Method 150.3: Determination of pH in Drinking Water

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Contents

1 SCOPE AND APPLICATION

1.1 Method

This method is to be used when obtaining pH measurements from drinking water. It applies to measurements of grab samples via bench-top and portable pH meters, and also to continuous pH measurement of drinking water via continuous pH monitoring instrumentation. This method is to be utilized when pH measurements are being submitted for compliance with daily monitoring requirements. Analysts should be skilled in the operation of the instrumentation and interpretation of the associated data. This method allows the use of any type of bench-top, portable, or continuous monitoring pH meter for compliance monitoring, and allows for the use of different technologies that conform to the constraints outlined in this method. Non-glass probes may be used provided method quality control (QC) parameters are met. This method is intended to measure drinking water pH with a resolution of 0.1 pH unit.

1.2 Means of Calibration and Calibration Verification

Calibration and calibration verification can be performed directly using a bench-top, portable, or continuous monitoring pH meter and reference pH buffers, or indirectly using a grab sample and calibrated bench-top or portable pH meter.

2 SUMMARY OF METHOD

A bench-top, portable, or continuous monitoring pH meter is used to measure the pH of drinking water using pH probes that include, but are not limited to, glass electrodes in combination with a reference potential, ion-selective field-effect transistor (ISFET) electrodes in combination with a reference potential, combination electrodes, and molecular sensors. Calibration and calibration verification can be performed directly or indirectly. Direct calibration and calibration verification involve measurement of reference pH buffers with the instrumentation. Alternatively, continuous monitoring pH meters may be calibrated or verified indirectly by using a grab sample from the sample stream and measuring the pH of the grab sample with a calibrated bench-top or portable pH meter. The continuous monitoring analyzer accuracy is verified or adjusted based on results from grab sample analyses.

3 DEFINITIONS

Calibration Verification – A process using a sample of known pH to verify pH meter calibration accuracy through the use of reference pH buffers or grab sample checks of continuous monitoring pH meters.

Portable pH Meter – A pH meter capable of being routinely transported to sampling sites for measuring sample pH to a resolution of 0.1 pH unit. Portable (also referred to as field pH meters) must be capable of user calibration or have a record of a pre-installed manufacturer calibration. Portable pH meters must be able to compensate for temperature manually or automatically.

Grab Sample – A discreet sample taken from the sample stream for measurement. Grab samples can also be used in the calibration verification and pH adjustment of continuous monitoring pH meters. The grab sample should be sampled near the continuous monitoring meter, must be measured as soon as possible, and must represent the conditions of the sample stream.

Bench-top pH Meter – A stand-alone pH meter capable of measuring sample pH to a resolution of 0.1 pH units. Bench (also referred to as laboratory) pH meters are typically user calibrated and must be able to

compensate for temperature manually or automatically.

Continuous Monitoring pH Meter – A pH meter directly connected to the sample stream and capable of measuring pH to a resolution of 0.1 pH unit. The system may use a flow-through, pipe mounted, or immersion electrode.

pH Probe – The electrode or sensor portion of the pH meter. The type of electrode can include, but are not limited to, glass electrodes in combination with a reference potential electrode, ion-selective field-effect transistor (ISFET) electrodes in combination with a reference potential electrode, combination measuring and reference electrodes, and molecular sensors.

Reference pH Buffer – A solution of known pH used to calibrate pH meters. This method requires the use of at least three reference pH buffers in meter calibration.

Safety Data Sheet (SDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire-fighting measures and reactivity data including storage, spill, and handling precautions.

4 INTERFERENCES

4.1 Manufacturer Recommendations for Probes

Refer to manufacturer recommendations regarding interferences specific to the probes used during analysis.

4.2 Probe Fouling

Periodically inspect the conditions of probes for fouling. Clean and maintain the probes according to manufacturer recommendations.

