



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

This standard is issued under the fixed designation D 5128; 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.

ε¹ NOTE—A footnote was editorially removed in June 1999.

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, utilizing a sealed, non-refillable, reference electrode. pH measurements of water of low conductivity are problematical 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.

1.3 *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:

- D 1129 Terminology Relating to Water²
- D 1193 Specification for Reagent Water²
- D 1293 Test Methods for pH of Water²
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water²
- D 3864 Practice for Continual On-Line Monitoring Systems for Water Analysis²
- D 4453 Practice for Handling of Ultra-Pure Water Samples²
- 2.2 *ASTM Proposal:*
- P 228 Proposed Test Methods for pH Measurement of Water of Low Conductivity³

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

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 of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement of Water. Current edition approved Oct. 26, 1990. Published February 1991.

² *Annual Book of ASTM Standards*, Vol 11.01.

³ Discontinued; see 1993 *Annual Book of ASTM Standards*, Vol 11.01. Replaced by Test Methods D 5464.

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, $\mu\text{S}/\text{cm}$	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

^AData courtesy of Ref (13). This data developed from algorithms originally published in Ref (14).

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

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, $\mu\text{S}/\text{cm}$	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

^AData courtesy of Ref (13). This data developed from algorithms originally published in Ref (14).