Standard Operating Procedure

pH using Multi-Parameter Water Quality Meters: Measurement, Meter Calibration, and Meter Maintenance

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1.0 INTRODUCTION

1.1 Purpose

To provide standardized procedures for the use and maintenance of *in situ* pH probes housed within multi-parameter water quality meters.

1.2 Scope of Work

These procedures are applicable for ambient surface water samples from lakes, streams, and tidal waters, and for wastewater samples.

2.0 MATERIALS

2.1 Equipment

The procedures described herein are applicable for use with the following multi-parameter water quality meters:

DRBC Name	Meter Make & Model	pH Probe
1. Coastal YSI	YSI 650 MDS + 6920 sonde	YSI 6561
2. Tristate #1	YSI 556 MPS	YSI 5564
3. Tristate #2	YSI 556 MPS	YSI 5564
4. EPA YSI	YSI 556 MPS	YSI 5564
5. Quanta	HydroLab Quanta	Quanta pH

All of these multi-parameter meters provide temperature compensation for pH readings.

2.2 Reagents & Chemicals

2.2.1 Standard Reagents

- pH 4.0 buffer
- pH 7.0 buffer
- pH 10.0 buffer

The above three NIST-traceable pH buffers will be routinely used for probe calibration and verification. Upon arrival at the lab, each buffer will be marked with the date received and, upon first opening and breaking the seal, the date first opened.

Fresh buffers (i.e., unused buffers directly from the manufacturer's container) will be used for all calibrations and verifications. Upon use, the buffer aliquots for calibration and verification will be discarded. In addition, pH buffers will be discarded upon expiration.

2.2.2 Additional Reagents for Quanta Multi-Parameter Meter

- Hach HydroLab KCl tablets (005376HY)
- Hach HydroLab pH electrolyte solution (005308HY; staturated KCl+AgCl)

Upon arrival at the lab, each container will be marked with the date received and, upon first opening and breaking the seal, the date first opened. Electrolyte solutions and tablets will be discarded following use, and any unused solutions will be discarded upon expiration.

3.0 PROCEDURES

3.1 Cleaning & Maintenance

Prior to calibration and use each day, examine the glass surfaces of the pH probe for oil, grease, or other fouling material. Should any material be found on the sensor, gently clean the sensor with a cotton swab (e.g., Q-tip) immersed in ethanol [*note: cotton may need to be removed from the swab tip to prevent excess pressure when cleaning the glass bulb; do not force the cotton swab between the sensor and the guard but rather remove cotton material so it more easily clears the gap*]. Following cleaning, rinse with plenty of tap water or distilled water. If significant problems with calibration and measurement are encountered, see Section 3.6 below on possible probe replacement.

3.2 Calibration

Calibrations must be conducted every day prior to use of the pH probe. Calibrations for pH include a 2-point calibration at the typical extremes of surface water pH, followed by a validation at an intermediate pH value. See each meter's users manual for specific instructions on accessing the calibration menus for that meter. The following provides step-by-step instructions for completing the calibration:

1. Rinse the pH probe and the calibration cup thoroughly with tap water.
2. Fill the calibration cup half-way with pH 4.0 buffer, immerse the probes into the buffer within the cup, and then remove the cup and pour the pH 4.0 buffer over the pH probe

and other sonde probes to displace any remaining tap water. Carefully shake free any remaining fluid from the calibration cup and the sonde.

