Designation: D6569 – 23

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

This standard is issued under the fixed designation D6569; 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 continuous determination of pH of water by electrometric measurement using the glass, the antimony or the ion-selective field-effect transistor (ISFET) electrode as the sensor.

1.2 This test method does not cover measurement of samples with less than 100 µS/cm conductivity. Refer to Test Method D5128.

1.3 This test method does not cover laboratory or grab sample measurement of pH. Refer to Test Method D1293.

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

1.5 *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.*

1.6 *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
D3370 Practices for Sampling Water from Flowing Process Streams
D3864 Guide for On-Line Monitoring Systems for Water Analysis
D5128 Test Method for On-Line pH Measurement of Water of Low Conductivity

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129, Test Method D1293 and Guide D3864.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *liquid junction potential, n*—the dc potential which appears at the point of contact between the reference electrode's salt bridge and the sample solution.

3.2.1.1 *Discussion*—Ideally this potential is near zero and is stable. However, in samples with extreme pH it becomes larger by an unknown amount and is a zero offset.

4. Summary of Test Method

4.1 pH is measured as a voltage between measuring electrode and reference electrode elements. The sensor assembly typically includes a temperature compensator to compensate for the varying output of the measuring electrode due to temperature.

4.2 The sensor signals are processed with an industrial pH analyzer/transmitter.

4.3 The equipment is calibrated with standard pH buffer solutions encompassing or in close proximity to the anticipated pH measurement range.

5. Significance and Use

5.1 pH is a measure of the hydrogen ion activity in water. It is a major parameter affecting the corrosivity and scaling properties of water, biological life in water and many applications of chemical process control. It is therefore important in water purification, use and waste treatment before release to the environment.

5.2 On-line pH measurement is preferred over laboratory measurement to obtain real time, continuous values for automatic control and monitoring purposes.

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.03 for Sampling of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement 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.

6. Interferences

6.1 Pressure and temperature variations may force process sample into the liquid junction of non-flowing junction reference electrodes and cause changes in the junction potential. Estimates of 0.2 to 0.5 pH errors from this source have been cited (**1**).[3]

6.2 Liquid junction potentials at the reference electrode can vary depending on the composition of the sample. Strong acids, bases and extremely high and low ionic strength samples develop liquid junction potentials different from typical calibrating buffer solutions (**2**). Where these conditions exist, the most stable junction potential is obtained using a flowing junction reference electrode—one that requires refilling with electrolyte solution. However, providing positive flow of electrolyte through the reference junction places limitations on the sample pressure that can be tolerated. Follow manufacturers' recommendations.

6.3 pH reference electrodes must not be allowed to dry. Electrolyte salts can crystallize in the liquid junction and produce a high liquid junction impedance. Subsequent pH measurements could be noisy, drifting or off-scale. When pH sensors are not in use, they should be typically stored wet per manufacturers' instructions.

6.4 There are several temperature effects on pH measurement. The pH electrode signal is described by the Nernst equation with its output proportional to the absolute temperature times the pH deviation from the isopotential point—usually 7 pH for glass electrodes. Compensation for this effect may be accomplished automatically with a temperature sensor integral to the combination pH probe and an algorithm in the instrument. Alternatively, some instruments may be set manually for a fixed temperature when a temperature signal is not available. Errors caused by deviations from the manual setting may be calculated from the following (for a conventional glass electrode system with 7 pH isopotential point).

$$\textit{Glass Electrode pH error} = \frac{(pH - 7) \times (T - Tf)}{Tf + 273} \quad (1)$$

where:

pH = uncorrected process pH,
T = process temperature (°C), and
Tf = temperature setting of fixed compensation (°C).

Other types of electrodes, (antimony, ISFET) have different isopotential points and therefore different corrections. Consult the manufacturer.

6.5 Solution temperature effects may be caused by changes in the sample, such as ionization of constituents, off-gassing, and precipitation, which occur with changes in temperature. These are generally small for many samples over moderate temperature ranges. In waste streams with variation in composition, such effects are usually not predictable. However, for samples with uniform or predictable composition with temperature changes >5 °C, one may determine the effect for the samples being measured and make the correction on all measurements. The pH to be reported is referenced to 25 °C unless another temperature is specified. Some process instruments have built-in solution temperature compensation which allows entry of a user-defined linear temperature coefficient into instrument memory for on-line correction of this effect. The temperature of the solution measured for pH should be monitored and recorded since this information may be critical to understanding the base state of the solution.

NOTE 1—For regulatory monitoring, correction for solution temperature effects should not be done without consulting the governing authority.

6.6 A small temperature influence can occur due to differences in the composition of measuring and reference half-cells. This is not compensated by any instrumentation. For this reason it is advisable to calibrate as near the measuring temperature as possible.

6.7 Coating of the measuring electrode may produce a slow or erroneous response since the sensing surface is in contact with the coating layer rather than the bulk sample. Flat surface electrodes and high sample flow velocity have been found to provide some self-cleaning effects. Cleaning may be accomplished manually using solvents, acids, detergents, etc. Cleaning may be automated by a number of approaches. See Appendix X1.

6.8 Abrasion of measuring electrode surfaces from particles in the sample can shorten sensor life. Where abrasive particles are present, the flow velocity past the electrode surface should be controlled low enough to minimize abrasion and provide satisfactory electrode life yet high enough to prevent particles from accumulating into a coating as in 6.7.

6.9 High pH conditions can produce an alkaline error as the glass pH sensor responds to sodium or other small cations in addition to hydrogen. This type of error is greater at higher temperatures. The result is always a negative error in the range of 0 to -1 pH depending on the pH, temperature, sodium concentration and sensor glass formulation. Some manufacturers have characterized the alkaline or sodium error sufficiently to closely estimate those errors. Some process ISFET electrodes do not experience these errors.

6.10 While fluorides in the sample do not interfere with the measurement, if present at pH below 5, they attack silica, greatly shortening the life of glass and ISFET electrodes.

6.11 Antimony electrode measurements are subject to major interferences from oxidizing or reducing species, non-linearity, irregular temperature characteristics and the physical condition of the electrode surface. However, the antimony electrode can withstand hydrofluoric acid which other electrodes cannot and this application is its primary use. The typical useful range of the antimony electrode is 3-9 pH. Performance is very application-dependent and should be carefully evaluated.

6.12 Electrical noise induced on the pH sensor-to-instrument cable can cause erratic and offset readings. Route pH signal cables separately from AC power and switching circuit wiring.

6.13 Electrical insulation leakage in electrode connectors and cable or cracking of a glass electrode membrane can cause

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