



Designation: D6569 – 23

Standard Test Method for On-Line Measurement of pH¹

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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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 $\mu\text{S}/\text{cm}$ 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).

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

where:

pH = uncorrected process pH,

T = process temperature (°C), and

T_f = 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.

the high impedance pH signal to be attenuated or completely lost. This results in a dead response where the measurement system will not give response away from the calibration point. Keep pH signal cables and connectors clean and dry. Preamplifiers are normally located close to pH sensors to minimize the distance high impedance signals must be transported—a help in minimizing noise interference in 6.12 as well.

6.14 Ground loop interference can occur if the pH measuring circuit is not galvanically isolated from earth ground, except for the electrodes themselves. Such interference can give an offset or off-scale reading when measuring in a grounded process installation but will give satisfactory response in grab samples or calibration solutions that are not grounded. Sources of ground loops include improper wiring of sensor cables, lack of isolation of analog or digital output signals from the measuring circuit, or a leaking sensor body which allows electrical contact of the sample to a part of the measuring circuit beyond the external electrode surfaces. Remove output wiring, check sensor wiring and observe readings to locate the cause of grounding problems.

6.15 Measurements on samples with conductivity less than 100 $\mu\text{S}/\text{cm}$ are vulnerable to streaming potentials, large junction potentials and other difficulties and are beyond the scope of this method. Use Test Method D5128.

7. Apparatus

7.1 Process Instrument:

7.1.1 The measuring system shall use a high impedance preamplifier, preferably located near the electrode but may be contained within the instrument, capable of measuring the high impedance pH sensor voltage. When located near the electrode, the preamplifier shall be sealed against moisture intrusion. A glass pH electrode measuring circuit must have at least 10^5 Megohm input impedance to preserve the signal. Some measuring circuits use a differential input and solution ground which can tolerate a higher reference junction impedance and reduce liquid junction potential errors.

7.1.2 The instrument shall provide indication, alarms, relays, isolated analog outputs and digital outputs as needed for the application. Where output signal isolation from the measurement circuit is not provided within the instrument, the signal must pass through an external signal isolator before connection to a grounded computer, data acquisition or control system. This will prevent ground loop errors in the measurement as described in 6.14.

7.1.3 Some instruments provide as a part of their measuring circuit, sensor diagnostics which check the impedance of the glass electrode, reference electrode or both to assure their integrity.

7.2 *Process Electrodes*—Although measuring and reference electrodes and the temperature compensator are described individually below, they may also be constructed into a single probe housing, frequently called a combination electrode. The different types of measuring electrodes and reference electrodes below are options: only one measuring electrode and one reference electrode are used for measurement.

7.2.1 *Glass Measuring*—The pH glass measuring electrode is by far the most common type of pH sensor. It shall have a

repeatable response as given in Test Method D1293. It shall have pH, temperature and pressure ratings suitable for the process conditions. It shall be conditioned in the process sample for at least 30 minutes or as recommended by the manufacturer before accurate readings can be taken.

7.2.2 *ISFET Measuring*—The ISFET measuring electrode along with its unique measuring circuit shall give response equivalent to a glass electrode measuring system. (ISFET electrodes typically require an adapter circuit to be compatible with glass electrode measuring instruments.)

7.2.3 *Antimony Measuring*—The antimony measuring electrode shall be pure polished antimony metal that has been conditioned by soaking in water to produce an oxide layer, according to manufacturer's instructions.

7.2.4 Non-Flowing Liquid Junction Reference:

7.2.4.1 The non-flowing reference electrode shall contain an electrode half-cell similar to the glass measuring electrode, if used, to cancel the temperature effects of the half-cells. It shall contain sufficient electrolyte with gelling agent or other means to restrict its loss and give acceptable life in the application. Despite the name “non-flowing,” the electrolyte is consumable as a trace amount of it diffuses through the junction into the sample. The only opening of the electrode is its interface with the process through its liquid junction—a small passage of porous ceramic, polymer, wood, fiber, ground glass surfaces or other material that allows electrical continuity with the sample while limiting loss of electrolyte. Some non-flowing reference electrodes are refillable.

7.2.4.2 For fouling processes containing sulfides, or other species that could react with the electrolyte, a second or double liquid junction shall be provided as a barrier to contamination or dilution of the inner electrolyte. A long path between the liquid junction and the inner half-cell is also helpful. Some electrode systems use another pH glass membrane within the reference electrode in place of a second junction. In that case, the intermediate electrolyte is a concentrated pH buffer which holds the reference potential constant.

7.2.4.3 For oil, grease or suspended solids-bearing samples, the liquid junction should have a relatively large surface area, typically greater than 15 mm^2 , to reduce the chances of becoming completely blocked.

7.2.5 Flowing Junction Reference:

7.2.5.1 The flowing junction reference electrode shall contain an electrode half-cell similar to the glass measuring electrode, if used, to cancel the temperature effects of the half-cells. It shall have a reservoir of electrolyte solution that is continuously forced through the liquid junction by gravity head or by external pressure. This type of electrode produces the most consistent junction potential under extreme process conditions and therefore is recommended especially for very high or low pH samples.