4.3 Temperature Effects

Temperature can affect the electrometric measurement of pH in two ways. The first is the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation. The second is the change of pH inherent in the sample at various temperatures. This is sample dependent and cannot be controlled. It should therefore be noted by reporting both the pH and temperature at the time of analysis.

5 SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely identified; each chemical compound should be treated as a potential health hazard unless otherwise determined, and exposure to these chemicals should be minimized. The laboratory or water system is responsible for maintaining documentation of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Safety Data Sheets (SDS) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.[1-4]

6 EQUIPMENT AND SUPPLIES

6.1 pH Meter

A bench-top, portable, or continuous monitoring pH meter may be used. A wide variety of instruments are

commercially available with various specifications and optional equipment. Meters must be capable of user calibration or have documentation of initial calibration from the manufacturer. Meters must be capable of automatic or manual temperature compensation. Results must be reported to the nearest 0.1 pH unit.

6.1.1 Continuous Monitoring pH Meter Special Considerations

6.1.1.1 Meter Adjustment and Grab Sample Location

Analysts must be capable of adjusting the continuous monitoring pH meter readout when comparing readings to stream grab sample results from a bench-top or portable pH meter during calibration or calibration verification. Grab sample location should be as near as possible to the continuous monitoring pH meter probe location.

6.1.1.2 Recording Readout

The meter must have a readout at its installation location and the readings must be continually recorded (hard copy chart or electronic data). For remote installations, the meter should also have the capability for transmission of the output to a centralized location.

6.1.1.3 Meter Alarm

The continuous monitoring pH meter should have the capability to activate an alarm when the pH is outside the normal operating range.

6.2 pH Probes

The pH probes include, but are not limited to, glass electrodes in combination with a reference potential electrode, ion-selective field-effect transistor (ISFET) electrodes in combination with a reference potential electrode, combination measuring and reference electrodes, and molecular sensors. Refer to manufacturer's recommendations regarding application.

6.2.1 Reference Potential Electrode

A calomel, silver-silver chloride or other reference electrode of constant potential may be used.

6.2.2 Continuous Monitoring Mounting Type

For continuous monitoring, electrode mounting may be flow-through, pipe mounted, or immersion. Probes should be installed so that they are in constant contact with the sample stream, even when not in use. Probes should also be installed as near the sampling point as possible.

7 REAGENTS AND STANDARDS

7.1 Reference pH Buffer Solutions

Reference buffers used in the calibration and calibration verification of pH meters are commercially available as liquids or in powder packets (powder packets require preparation; follow vendor's instructions). Typical pH buffer solutions have pH values near 4, 7, and 10. Buffer solution pH values are dependent upon temperature. Refer to the manufacturer specifications for each buffer used and adhere to the specified expiration dates. If using the same aliquots of pH reference solutions for multiple calibrations and calibration verifications, users should change out solutions weekly to prevent contamination and potential changes to reference pH.

8 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Representative Samples

Samples should be analyzed immediately after collection in order to best represent conditions at the sample collection location. If using a grab sample, the grab sample collection point should be as close as possible to the location where the sample enters the continuous monitoring pH meter. A sample line may be equipped with a valve that allows for intermittent grab sampling with minimal disruption of flow to the meter. Grab samples must be representative of conditions where the sample stream enters the continuous monitoring pH meter.

8.2 Sample Collection

Collect approximately 100 mL of sample in a clean plastic or glass container. Minimize sample aeration and the presence of air bubbles, which can interfere with analysis. Do not store samples.

Note: The use of temperature compensation with off-line or continuous monitoring pH meters will compensate for Nernst equation-related differences in pH between measurements of samples at different temperatures. However, temperature directly impacts dissociation and sample hydrogen ion concentration, which cannot be compensated for in samples. Therefore, the temperature should always be recorded at the time of sampling, and analysts should not allow the temperature of the sample after collection to change by more than 5 °C before analysis.

