Standard Operating Procedure

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

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Author: _____ 3/7/2011
Erik L. Silldorff (Aquatic Biologist) Date

Approved: _____ 3/9/2011
Thomas J. Fikslin (Branch Manager & Lab Supervisor) Date

1.0 INTRODUCTION

1.1 Purpose

To provide standardized procedures for the use and maintenance of *in situ* Dissolved Oxygen (D.O.) 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 integration for D.O. readings.

2.2 Reagents & Chemicals

2.2.1 Standard Reagents

- distilled or deionized water
- electrolyte buffer (KCl solutions that vary by manufacturer)

Distilled water will routinely be used for probe calibration. In addition, regular servicing of the D.O. membrane will be required, with use of an electrolyte buffer within and under the replacement membranes. 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 D.O. membrane replacements and servicing. Upon use, the buffer aliquots will be discarded, and buffers will be discarded upon expiration.

2.2.2 Additional Reagents for Winkler Titration

- LaMotte-brand Manganous Sulfate solution (#4167-G)
- LaMotte-brand Alkaline Potassium Iodide Azide (#7166-G)
- LaMotte-brand Sulfamic Acid Powder (#6286-H)
- LaMotte-brand Sodium Thiosulfate, 0.025 N (#4169-H)
- LaMotte-brand Starch Indicator Solution (#4170WT-G)

These five reagents will be used with the LaMotte Winkler Titration kit for field-based verifications of dissolved oxygen sensors. Upon arrival at the lab, each reagent container will be marked with the date received and, upon first opening and breaking the seal, the date first opened. Fresh reagents (i.e., unused reagents directly from the manufacturer's container) will be used for all calibrations and verifications. Reagents will be discarded following use, and any unused solutions will be discarded upon expiration. In addition, a new (unopened) bottle of Sodium Thiosulfate will be opened each quarter in which field measurements of D.O. are taken. The Certificate of Analysis for each Sodium Thiosulfate lot will be obtained from the manufacturer and kept on file for a minimum of 5 years.

2.3 Supplies

2.3.1 Standard Supplies

- D.O. membranes (see manufacturer's specifications)
- dissecting scissors

2.3.2 Additional Supplies for Winkler Titration

- LaMotte-brand 1 gram measuring spoon (#0697)
- LaMotte-brand Direct Reading Titrator (#0377; looks like a plastic syringe)
- LaMotte-brand 25 mL test tube w/ cap (#0608)
- LaMotte-brand 60 mL sample bottle (#0688-DO)

3.0 PROCEDURES

3.1 Cleaning & Maintenance

On the day preceding calibration and field work, examine the D.O. membrane for any wrinkles, bubbles below the membrane, or fouling / growth on the membrane itself. Should any of these issues be identified, replace the D.O. membrane and D.O. electrolyte according to the manufacturer's instructions. If possible, wait overnight (4-12 hrs) to allow the new D.O. membrane to set before calibration and use. If significant problems with calibration and measurement are encountered, see Section 3.6 below on possible servicing or probe replacement.

3.2 Calibration

Calibrations must be conducted every day prior to use of the Dissolved Oxygen probe. Because the oxygen readings for these meters depend on atmospheric pressure and thus elevation above sea level, it is important to calibrate the D.O. probe at or near the elevation where the probe will be used (e.g., calibrating at sea level for use at 2000 ft elevation will lead to erroneous readings). Daily calibrations will be conducted by saturating a small volume of air with distilled water and setting the equilibrium readings to 100% D.O. saturation. In addition, the D.O. readings for each meter need to be verified at least weekly during use with a field-based Winkler Titration. See each meter's users manual for specific instructions on accessing the calibration menus for that meter.

