Designation: D5128 – 14 (Reapproved 2022)

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

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 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 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance 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:*[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.

[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.

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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 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, µS/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, µS/cm	Sample pH	Δ pH Error from Additional 1 mg/L HCl Contaminate
0.001	0.060	6.94	Δ2.38
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**).

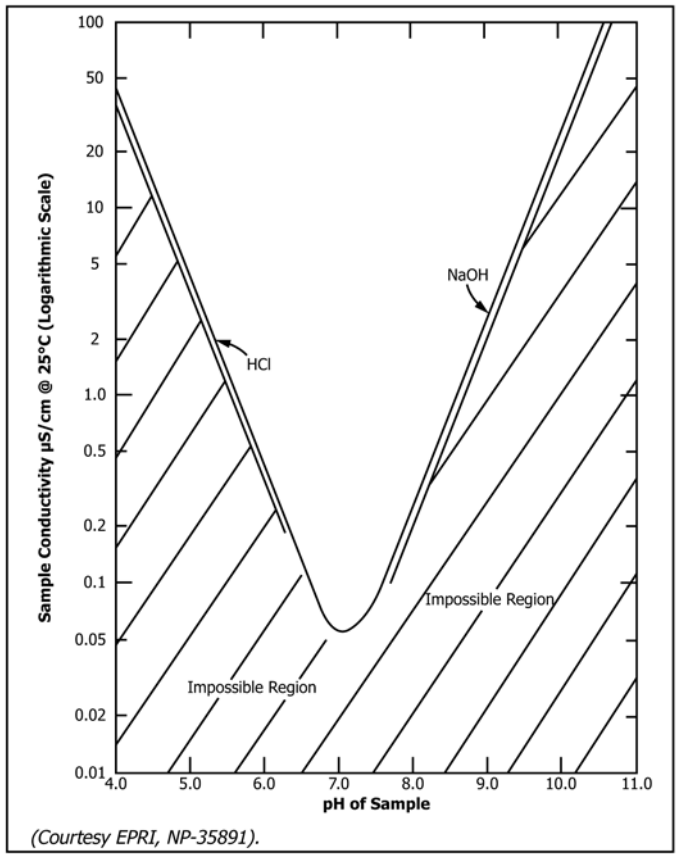

FIG. 1 Restrictions Imposed by the Conductivity pH Relationship

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.

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**). 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 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