

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 (ϵ) 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 $\mu\text{S}/\text{cm}$ (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 standard.

1.4 *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](#)

[D3864 Guide for On-Line Monitoring Systems for Water Analysis](#)

[D4453 Practice for Handling of High Purity Water Samples](#)

[D5464 Test Method for pH Measurement of Water of Low Conductivity](#)

3. Terminology

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

3.2 Definitions of Terms Specific to This Standard:

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**).³

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.

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.

¹ This test method is under the jurisdiction of ASTM Committee [D19](#) on Water and is 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.

Current edition approved Jan. 1, 2014. Published January 2014. Originally approved in 1990. Last previous edition approved in 2009 as D5128 – 09. DOI: 10.1520/D5128-14.

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 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^A

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, $\mu\text{S/cm}$	Sample pH	Δ pH Error from Additional 1 mg/L NaOH Contaminate
0.001	0.055	7.05	Δ 2.35
0.010	0.082	7.45	Δ 1.95
0.100	0.625	8.40	Δ 1.03
1.0	6.229	9.40	Δ 0.30
8.0	49.830	10.30	Δ 0.05

^A Data courtesy of Ref (1). ^B This data developed from algorithms originally published in Ref (2).

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

TABLE 2 Calculated Conductivity and pH Values at 25°C of Low Concentrations of HCl in Pure Water^A

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, $\mu\text{S/cm}$	Sample pH	Δ pH Error from Additional 1 mg/L HCl Contaminate
0.001	0.060	6.94	Δ 2.38
0.010	0.134	6.51	Δ 1.95
0.100	1.166	5.56	Δ 1.03
1.0	11.645	4.56	Δ 0.30
8.0	93.163	3.66	Δ 0.05

^A Data courtesy of Ref (1). This data developed from algorithms originally published in Ref (2).

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.

5.3 Conventional pH measurements are made in solutions that contain relatively large amounts of acid, base, or dissolved salts. Under these conditions, pH determinations may be made quickly and precisely. Continuous on-line pH measurements in water samples of low conductivity are more difficult (4, 5).

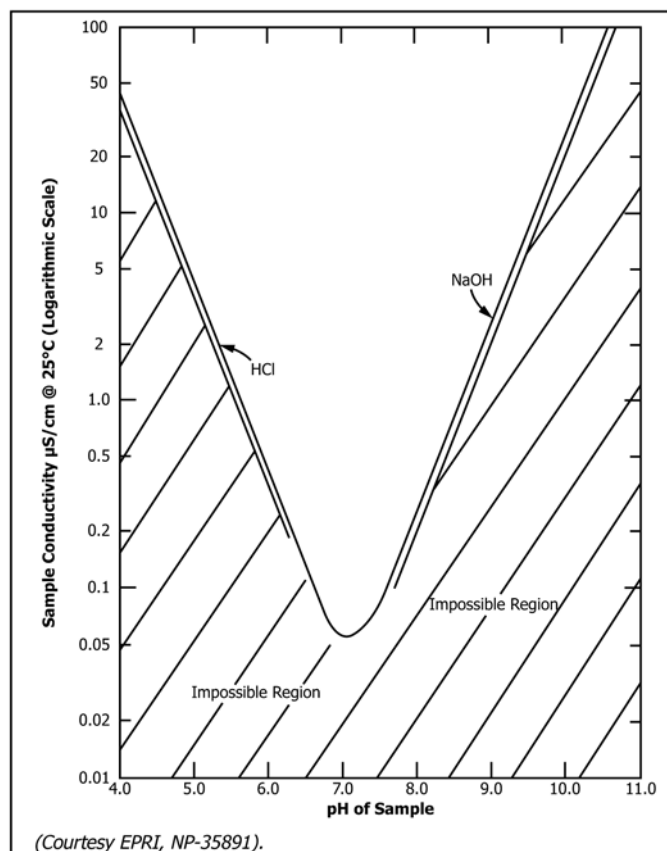


FIG. 1 Restrictions Imposed by the Conductivity pH Relationship

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) 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

TABLE 3 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
	$\mu\text{S/cm}$	pH	$\mu\text{S/cm}$	pH	
0	0.056	7.00	0.508	5.89	Δ 1.11 pH
0.12	1.462	8.73	1.006	8.18	Δ 0.55 pH
0.51	4.308	9.20	4.014	9.09	Δ 0.11 pH
0.85	6.036	9.34	5.788	9.26	Δ 0.08 pH
1.19	7.467	9.44	7.246	9.38	Δ 0.06 pH

^A Data extracted from Ref (8).

KCl electrolyte leakage from the pH reference half-cell can also affect the sample. Refer to Practice D4453 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 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 buffer solutions, that have a higher ionic strength than the pure water sample stream, causes significant change in the liquid junction potential of sealed reference electrodes from what it is in a low conductivity sample, resulting in pH measurement 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 that have been exposed to the much higher ionic strength of 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 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.

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°C. This is typically set into the

TABLE 4 pH versus Specific Conductivity At 25°C^A

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.

Ammonia, mg/L NH ₃	Ammonium Hydroxide, mg/L NH ₄ OH	pH	Specific Conductivity, μS/cm
0.10	0.21	8.65	1.24
0.15	0.31	8.79	1.72
0.20	0.41	8.89	2.15
0.25	0.51	8.96	2.54
0.30	0.62	9.02	2.91
0.35	0.72	9.07	3.25
0.40	0.82	9.11	3.57
0.45	0.93	9.15	3.88
0.50	1.03	9.18	4.17
1.00	2.06	9.38	6.58
1.50	3.09	9.49	8.47
2.00	4.11	9.56	10.08

^A Data courtesy of Ref (1). This data developed from algorithms originally published in Ref (2).

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).

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 electrode should be

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

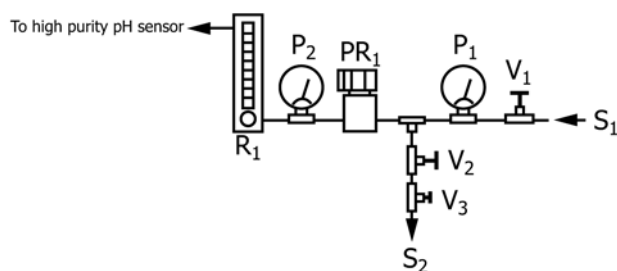
8.1 *Commercial Buffer Solutions*—Commercially available prepared buffers traceable to National Institute of Standards and Technology (NIST) standards should be adequate for the calibration procedures in 9.2 – 9.5. These commercial buffer solutions usually have pH values near 4, 7, 9, and 10 pH at 25°C. 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 Method A in Test Method D1293 for the preparation of reference buffer solutions if desired.

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.



S ₁ = sample inlet, 6.35 mm stainless steel tube fitting	PR ₁ = secondary pressure regulator, 0 – 172.4 kPa (gage)
V ₁ = high pressure sample inlet shut-off valve	R ₁ = rotameter, with control valve, 0 – 600 mL/min
P ₁ = sample inlet pressure gauge 0 – 689.4 kPa (gage)	P ₂ = flow-cell pressure gauge, 0 – 182.4 kPa (gage)
V ₂ = grab sample valve / on-off	
V ₃ = tamper resistant flow rate valve, max. 200 mL/min at specified system pressure	
S ₂ = grab sample outlet	

FIG. 2 Schematic Sample System

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 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 flow cell for a minimum of 15 minutes before using measurements.

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 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.

NOTE 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.