9 QUALITY CONTROL

Quality control (QC) procedures are incorporated into analytical methods in order to demonstrate that the results are valid and within the accuracy and precision ranges needed for protection of public health. The following sections detail the QC procedures that are required for bench-top, portable, and continuous monitoring pH meters. The Initial Demonstration of Capability (IDC) and ongoing QC criteria are summarized in Section 16, Tables 1 and 2. The laboratory or water system is required to maintain performance records that define the quality of data generated. For regulatory drinking water monitoring applications, additional QC and documentation may be specified by the associated primacy agency.

9.1 Bench-top and Portable pH Meter Initial Demonstration of Capability (IDC)

9.1.1 IDC frequency

An IDC must be successfully performed by each analyst prior to analyzing field samples and following any instrument maintenance. Calibrate as described in Section 10 prior to conducting the IDC.

9.1.2 Demonstration of Precision

Analyze four separate aliquots of a reference buffer of known pH. Samples should be continuously and gently stirred to minimize the presence of air bubbles. If mechanical stirring is not available, the sample should be gently swirled. Allow for the measurement to stabilize. Calculate the standard deviation of the replicates. The standard deviation must be ≤0.1 pH units.

9.1.3 Demonstration of Accuracy

Using the four replicates from the Demonstration of Precision, calculate the average measured pH. The result must be within ±0.1 pH units of the true pH value.

9.2 Bench-top and Portable pH Meter Ongoing QC

9.2.1 Bench-top or Portable pH Meter Calibration Verification

A single reference buffer of known pH must be analyzed at least daily or at the time of measurement for systems that monitor less frequently. The sample should be continuously and gently stirred to minimize the presence of air bubbles. If mechanical stirring is not available, the sample should be gently swirled. Allow the measurement to stabilize. The calibration verification reference buffer sample measurement must be within ±0.1 pH units of the true pH value. If the calibration verification fails, the instrument must be recalibrated (Section 10.1). If the calibration verification continues to fail, the pH meter or electrode may need maintenance or replacement.

9.3 Continuous Monitoring pH Meter QC using a Removable Probe

9.3.1 IDC and On-going QC

Follow the IDC and Ongoing QC procedures as discussed in Sections 9.1 and 9.2 by removing the probe from the sample stream and placing the probe in separate containers of the reference buffer solution. Rinse the probe with distilled water in between placement.

9.4 Continuous Monitoring pH Meter QC using a Grab Sample

9.4.1 IDC and On-going QC

The bench-top or portable pH meter used in the grab sample analysis must meet the IDC and Ongoing QC as described in Sections 9.1 and 9.2.

9.4.2 Continuous Monitoring pH Meter Calibration Verification

When using continuous monitoring pH meters, grab samples may be collected following the procedure in Section 8 and measured using a bench-top or portable pH meter. The sample should be continuously and gently stirred to minimize the presence of air bubbles. If mechanical stirring is not available, the sample should be gently swirled. Allow for the measurement to stabilize. Compare the result obtained from the bench-top or portable pH meter to the readout of the continuous monitoring pH meter. The results must not deviate by more than ±0.2 pH units. If the verification check fails, refer to Section 10.3 for calibration.

9.4.3 Verification Frequency

A grab sample must be verified daily or at the time of measurement for systems that monitor less frequently.

9.4.4 Optional Grab Sample Duplicate

Analysis of duplicate grab samples (two samples collected at the same time) provides an estimate of the precision of the grab sample analyses that are used to verify the accuracy of the continuous monitoring pH meter. Poor grab sample precision can cause problems in the analyzer adjustment. Analysis of grab sample duplicates is suggested when there are difficulties in adjusting the continuous monitoring meter to agree with the grab sample measurement. Results from grab sample duplicates should be within ±0.2 pH units. If the Sample and the Sample Duplicate result falls outside the designated range, analyze two aliquots of a reference buffer with the bench-top or portable pH meter to verify that the grab sample method is in control.

9.5 Additional QC

Laboratories and water systems are encouraged to institute additional QC practices to meet their specific

needs.