3. Fill the calibration cup to the appropriate level (½ full for YSI meters; ¾ full for Quanta) with fresh pH 4.0 buffer.
4. Allow the pH readings on the meter to stabilize (minimum of 60 seconds) before calibrating to the pH 4.0 buffer. Record on the calibration bench sheet the initial reading immediately prior to calibration, whether the reading was calibrated, and the final reading on the meter. The time of meter calibration is also recorded on the calibration bench sheet along with a signature of the analyst performing the calibration.
5. Rinse the calibration cup and pH probe (and other affected probes) thoroughly with tap water.
6. Fill the calibration cup half-way with pH 10.0 buffer, immerse the probes into the buffer within the cup, and then remove the cup and pour the pH 10.0 buffer over the pH probe and other sonde probes to displace any remaining tap water. Carefully shake free any remaining fluid from the calibration cup and the sonde.
7. Fill the calibration cup to the appropriate level (½ full for YSI meters; ¾ full for Quanta) with fresh pH 10.0 buffer.
8. Allow the pH readings on the meter to stabilize (minimum of 60 seconds) before calibrating to the pH 10.0 buffer. Record on the calibration bench sheet the initial reading immediately prior to calibration, whether the reading was calibrated, and the final reading on the meter.
9. Rinse the calibration cup and pH probe (and other affected probes) thoroughly with tap water.
10. Fill the calibration cup half-way with pH 7.0 buffer, immerse the probes into the buffer within the cup, and then remove the cup and pour the pH 7.0 buffer over the pH probe and other sonde probes to displace any remaining tap water. Carefully shake free any remaining fluid from the calibration cup and the sonde.
11. Fill the calibration cup to the appropriate level (½ full for YSI meters; ¾ full for Quanta) with fresh pH 7.0 buffer.
12. Allow the pH readings on the meter to stabilize (minimum of 60 seconds) before reading this intermediate verification value. Record on the calibration bench sheet the final stabilized reading for this pH 7.0 buffer.
13. Rinse the calibration cup and pH probe (and other affected probes) thoroughly with tap water, and prepare for either further calibrations or for storage and travel (see 3.5 below)

3.3 Validation of Calibration During Use

In addition to daily pH calibrations prior to use, the pH calibration needs to be validated when the pH meter is in use for longer than a 3 hour period, and at 3 hour intervals thereafter during use. The pH validation will include, at a minimum, a spot check of the pH 7.0 buffer and a recording of the pH reading and the time of validation in field notebooks (these records will be transferred to the calibration bench sheet upon return to the lab). If the pH differ by more than 0.2 units from the standard value (i.e., pH reads less than 6.80 or greater than 7.20), the pH probe needs to be re-calibrated prior to further use.

3.4 Measurement Procedures

3.4.1 Streams & Rivers

Attach the probe guard and deploy the sonde within a representative area of appreciable flow to provide adequate mixing around the probes. Turn the meter on, record the time on the data sheet, and wait an initial 60 seconds before checking pH readings. From 60 seconds onward, observe the pH readings and record an initial pH reading and the time of measurement when pH values stabilize (e.g., no change more than 0.02 units within 10 seconds). Record a duplicate reading and the time of the measurement at least 60 seconds following the initial reading and up to 10 minutes following that reading. Retrieve the sonde, retain a small volume of either tap water or surface water within the travel cup, and finish packing the meter for travel.

3.4.2 Tidal Waters

Attach the probe guard and deploy the sonde within the water column and a minimum of 10 cm above the bottom. Turn the meter on, record the time on the data sheet, and wait an initial 60 seconds before checking pH readings. If the probes are situated in adequate flow, no special care is needed. However, if the measurements are taken at slack tide or from a quiescent location, ensure adequate flow around the probes by either gentle movement of the sonde or by utilizing a flow inducing device (e.g., stirrer, pump). Starting 60 seconds following deployment / turning on the electronics, observe the pH readings and record an initial pH reading and the time of measurement at the point when pH values stabilize (e.g., no change more than 0.02 units within 10 seconds). Record a duplicate reading and the time of the measurement at least 60 seconds following the initial reading and up to 5 minutes following that reading. Retrieve the sonde, retain a small volume of either tap water or surface water within the travel cup, and finish packing the meter for travel [*note: if brackish or saline waters are used for storage in the travel cup, flush the probes and replace with tap water upon return to the lab, office, or motel; see 3.4 below*].

3.4.3 Lakes & Ponds

Attach the probe guard and deploy the sonde within the water column and a minimum of 10 cm above the bottom. Turn the meter on, record the time on the data sheet, and wait an initial 60 seconds before checking pH readings. Ensure adequate flow around the probes by either gentle movement of the sonde or by utilizing a flow inducing device (e.g., stirrer, pump). Starting 60 seconds following deployment / turning on the electronics, observe the pH readings and record an initial pH reading and the time of measurement at the point when pH values stabilize (e.g., no change more than 0.02 units within 10 seconds). Record a duplicate reading and the time of the measurement at least 60 seconds following the initial reading and up to 5 minutes following that reading. Retrieve the sonde, retain a small volume of either tap water or surface water within the travel cup, and finish packing the meter for travel.

