line pH measurements to be more error-free **(5)**.

A1.1.2.6 The STC correction in pH instruments must be disabled during buffer calibration because the temperature coefficient of buffer solutions is different from the coefficient of the sample. In most instruments this is done automatically. As a result, if the buffer solution is not at the reference temperature, the pH measured in a buffer solution with the STC active will normally differ from the buffer value entered during calibration. pH measurement with the STC active is only correct back in the sample.

# **D5128 − 14 (2022)**

# **TABLE A1.1 pH as a Function of Temperature for Different Matrixes** *<sup>A</sup>***,***<sup>B</sup>*



*<sup>A</sup>* See [A1.1.2.3](#page-5-0) Matrix No.

1: 4.84 mg/L SO<sub>4</sub>  $=$ ,

2: 0.272 mg/L NH<sub>3</sub> + 20 µg ⁄L N<sub>2</sub>H<sub>4</sub>,

3: 1.832 mg/L NH<sub>3</sub> + 10.0 mg/L morpholine + 50 µg */*L N<sub>2</sub>H<sub>4</sub>, and<br>4: 3.0 mg/L PO<sub>4</sub> at 2.7 Na <sup>+</sup>: PO<sub>4</sub> <sup>±p</sup> + 0.30 mg/L NH<sub>3</sub>.<br><sup>*B*</sup> Values calculated by John Riddle, NUS Corporation, Pittsburgh, PA.