10 CALIBRATION

Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care for the probes is required as prescribed by the manufacturer. The analyst should refer to the particular manufacturer's instructions.

10.1 Bench-top and Portable pH Meter Calibration

10.1.1 Calibration Guidelines

If a pH meter is capable of user calibration, then it must be calibrated using the following guidelines. Follow the manufacturer's instructions. Calibrate each meter at a minimum of two pH levels that bracket the expected pH of the samples and are approximately three pH units or more apart. Typically, for drinking water, 2-point calibrations are performed using the pH 7.0 and pH 10.0 buffers. The buffers should be continuously and gently stirred to minimize the presence of bubbles. Allow for the measurement to stabilize.

10.1.2 pH Buffer Verification

Following calibration, analyze another reference pH buffer (e.g., pH 4 buffer) for calibration verification. The result must be within ±0.1 pH units of the true pH value.

10.1.3 Calibration Frequency

Calibration must be carried out at least weekly or at the time of measurement for systems that monitor less frequently and must be performed if the daily calibration verification sample (Section 9.2.1) does not meet QC.

10.1.4 Factory Calibration Documentation

If a pH meter uses a pre-installed factory calibration, documentation must be provided by the manufacturer that the meter was initially calibrated and that the meter requires no further user calibration. Calibration must be verified as described in Section 9.2.1.

10.2 Continuous Monitoring pH Meter Calibration using a Removable Probe

10.2.1 User Calibration Capability

The continuous monitoring meter must be capable of user calibration in order to perform the steps described in Sections 10.2.2 – 10.2.4.

10.2.2 Calibration Guidelines

Calibrate the electrode at a minimum of two pH levels that bracket the expected pH of the water and are approximately three pH units or more apart. Typically, for drinking water, 2-point calibrations are performed using the pH 7.0 and pH 10.0 buffers. The buffers should be continuously and gently stirred to minimize the presence of bubbles. If mechanical stirring is not available, the sample should be gently swirled. Allow for the measurement to stabilize.

10.2.3 pH Buffer Verification

Following calibration, analyze another reference pH buffer. The result must be within ±0.1 pH units of the

true pH value.

10.2.4 Calibration Frequency

Calibration must be carried out at least weekly or at the time of measurement for systems that monitor less frequently and must be carried out if the daily calibration verification sample (Section 9.3.1) does not meet QC.

10.3 Continuous Monitoring pH Meter Calibration using a Grab Sample

10.3.1 Calibration Guidelines

The bench-top or portable pH meter must be calibrated prior to use against at least two buffers and calibration must be verified with another buffer as outlined in Section 10.1, unless a factory calibration is used (Section 10.1.4). It is not necessary that reference pH buffers be at the same temperature as the sample stream for temperatures typically observed in drinking water sample lines.

10.3.2 Initial Calibration

The continuous monitoring pH meter system should be initially calibrated by the manufacturer (with documentation) or against two reference buffers as outlined in Section 10.2 before being placed into service.

10.3.3 Grab Sample Adjustment

Collect a grab sample of the flowing stream from a point as close to the meter as possible. A sample line may be equipped with a valve that allows for intermittent grab sampling with minimal disruption of flow to the meter. Separate sampling lines are acceptable as long as samples are representative of where the sample stream enters the continuous monitoring pH meter. Measure the pH of this grab sample as quickly as possible with a bench-top or portable pH meter. The sample should be continuously and gently stirred to minimize the presence of bubbles. If mechanical stirring is not available, the sample should be gently swirled. Allow for the measurement to stabilize. Adjust the calibration control of the continuous monitoring pH meter to the reading obtained.

10.3.4 Temperature Effects

The temperature and condition of the grab sample must remain constant (±5 °C) until its pH has been measured by the bench-top or portable pH meter. The temperature of the sample should be measured and recorded. The pH meter should compensate for any Nernst equation-related differences in temperature, but it is recommended that the analyst acclimate the probe to the sample temperature prior to measurement.