3.2.1 Daily D.O. % Saturation Calibrations

Daily D.O. calibrations will use the following step-by-step "Percent Saturation" method:

1. Rinse the D.O. probe and other sonde probes with distilled or deionized water.
2. Gently dry the D.O. membrane with a paper towel, including the seams at the O-rings.
3. Rinse the travel cup with distilled or deionized water, and place a small volume of distilled or deionized water in the bottom of the travel cup so that neither the temperature probe nor the D.O. membrane are immersed in or touching the water when the cup is placed on the sonde [*note: tap water with specific conductance less than 500 µS/cm may be used if distilled water is unavailable*]
4. Place the travel cup on the sonde in the upright position but with little or no engaging of the threads in order minimize airflow and interchange to the outside lab while maintaining a connection to the atmospheric pressure outside the cup [*note: the intent is to provide an environment around the probes that reaches 100% humidity in*

a short time (< 10 min) without sealing and pressurizing the travel cup around the probes].

5. Record the time the D.O. % Saturation set-up is completed on the calibration bench sheet, along with details of water source and set-up. Beginning no sooner than 60 seconds following set-up, start recording on the calibration bench sheet the sonde's temperature, Dissolved Oxygen (mg/L), and D.O. % Saturation along with the time of reading; make repeated readings and recordings at between 1 minute and 5 minute intervals.
6. Once D.O. % Saturation values stabilize (approximately 10 minutes), calibrate the D.O. % Saturation to 100% (*see additional specifications in each users manual on this final step*). On the calibration bench sheet, record the final D.O. % saturation value immediately before calibration, the fact that the calibration was completed, and the final D.O. % saturation value following calibration.
7. Record the current barometric pressure on the calibration bench sheet and during entry for the D.O. calibration. Barometric pressure is best measured on-site using either the hand-held display unit from the Coastal YSI (650 MDS) or the EPA YSI (556 MPS). However, barometric pressure can also be determined via translating National Weather Service sea-level readings at the nearest weather station to the proper units and the elevation at which calibrations are conducted [*see Section 5.1.3 in the Quanta users manual for details*].
8. Prepare the meter for either further calibrations or for storage and travel (see 3.5 below)

3.2.2 Weekly D.O. Winkler Titrations & Validations

Winkler titrations for determining Dissolved Oxygen concentrations (mg/L) need to be completed at a minimum of once per week for any D.O. probe being used for field measurements. Typically, these measurements will be completed in the field at a stream or river sampling site with adequate flow and where water temperature and D.O. concentrations are relatively stable over the 10-15 minutes needed for completing the Winkler titration. These weekly titrations, however, can be completed in the lab using a circulating water bath that has been allowed to reach equilibrium conditions over a minimum of 4 hours. If the Winkler titrations are completed in the field, the calibration bench sheet needs to be taken into and completed in the field, or the required information needs to recorded in field notebooks and transferred to the calibration bench sheet upon return to the lab.

For the paired water quality meter and Winkler readings, first deploy the water quality meter's sonde (with guard) into an area of the stream or river with adequate flow near the

stream bank (see 3.3.1 below). Once the meter is turned on and beginning to equilibrate, record the time of set-up for the water quality meter and begin the Winkler titration. Currently, the DRBC is using a Lamotte Winkler Titration kit (#7414) for conducting these titrations. The kit includes both detailed and simplified instructions for completing the Winkler titration. The following is a step-by-step guide for completing the titration that is based on the original instruction materials:

1. Rinse the D.O. sample bottle thoroughly using sample water. To take the sample, place the cap on the bottle, immerse the bottle fully underwater, remove the cap underwater, and allow the sample bottle to fill. Ensure that no air remains in the sample bottle, and place the cap back on the sample bottle while still underwater.
2. Back at the sample staging area, remove the cap from the sample bottle and immediately add the following reagents:
    a. 8 drops of Manganous Sulfate Solution (#4167-G)
    b. 8 drops of Alkaline Potassium Iodide Azide (7166-G)

