



Designation: D 6569 – 05

Standard Test Method for On-Line Measurement of pH¹

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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 D 5128.

1.3 This test method does not cover laboratory or grab sample measurement of pH. Refer to Test Method D 1293.

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

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

D 1293 Test Methods for pH of Water

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water

D 3370 Standard Practices for Sampling Water from Closed Conduits

D 3864 Guide for Continual On-Line Monitoring Systems for Water Analysis

D 5128 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 D 1129, Method D 1293 and Practice D 3864.

3.2 *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 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.

3.2.1 *liquid junction potential*—the dc potential which 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 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.

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

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

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)

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 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 Method **D 5128**.

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 **D 1293**. 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. Its 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.