11 PROCEDURE

11.1 Bench-top and Portable pH Meters

11.1.1 Meter Installation, Operation, and Maintenance

Follow the manufacturer's instructions for installation, operation, and maintenance of the bench-top pH meter. Refer the manufacturer's instructions for operation and maintenance of the portable pH meter.

11.1.2 Calibration Frequency

The bench-top or portable pH meter must be calibrated weekly as outlined in Section 10.1.

11.1.3 Verification Frequency

Between calibrations, the bench-top or portable pH meter calibration must be verified daily as described in Section 9.2.

11.1.4 Sample Collection

Place no more than 100 mL of sample in an appropriately sized container for the analysis, since larger volumes of sample can lead to longer equilibration times. Be sure to pre-rinse the container with a small volume of the sample and discard prior to filling the container with the sample that will be measured.

11.1.5 Rinsing Probe

Rinse the sensor or electrode with distilled water and insert the sensor or electrode into the container ensuring the probe is in complete contact with the sample.

11.1.5.1 Portable pH Meters and Temperature

Portable pH meters may be used in more extreme temperature conditions than where bench-top pH meters are used. Portable meters must be capable of automatic or manual temperature compensation. To mitigate other temperature effects, it is recommended that the pH probe be allowed to reach sample temperature by placing the probe in the sample for several minutes prior to analysis.

11.1.6 Sample Stirring

During pH analysis, samples should be stirred using a magnetic stirrer. If magnetic stirring is unavailable, the sample should be swirled with care to not let the probe touch the sides of the container. Care should also be taken to not promote bubble formation.

11.1.7 Measurement

Measure the pH of the sample to the nearest 0.1 pH unit and record the temperature of the sample in °C.

11.1.8 Probe Care

Maintain, store, and clean probes or portable meters as needed according to the manufacturer's instructions.

11.2 Continuous Monitoring pH Meter

11.2.1 Meter Installation, Operation, and Maintenance

Follow the manufacturer's instructions for installation, operation, and maintenance of the continuous monitoring pH meter.

11.2.2 Calibration Frequency

The continuous monitoring pH meter must be calibrated weekly if using removable electrodes as outlined in Section 10.2 and initially before use if using a grab sample as described in Section 10.3.

11.2.3 Verification Frequency

After calibration, the continuous monitoring pH meter calibration must be verified daily as described in Sections 9.3 and 9.4.

11.2.4 Stream Contact

Ensure there is proper flow through the continuous monitoring pH meter and that the probe or sensor is in

complete contact with the sample stream.

11.2.5 Measurement

Measure the pH of the sample to the nearest 0.1 pH unit and record the temperature of the sample in °C.

12 DATA ANALYSIS AND CALCULATION

Meters read directly in pH units. Report pH to the nearest 0.1 pH unit and temperature to the nearest °C.

13 POLLUTION PREVENTION

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the waste management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

Quantity of a chemical purchased should be based on expected usage during its shelf-life, disposal cost, and environmental impact of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

For information about pollution prevention that may be applicable to laboratory operations, consult *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards*.[5]

14 WASTE MANAGEMENT

The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents are used. The matrixes of concern are drinking water. However, the Agency requires that waste management practices be conducted consistent with all applicable rules and regulations, and that the air, water, and land are protected by minimizing and controlling all releases from bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

15 REFERENCES

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16 TABLES AND FLOWCHARTS

Table 1A. Bench-top or Portable pH Meter Initial Demonstration of Capability (IDC) Quality Control Requirements