3.4.4 Wastewater

Attach the probe guard and deploy the sonde within the water column and a minimum of 10 cm above the bottom of any structure. Turn the meter on, record the time on the data sheet, and wait an initial 60 seconds before checking pH readings. If the probes are situated in adequate flow, no special care is needed. However, if the measurements are taken from a quiescent location, ensure adequate flow around the probes by either gentle movement of the sonde or by utilizing a flow inducing device (e.g., stirrer, pump). Starting 60 seconds following deployment / turning on the electronics, observe the pH readings and record an initial pH reading and the time of measurement at the point when pH values stabilize (e.g., no change more than 0.02 units within 10 seconds). Record a duplicate reading and the time of the measurement at least 60 seconds following the initial reading and up to 5 minutes following that reading. Retrieve the sonde, place a small volume of either tap water or pH buffer within the travel cup (*do not use wastewater!*), and finish packing the meter for travel.

3.5 Storage

Except when no other sanitary water is available, distilled or deionized water should ***not*** be used for storage of pH and other water quality probes due to its low ionic strength. Instead, tap water, clean surface water, or pH 4.0 buffer should be used for storage. For short-term storage (a day or less), tap water or clean surface water is preferred [*note: brackish or saline water can be used for short term storage of a day or less, but the*

probes must be rinsed thoroughly and the storage cup water replaced upon return to the lab, office, or motel]. For moderate lengths of storage (up to 2 weeks), tap water should be used for storage in the travel cup. For long-term storage (a month or longer), pH 4.0 buffer solution must be used to prevent damage to the pH probe (pH 4.0 buffer can also be used for shorter-term storage, but greater care with calibration and verifications must be used). It is important to note that maintaining some fluid in the cup is more important than the source of water. As a result, if the preferred water source is not immediately available, use a small volume of the available water source (e.g., water bottle) for short-term storage but immediately and thoroughly rinse the sensors at the earliest opportunity, and replace the fluid within the travel cup with the recommended water source.

In both short-term and moderate storage, fill the travel cup with approximately ½ inch (1 cm) of water and secure the travel cup to prevent evaporation. A small volume of water is necessary to simultaneously maintain a moist, humid environment within the storage cup while preventing immersion of any probe in the storage fluid. Long-term immersion within any storage fluid can result in sensor drift and/or shorten the sensor lifetime.

3.6 Probe Replacement

The pH readings and calibrations should be monitored for drift and errant readings. If the pH readings take many minutes (up to 30+ minutes) to completely stabilize, or if the initial readings during calibration of the pH buffers are off by more than 0.5 units, or if other problems with the pH readings occur, then the pH sensor may need replacement or re-servicing. The appropriate steps vary, however, with the manufacturer of the pH probe.

3.6.1 YSI Probes

At the time of this draft (Feb-2011), the YSI probes typically are lasting only around 1 year before they become problematic. Thus, YSI probes will likely need to be replaced on an approximately yearly basis, although some probes have been dying in 6 months or less. When a YSI probe begins having trouble, it is likely time to discard the probe and install a new probe on the meter [*note: see Users Manuals for additional steps that can be taken to try to re-condition a failing probe (pg. 94 in 556 manual & pg.2-117 in 6-series manual)*]. One or more replacement probes are typically kept in the lab within the calibration supply drawer (556 models) but probes may need to be ordered from the manufacturer or a re-supplier (e.g., Fondriest). See each users manual for detailed methods on probe replacement.

3.6.2 Quanta Probes

The Quanta pH probe typically does not need to be replaced. Instead, the Quanta pH probe has a glass bulb (cleaning necessary; see 3.1 above) and a serviceable reference sleeve. This reference sleeve needs attention when pH readings become problematic. The pH reference sleeve is the blue- or green-colored translucent cylinder situated adjacent to the glass pH bulb. The most common requirement for this reference sleeve is the replacement of the internal electrolyte solution (KCl + AgCl) and the addition of KCl tablets to maintain the KCl saturation. An indication that such replacement is needed is the low volume of particulate / crystalline KCl seen within the reference sleeve. In addition, at the end of the sleeve is a porous Teflon reference junction unit that is critical for pH measurement. If reasonable pH readings are not attained after replacement of the electrolyte and addition of KCl tablets within the reference sleeve, then the Teflon reference junction piece may need replacement. For full details on both the reference sleeve and the reference junction, see pgs. 23-24 of the Quanta users manual.

3.7 Quality Control

Original calibration records will be retained within the lab for a period no less than 5 years. These calibration records will clearly indicate the meter and/or probe being calibrated, the date and time of calibration, and the analyst conducting the calibration. Any calibration checks or validations will also be recorded and transferred to the calibration bench sheet.