

FT 1100. Field Measurement of Hydrogen Ion Activity (pH)

Use in conjunction with:

- FT 1000 General Field Testing and Measurement
- FQ 1000 Field Quality Control Requirements
- FS 1000 General Sampling Procedures
- FD 1000 Documentation Procedures

1. Equipment and Supplies

1.1. Field Instrument: Use any pH meter consisting of a potentiometer, a glass electrode, a reference electrode, and a temperature-compensating device.

1.1.1. For routine fieldwork use a pH meter accurate and reproducible to at least 0.2-unit in the range of 0.0 to 14.0 units, and equipped with temperature-compensation adjustment. Record the pH value in pH units to one decimal place.

1.1.2. Advanced silicon chip pH sensors (with digital meters) may be used if demonstrated to yield equivalent performance to glass electrode sensors for the intended application.

1.2. Standards: Purchased or laboratory-prepared standard buffer solutions of pH values that bracket the expected sample pH range. Use buffers with nominal values of 4.0, 7.0 and 10.0 units for most situations. If the sample pH is outside the range of 4.0 to 10.0, then use two buffers that bracket the expected range with the pH 7 buffer being one of the two buffers. Alternatively, prepare appropriate standards per table I in method SM4500-H⁺-B.

1.3. Recordkeeping and Documentation Supplies:

- Field notebook (w/ waterproof paper is recommended) or forms
- Indelible pens

2. Calibration and Use

2.1. General Concerns

2.1.1. The acceptance criterion for the initial calibration or the calibration verification is a reading of the standard within +/- 0.2-unit of the expected value.

2.1.2. On a weekly basis, check the calibration to ensure the % theoretical slope is greater than 90% (if applicable to your instrument type).

2.1.2.1. Note the % slope in the calibration records.

2.1.2.2. A % slope of less than 90% indicates a bad electrode that must be changed or repaired.

2.1.2.3. If % slope cannot be determined on your meter, or the manufacturer's optimum specifications are different, follow the manufacturer's recommendation for maintaining optimum meter performance.

2.2. Interferences

2.2.1. Sodium at pH \geq 10.0 units can be reduced or eliminated by using a low sodium error electrode.

- 2.2.2. Coatings of oils, greases, and particles may impair the electrode's response. Pat the electrode bulb dry with lint-free paper or cloth and rinse with de-ionized water. For cleaning hard-to-remove films, use acetone very sparingly so that the electronic surface is not damaged.
- 2.2.3. Temperature effects on the electrometric measurement of pH are controlled by using instruments having temperature compensation or by calibrating the meter at the temperature of the samples.
- 2.2.4. Poorly buffered solutions with low specific conductance ($< 200 \mu\text{mhos/cm}$) may cause fluctuations in the pH readings. Equilibrate electrode by immersing in several aliquots of sample before taking pH.
- 2.2.5. Ensure stable sample and sensor temperature before calibrating or taking sample readings. Drifting sensor or sample temperature may produce erroneous sample measurements, calibrations, or verifications.
- 2.2.6. Thoroughly rinse the pH sensor with deionized water or fresh buffer standard when calibrating or verifying the calibration or when taking sample measurements. For in-situ measurements, ensure adequate flushing of the sensor with fresh sample water prior to taking measurements. Any residual standard, sample or deionized water remaining on the sensor may affect the measurement of the subsequent standard or sample. This is especially true when samples or standards of widely different pH value are successively measured.
- 2.2.7. Drifting readings or an inability to calibrate the sensor may also indicate a fouled electrode. Clean the electrode per the manufacturer's instructions or replace.
- 2.3. Calibration: Follow the manufacturer's calibration instructions specific to your meter. Most instruments allow for a two-point calibration and a few models can perform a three-point calibration. Use the appropriate number of standard buffer solutions for calibration. Do not reuse buffers for initial calibrations.
 - 2.3.1. Rinse the probe with de-ionized water (DI) before and between each standard buffer solution.
 - 2.3.2. Follow the calibration activities specified in FT 1000, section 2.2.
 - 2.3.2.1. Perform an initial calibration using at least two buffers. Always use a pH 7 buffer first.
 - 2.3.2.2. If the pH sample range is expected to be wider than the range established by a two-point calibration (e.g., some samples at pH 4 and others at pH 8), then add a third calibration point. If the instrument cannot be calibrated with three buffers, the third buffer may be used as the initial calibration verification to extend the range.
 - 2.3.2.3. After initial calibration, immediately perform an initial calibration verification (ICV). Read a buffer as a sample. To be acceptable, a calibration verification must be within ± 0.2 pH units of the stated buffer value. For example, if reading the pH 4.0 buffer, the result must be in the 3.8 to 4.2 range. Certain regulatory programs may have more stringent acceptance criteria.
 - 2.3.2.4. After sample measurement(s), perform a continuing calibration verification (CCV). Read a buffer as a sample. To be acceptable, a

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calibration verification must be within +/- 0.2 pH units of the stated buffer value. This CCV (if within acceptance criteria) can be used as the beginning of the chronological bracket. Certain regulatory programs may have more stringent acceptance criteria.

