


SOP-C-120

Determination of pH

Revision 11

Approval:



Laboratory Manager

3-12-24

Date



Concurrence

03-12-2024

Date

Effective date: 3-31-24

Renewal date: _____ Initials: _____

SOP-C-120
Determination of pH

- i. **Identification of the method**
 - a. SM 4500-H⁺ (approved 2018) and EPA 9045C (approved 1995)
- ii. **Applicable matrix or matrices**
 - a. Waters or aqueous solutions and suspensions
- iii. **Limits of detection and quantitation**
 - a. Normal limits are from 1 to 10 pH units without specialized probes.
 - b. Report to the nearest 0.1 pH Standard Units.
- iv. **Scope and application, including parameters to be analyzed**
 - a. Calibration and verification are done near the pH of the solution or sample being measured.
- v. **Summary of the method**
 - a. Electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode.
- vi. **Definitions**
 - a. pH- indicator of acidity or basicity, defined as the negative logarithm of the hydrogen ion concentration in an aqueous solution
 - b. Standard Units (S.U.)- an assigned numeric value of pH
 - c. ATC (Automatic Temperature Compensation)- a feature found on most pH meters which corrects for temperature differences between calibration standards and samples measured.
- vii. **Interferences**
 - a. The glass electrode is relatively free from interference from color, turbidity, colloidal matter, oxidants, reductants, or high salinity, except for a sodium error at pH > 10. This error may be reduced by using special "low sodium error" electrodes, which are not in use at this time.
 - b. Extreme temperatures will interfere with pH measurement, even using ATC.
 - c. Oils and greases can foul the probe.
 - d. pH measurements are affected by temperature in two ways: mechanical effects that are caused by changes in the properties of the electrodes and chemical effects caused by equilibrium changes. In the first instance, the slope increases with increasing temperature and electrodes take time to achieve thermal equilibrium. This can cause long-term drift in pH. Because chemical equilibrium affects pH, standard pH

SOP-C-120
Determination of pH

buffers have a specified pH at indicated temperatures. Always report temperature at which pH is measured.

- e. Combination electrodes incorporate the glass and reference electrodes into a single probe. Use a “low sodium error” electrode that can operate at high temperatures for measuring pH over 10 because standard glass electrodes yield erroneously low values. For measuring pH below 1 standard glass electrodes yield erroneously high values; use liquid membrane electrodes instead.

viii. Safety

- a. Refer to QAM-S-101, “Laboratory Safety,” for general laboratory safety.

ix. Equipment and supplies

- a. Accumet AB 150 pH/Millivolt Meter, or equivalent.
- b. Accumet pH Electrode with Ag/AgCl reference system, combination probe, or other equivalent electrode.
- c. Magnetic stirrer and Teflon-coated stirring bar.
- d. Thermometer or temperature sensor for automatic compensation
- e. Beakers: Preferably use polyethylene or TFE beakers.
- f. Flow chamber: Use for continuous flow measurements or for poorly buffered solutions.

x. Reagents and standards

- a. Reagents
 - i. Deionized water (DI) for rinsing
- b. Standards (refresh daily from the stock)
 - i. pH 7 buffer solution, commercially prepared
 - ii. pH 10 buffer solution, commercially prepared
 - iii. pH 4 buffer solution, commercially prepared
 - iv. other levels of buffer solutions as appropriate for the samples tested

xi. Sample collection, preservation, shipment and storage

- a. Holding Time: as soon as possible; pH is best measured in the field. If not possible, pH is measured as soon as practicable in the laboratory and data are designated as Laboratory pH with temperature, time and date labels.
- b. Refrigerate sample to $>0\text{--}\leq 6^{\circ}\text{C}$ if not measured immediately.
- c. Samples are not collected or delivered by the laboratory.

xii. Quality control

SOP-C-120
Determination of pH

- a. Refer to QAM-Q-101, "Laboratory Quality Control," for quality control requirements.

xiii. Calibration and standardization

- a. Calibration for this instrument consists of two-buffer set points with one other buffer calibration check in accordance with QAM-I-105, "Operation and Calibration of the pH Meter." The range of buffer standards generally bracket the pH of the samples analyzed.
- b. Before initial analysis of the day, perform a two-buffer set point calibration using two of pH 4.0, 7.0, or 10.0 buffer solutions in accordance with QAM-I-105, "Operation and Calibration of the pH Meter". The pH 10.0 & 7.0 buffers are for routine waters, solutions and suspensions. When analyzing wastes or samples with extreme higher or lower pH, use a more appropriate buffer closer to the expected pH range. Other buffers may be used to achieve desired range of measurement.
- c. Record the lot of the pH buffer, the temperature at the time of the reading and the slope in percent for each pH buffer used.
- d. Perform a calibration verification on at least one other pH buffer, usually 7.0 pH. A ICV/CCV is of a different source than the calibration buffers, but the LCS may be one of the calibration buffers. If the observed readings are within ± 0.1 pH units, acceptance criteria have been met.