Type of pH Meter	Method Reference	Requirement	Specification	Acceptance Criteria
Bench-top or Portable pH Meter	10.1	Calibration	Calibrate using two reference pH buffers that bracket the expected pH of the samples. Analyze a third reference pH buffer following the two-point calibration. Calibrate weekly or at the time of measurement for systems that monitor less frequently.	Following calibration, the third reference pH buffer must be within ±0.1 pH units of the true pH value. Note: Meters with pre-installed factory calibrations may be used with proper documentation and must be verified using the discussed procedures.
Bench-top or Portable pH Meter	9.1.2	Demonstration of Precision	Analyze four replicate reference pH buffers. Calculate the standard deviation of the replicates.	The standard deviation must be ≤0.1 pH units.
Bench-top or Portable pH Meter	9.1.3	Demonstration of Accuracy	Analyze four replicate reference pH buffers. Calculate the mean measured pH.	The mean measured pH must be within ±0.1 pH units of the true pH value.

Table 1B. Continuous Monitoring (Removable Electrode) pH Meter Initial Demonstration of Capability (IDC) Quality Control Requirements

Type of pH Meter	Method Reference	Requirement	Specification	Acceptance Criteria
Continuous monitoring pH Meter (Using Removable Electrode)	10.2	Calibration	Calibrate using two reference pH buffers that bracket the expected pH of the samples. Analyze a third reference pH buffer following the two-point calibration. Calibrate weekly or at the time of measurement for systems that monitor less frequently.	Following calibration, the third reference pH buffer must be within ±0.1 pH units of the true pH value.
Continuous monitoring pH Meter (Using Removable Electrode)	9.3.1	Demonstration of Precision	Analyze four replicate reference pH buffers. Calculate the standard deviation of the replicates.	The standard deviation must be ≤0.1 pH units.
Continuous monitoring pH Meter (Using Removable Electrode)	9.3.1	Demonstration of Accuracy	Analyze four replicate reference pH buffers. Calculate the mean measured pH.	The mean measured pH must be within ±0.1 pH units of the true pH value.

Table 1C. Continuous Monitoring (Grab Sample) pH Meter Initial Demonstration of Capability (IDC) Quality Control Requirements

Type of pH Meter	Method Reference	Requirement	Specification	Acceptance Criteria
Continuous monitoring pH Meter (Using Grab Sample)	10.3	Calibration	Initial Calibration by manufacturer with documentation or calibrated according to Section 10.3. Calibration control adjusted based on comparison between bench-top or portable pH meter and continuous monitoring pH meter. Compare daily or at the time of measurement for systems that monitor less frequently.	Calibration control must be adjusted when comparison results is >0.2 pH units.
Continuous monitoring pH Meter (Using Grab Sample)	9.4.1	Demonstration of Precision, Demonstration of Accuracy	The bench-top or portable pH meter used in the grab sample analysis must meet the IDC as described in Section 9.1.	For bench-top or portable pH meter IDC, see Sections 9.1.2 and 9.1.3.

Table 2. Ongoing Quality Control Requirements

Type of pH Meter	Method Reference	Requirement	Specification	Acceptance Criteria
Bench-top or Portable pH Meter	9.2	Calibration Verification	A single reference pH buffer analyzed daily or at the time of measurement for systems that monitor less frequently.	The calibration verification sample must be within ±0.1 pH units of the true pH value.
Continuous monitoring pH Meter (Using Removable Electrode)	9.3	Calibration Verification	A single reference pH buffer analyzed daily or at the time of measurement for systems that monitor less frequently.	The calibration verification sample must be within ±0.1 pH units of the true pH value.
Continuous monitoring pH Meter (Using Grab Sample)	9.4	Calibration Verification	Daily or at the time of measurement for systems that monitor less frequently analyze a grab sample from the stream and compare with a bench-top or portable pH meter. The laboratory pH meter used in the grab sample analysis must meet the on-going QC as described in Section 9.2.	The compared results must not deviate by more than ±0.2 pH units.
Continuous monitoring pH Meter (Using Grab Sample)	9.4.4	Optional Grab Sample Duplicate	Analyze duplicate grab samples to verify the accuracy of the continuous monitoring pH meter.	Results from grab sample duplicates should be within ±0.2 pH units.