    After adding the reagents, cap the bottle and mix the solution by inverting the sample bottle several times. Then set the bottle down and allow the precipitate to settle (minimum: all precipitate below the shoulder of the sample bottle).
3. Using the 1 gram spoon, add one level measure of Sulfamic Acid Powder (6286-H). Cap the bottle and invert the bottle repeatedly to mix and dissolve all Sulfamic Acid Powder and all precipitate. [note: the sample should be be clear yellow to orange in color as long as some dissolved oxygen]
4. Fill the titration test tube to the 20 mL line (bottom of meniscus) and replace the cap on the test tube.
5. Expel all air from Titrator (small plastic syringe), insert the Titrator into the open hole in the Sodium Thiosulfate bottle (4169-H) and then invert the Sodium Thiosulfate bottle with the Titrator sealing the hole. In this inverted position, slowly withdraw the plunger to fill the Titrator with Sodium Thiosulfate solution until the solution aligns with the 0 on the scale. If any air bubbles remain in the Titrator, expel them by re-injecting the Sodium Thiosulfate solution back into the bottle while remaining in this inverted position. Once the Titrator is filled to the 0 line without any entrained air bubbles, turn the bottle upright and remove the Titrator.
6. Observe the sample solution within the test tube; if already a very pale yellow, skip ahead to step 8 (addition of Starch Indicator).
7. Insert the tip of the Titrator into the test tube cap and begin to slowly titrate the Sodium Thiosulfate solution into the fixed sample solution within the test tube. Continue titrating until the original yellow-brown color changes to a very pale yellow color, gently swirling the test tube between drops to mix the contents.

8. Carefully remove the Titrator (*do not disturb the Titrator plunger!*) and test tube cap, and then add 8 drops of Starch Indicator Solution (4170WT-G) to the test tube, swirling the test tube to evenly distribute the blue color.
9. Replace the test tube cap and Titrator onto the test tube, and continue the titration and mixing via gentle swirling of the test tube after each Sodium Thiosulfate drop. Continue adding Sodium Thiosulfate drop-by-drop until the blue color completely disappears upon mixing and fails to return. [*note: if the D.O. concentration is greater than 10 mg/L, the Titrator will need to refilled and steps 5, 6, 7, and 9 repeated to reach the clear color endpoint*]
10. Record the final Winkler titration test result by directly reading the D.O. concentration from the scale on the Titrator [*note: if a second Titrator was needed, remember to add 10 mg/L to the reading on the scale*]. The test result, the time of titration, and the simultaneous water quality meter readings (water temperature, D.O. concentration, D.O. % saturation) need to be recorded.
11. Discard the sample and the Sodium Thiosulfate remaining within the Titrator. Carefully rinse the sample bottle and the test tube and return them to the kit.

3.3 Measurement Procedures

3.3.1 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 Dissolved Oxygen readings. From 60 seconds onward, observe the D.O. readings and record an initial D.O. reading and the time of measurement when pH values stabilize (e.g., no change more than 0.05 mg/L 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.

3.3.2 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 Dissolved Oxygen 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 D.O. readings and record an initial D.O. reading and the time of measurement at the point when D.O. values stabilize (e.g., no change more than 0.05 mg/L 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*].

3.3.3 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 Dissolved Oxygen 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 D.O. readings and record an initial D.O. reading and the time of measurement at the point when D.O. values stabilize (e.g., no change more than 0.05 mg/L 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.

3.3.4 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 Dissolved Oxygen 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 D.O. readings and record an initial D.O. reading and the time of measurement at the point when D.O. values stabilize (e.g., no change more than 0.05 mg/L 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.

3.4 Storage

Except when no other sanitary water is available, distilled or deionized water should ***not*** be used for storage of Dissolved Oxygen 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-term 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.

3.5 Probe Replacement

Most Dissolved Oxygen issues can be resolved by replacing the D.O. membrane and sensor electrolyte (see Section 3.1). The anode and cathode within the sensor and beneath the membrane can also become fouled from use and by exposure to varying materials. If the anode or cathode beneath the membrane look discolored or fouled in any way, and erratic D.O. behavior cannot be resolved by membrane replacement, consider

servicing the D.O. components before replacing the D.O. probe entirely. Details on in-lab and professional servicing of the D.O. sensors can be found in the users manuals for each instrument. If these more comprehensive attempts to rectify the D.O. probe are unsuccessful, however, the D.O. probe may need replacement (an infrequent requirement). Contact the manufacturer for part and/or servicing options for each meter.

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.