xiv. Procedure

- a. Prior to analysis, refrigerated samples are warmed to about the same temperature as the standard buffer solutions. If ATC is not used, bring samples to within $\pm 1^{\circ}\text{C}$ of calibration standards used.
- b. For soils, sediments and other solids, make an aqueous suspension by mixing the sample with DI water at a 1:1 ratio. The mixture is continuously stirred for 5 minutes, and then allowed to stand for about 1 hour prior to determination of pH in the aqueous phase as described below.
- c. Place sample in a clean glass beaker or other suitable container and mix the sample with stir bar or rod.
- d. Verify there is sufficient sample volume to cover sensing elements of the electrodes and to give adequate clearance for the stir bar.

SOP-C-120
Determination of pH

- e. Rinse electrode with deionized water and ensure air port is open (if present), then rinse at least 3 times with the sample.
- f. While stirring, place electrode in sample.
- g. Press “stdby” button to put meter into active mode.
- h. After reading stabilizes, read the pH value on the display.
- i. Record pH to the nearest 0.1 unit in the log.
- j. Rinse electrodes with deionized water between measurements. For less clean samples, also rinse electrode with a small amount of the next sample to be measured before placing into fresh sample.
- k. Perform ICV/CCV/LCS/LCSD checks by measuring one standard at pH 7. ESDMS or current LIMS may calculate acceptability of the check.
- l. Press “stdby” button to return meter to Standby mode.
- m. Close air port on electrode (if present).
- n. Store probe in pH 4 buffer.
- xv. Data analysis and calculations**
 - a. None. When using ATC, report pH adjusted to 25°C, otherwise report the temperature at which the pH was measured.
 - b. Report the time/date of both sample collection and pH measurement to show it was done within 15 minutes.
- xvi. Method performance**
 - a. Method performance, data assessment and acceptance, corrective action: refer to QAM-Q-101, "Laboratory Quality Control". Any pH data measured in the laboratory is designated as such. Per 40 CFR 136, pH is measured immediately on samples in the field.
- xvii. Pollution prevention**
 - a. Refer to QAM-W-101, “Disposal of Laboratory Waste,” for general waste management and pollution control requirements.
- xviii. Data assessment and acceptance criteria for quality control measures**
 - a. CCV, LCS, LCSD measurements are acceptable if they are within 0.1 S.U. of expected values.
 - b. Refer to QAM-Q-101, “Laboratory Quality Control,” or project plans for other general quality control requirements.
- xix. Corrective actions for out-of-control data**
 - a. Refer to QAM-Q-105, “Corrective Actions,” for corrective action implementation.

SOP-C-120
Determination of pH

xx. Contingencies for handling out-of-control or unacceptable data

- a. Refer to QAM-Q-105, "Corrective Actions," and QAM-Q-101, "Laboratory Quality Control," for handling out-of-control or unacceptable data.

xxi. Waste management

- a. Refer to QAM-W-101, "Disposal of Laboratory Waste," for general waste management and pollution control requirements. No hazardous waste is generated by this procedure, unless the sample is hazardous initially.

xxii. References

- a. Fisher Scientific Accumet® Basic (AB) Benchtop Meters, 68X613601, Revision 0, Fisher Scientific, July 2012.
- b. Combination pH Electrodes with Silver/Silver Chloride References, Accumet, 257151-001, Rev. B, 12/10.
- c. National Environmental Laboratory Accreditation Conference (TNI Standard), The NELAC Institute, 2016.
- d. Standard Methods for the Examination of Water and Wastewater, latest online edition, ed. by Arnold E. Greenberg, et al., APHA, AWWA, Washington D.C., Method 4500 H+ A&B (approved 2018).
- e. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Version 2, Method 9045C, EPA, Cincinnati, Ohio, 1997.
- f. Guidelines Establishing Test Procedures for the Analysis of Pollutants, 40 CFR 136.3, Title 40, Volume 20, Code of Federal Regulations, U.S. Government Printing Office, July 1, 2012.

xxiii. Any tables, diagrams, flowcharts and validation data

- a. none