7.2.6 Temperature Compensator:

7.2.6.1 The temperature compensator shall provide rapid temperature response corresponding to the temperature of the glass membrane. It's temperature signal is used to compensate for output variations of the measuring electrode due to

temperature—called the Nernst effect. Where process temperature is stable or where sample pH is always near the isopotential point, typically 7, the temperature compensator may be omitted and a fixed temperature setting may be used in the instrument. See 6.4.

7.2.6.2 For samples that change ionization significantly with temperature, the temperature signal may also be used for solution temperature compensation in measuring instruments so equipped. See 6.5.

7.2.7 *Electrode Mounting Types:*

7.2.7.1 The sensing tip of the electrodes shall be immersed under all process conditions to assure a reliable measurement and to prevent the reference electrode from drying out. Provision must be made when a process is shut down for keeping the reference junction wetted.

7.2.7.2 Submersion electrodes shall provide pipe thread or other means of sealing a support conduit to carry their signal leadwire(s) up out of the solution and keep the wiring and any connectors completely dry. Protection of the fragile glass membrane or ISFET sensor surface shall be provided.

7.2.7.3 Insertion electrodes shall have a pipe thread or other means of sealing the electrode into a pipe or side of a tank suitable for the process pressure. For side of tank mounting, most electrodes require mounting with the sensing end of the probe sloped downward at least 15 degrees below horizontal. This assures that the electrolyte of the glass measuring and the reference electrodes maintains continuity with the inner surfaces of the membrane and liquid junction, respectively. Because pH electrodes require periodic calibration, insertion mounting is recommended only in processes that shut down frequently. For long-term continuous processes, electrodes may be installed in a side stream that can be isolated from the main process line by valves. With a side stream, care must be taken to ensure sufficient pressure drop in the main line to force a flow through the side stream. Side stream discharge to drain may be used and this gives an added benefit of reduced pressure on the electrode. For recommendations on sampling, refer to Practice C of D3370.

7.2.7.4 Flow-through chambers for electrodes shall provide means for sealing the electrodes into the chamber. Flow-through installation may also benefit from location in a side-stream as in 7.2.7.2.

7.2.7.5 Retractable electrode mountings (also called wet-tap or removable mountings) allow removal of the electrode from a pressurized process line or tank without shutting down the process. They use a valve or other sealing means to block process pressure before the electrode is removed. Retractable mountings are useful for obtaining the fastest response to process conditions but they subject the electrode to full process pressure, temperature and flow velocity. Some retractable mountings include manual or automated provision for electrode withdrawal and introduction of cleaning and calibrating solutions into the cavity around the electrode tip. See X1.4.1.

7.2.8 Electrode life is dependent on conditions of the sample. High temperature or pressure cycling or both causes expansion and contraction of electrodes which can deplete the electrolyte. Some experience indicates the life of pH electrodes is inversely proportional to the operating temperature (3). High

temperature at high pH will cause chemical attack of glass electrode membranes (shortening life) and a degradation of response—both slower in time and reduced in electrical output. Some formulations of glass membranes are more resistant to these conditions. Consult the manufacturer.

8. Reagents

8.1 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type IV or better, of Specification D1193.

8.2 *Commercial pH Buffer Solutions*, traceable to standard reference materials from the National Institute of Standards and Technology (NIST) or traceable to another internationally recognized standards agency are used for calibration of on-line electrode systems. Refer to buffer solution manufacturer's literature for details on composition, pH value versus temperature, shelf life, etc. Additional information is included in Test Method D1293. pH buffer solutions with pH greater than 7 will absorb carbon dioxide from the atmosphere and develop a lower pH value over time. Keep buffer solutions sealed except when dispensing and do not store for more than one year or per manufacturer's instructions. Buffer solutions may also be made up from pre-weighed, packaged salts dissolved in a precise volume of water, per manufacturer's instructions.

8.3 *Dilute Hydrochloric Acid* (50 g HCl/L), dilute 11.2 mL of 37.5 % HCl in water to make 100 mL.

9. Calibration

9.1 *Buffer Solution Calibration:*

9.1.1 Buffer solution calibration is the ultimate standard for pH measurement. See 8.2. Two commercial pH buffer solutions are used for process system calibration. The two buffer solution pH values should bracket the range of measurement, if possible.

9.1.2 For a new pH sensor, condition it as in 10.1. Set the process instrument or external controls to hold any pH signal, alarms, etc. in a safe range during the upset in pH measurement that occurs when electrodes are removed. Some instruments have a built-in function for this purpose. Close isolation valves, if used, and remove the electrode from the process.

9.1.3 If electrode cleaning requires chemicals or physical scrubbing, do this as a separate step before calibration and place the sensor back in the process long enough for it to reacclimate to sample conditions.

9.1.4 Remove the electrode and rinse its surfaces well with water to prevent contamination of buffer solutions.

9.1.5 Following the instrument manufacturer's instructions, immerse the electrode sequentially in the two buffer solutions, rinsing between and performing the steps for two-point calibration. Allow sufficient time for the pH and temperature to reach equilibrium and for the readings to stabilize in the buffer solutions. Discard used buffer solutions.

9.1.6 For highest accuracy, heat or cool the buffer solutions to approximate the process temperature to eliminate the temperature influence described in 6.6. In addition, buffer solutions change pH with temperature. It is important to use the pH value of the buffer solution at its temperature during calibration. This