- 2.4. Measuring pH *in situ*: After calibrating the multi-probe sensors as outlined in 2.3 above, follow the meter's instructions to select the display for reading the pH of the sample. Immerse the probe at the desired depth in the water and wait for stabilization of the reading before recording the measurement.
- 2.5. Measuring pH in Flow-through Cells: When using a flow-through cell, the procedure described above in section 2.4 is applicable.
- 2.6. Measuring pH in Samples: After an acceptable initial calibration or calibration verification, follow these procedures to take a pH reading of a freshly collected sample (within 15 minutes of collection).
 - 2.6.1. Pour enough of the fresh sample into a clean cup to take the reading.
 - 2.6.2. Place the pH electrode in the sample (in the cup) and swirl the electrode.
 - 2.6.3. Wait for stabilization, and read the pH value.
 - 2.6.4. Turn the meter off after the last sample reading, rinse the electrode thoroughly with de-ionized water and replace the electrode's cap.
3. PREVENTIVE MAINTENANCE: Refer to FT 1000, section 3.
4. DOCUMENTATION
 - 4.1. Standard and Reagent Documentation: Document information about standards and reagents used for calibrations, verifications, and sample measurements.
 - 4.1.1. Note the date of receipt, the expiration date and the date of first use for all standards and reagents.
 - 4.1.1.1. Document acceptable verification of any standard used after its expiration date.
 - 4.1.2. Record the concentration or other value for the standard in the appropriate measurement units.
 - 4.1.2.1. Note vendor catalog number and description for preformulated solutions as well as for neat liquids and powdered standards.
 - 4.1.2.2. Retain vendor assay specifications for standards as part of the calibration record.
 - 4.1.3. Record the grade of standard or reagent used.
 - 4.1.4. When formulated in-house, document all calculations used to formulate calibration standards.
 - 4.1.4.1. Record the date of preparation for all in-house formulations.
 - 4.1.5. Describe or cite the procedure(s) used to prepare any standards in-house (DEP SOP or internal SOP).
 - 4.2. Field Instrument Calibration Documentation: Document acceptable calibration and calibration verification for each instrument unit and field test or analysis, linking this record with affected sample measurements.

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- 4.2.1. Retain vendor certifications of all factory-calibrated instrumentation.
- 4.2.2. Designate the identity of specific instrumentation in the documentation with a unique description or code for each instrument unit used.
 - 4.2.2.1. Record manufacturer name, model number, and identifying number such as a serial number for each instrument unit.
- 4.2.3. Record the time and date of all initial calibrations and all calibration verifications.
- 4.2.4. Record the instrument reading (value in appropriate measurement units) of all calibration verifications.
- 4.2.5. Record the name of the analyst(s) performing the calibration.
- 4.2.6. Document the specific standards used to calibrate or verify the instrument or field test with the following information:
 - Type of standard or standard name (e.g., pH buffer)
 - Value of standard, including correct units (e.g., pH = 7.0 SU)
 - Link to information recorded according to section 4.1 above
- 4.2.7. Retain manufacturers' instrument specifications.
- 4.2.8. Document whether successful initial calibration occurred.
- 4.2.9. Document whether each calibration verification passed or failed.
- 4.2.10. Document any corrective actions taken to correct instrument performance according to records requirements of FD 3000.
 - 4.2.10.1. Document date and time of any corrective action.
 - 4.2.10.2. Note any incidence of discontinuation of use of the instrument due to calibration failure.
- 4.2.11. Describe or cite the specific calibration or verification procedure performed (DEP SOP or internal SOP).
- 4.3. Record all field-testing measurement data, to include the following:
 - Project name
 - Date and time of measurement or test (including time zone, if applicable)
 - Source and location of the measurement or test sample (e.g., monitoring well identification number, outfall number, station number or other description)
 - Latitude and longitude of sampling source location (if required)
 - Analyte or parameter measured
 - Measurement or test sample value
 - Reporting units
 - Initials or name of analyst performing the measurement
 - Unique identification of the specific instrument unit(s) used for the test(s)