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Massachusetts Water Watch Partnership

Standard Operating Procedure Lakes-4

For Dissolved Oxygen

Revision 0

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Overview

This procedure describes how to collect a lake grab sample for dissolved oxygen and how to fix the sample for transportation. Also included is the analytical determination of dissolved oxygen in the laboratory using a digital titrator.

1.0 Field Equipment List

___ Modified Wisconsin Sampler with 60 ml Dissolved Oxygen bottle inside

___ Calibrated line

___ Thermometer (depth-electronic or manual)

___ D.O. chemicals - Powder pillows #1, #2, and #3

___ Scissors

___ Field data sheet and pencils

___ Marble

___ Cooler

___ Ice

___ Frozen koolits

___ Zip-loc bags (1 gallon size)

2.0 Sampling Protocol

2.1 Check your data sheet for the depth of water at the sampling site. Subtract 0.4 meters (two marks on the calibrated line) from this depth. This will be the depth to collect the dissolved oxygen sample.

2.2 Lower Wisconsin sampling bottle to desired depth. Check that no bubbles are coming from the sampler.

2.3 Give a short, sharp yank on the lowering line to pull intake and outlet plugs. Wait until all bubbles disappear at the surface. It takes about 90 seconds for the bottle to fill).

2.4 Retrieve bottle.

3.0 Fixing the Sample

3.1 The following is best done by two persons: Volunteer 1 carefully unscrews and removes sampler top to avoid spilling any water, then extracts D.O. bottle from sampler.

3.2 Volunteer 2 places the thermometer in the Wisconsin sampling bottle (not in the D.O. bottle).

3.3 Volunteer 1 holds D.O. bottle and cap.

3.4 Volunteer 2 pours D.O. reagent #1 (manganous sulfate) into D.O. bottle; then pours reagent #2 (alkaline iodide-azide) into the D.O. bottle. Do not be concerned if a small amount of water overflows the bottle, but do be careful not to introduce any bubbles.

3.5 Volunteer 1 carefully caps bottle to avoid trapping air bubbles inside (the cap is shaped like a cone to minimize this; holding the cap 1" above the lip, let go of the cap so it drops neatly inside the bottle).

3.6 Holding the D.O. bottle and with index finger on the cap to prevent its dislodging, Volunteer 1 inverts bottle 50 times (or until reagents dissolve) with a motion like turning a doorknob clockwise and counterclockwise in succession.

3.7 Allow bottle to sit for 5 minutes. A brownish flocculent material should accumulate on the bottom. [If the floc never settles, proceed with next step but make a note on field sheet that sample should be flagged.]

3.8 Meanwhile, Volunteer 2 removes thermometer from Wisconsin sampler, reads the temperature and notes it on the field data sheet.

3.9 Volunteer 1 carefully removes cap of D.O. bottle by twisting slightly and lifting.

3.10 Volunteer 2 pours reagent #3 (sulfamic acid) into bottle.

3.11 Carefully drop marble into bottle. (This step is optional and is meant to avoid air bubbles when you cap the bottle.)

3.12 Carefully drop the cap in the bottle again and repeat bottle inversion process. The liquid will turn a yellow color: the stronger the color, the more dissolved oxygen.

3.13 On lake field sheet, record sample ID, depth of sampling, and write ‘DO’ in Chemistry column.

4.0 Transporting the Sample

4.1 The process you have just completed has "fixed" the dissolved oxygen as a reasonably stable compound.

4.2 Store in the cooler for delivery to the lab.

4.3 If you cannot put ice directly in your cooler because you store other materials in there, use a gallon-size zip-loc bag filled with ice. Put your sample in that zip-loc

bag, zip shut and place in cooler with koolit.

4.4 Deliver to lab within 8 hours of collection.

5.0 Lab Equipment List[1]

___ Hach digital titrator

___ Hach sodium thiosulfate (0.2 N) titration cartridge with clean delivery tube

___ Starch indicator solution with drop dispenser

___ Clean 60 ml BOD bottle for QC sample

___ Fixed lake water samples

___ Graduated cylinders, 100 and 50 ml

___ Erlenmeyer flask or beaker, 100 ml

___ Distilled water

___ Magnetic stirrer and stirring bar (optional)

___ Lab sheet and pencils

___ Safety goggles and gloves

6.0 Quality Control Protocol using EAL[2] QC sample

To obtain a QC sample from UMass-EAL, call the EAL Director at 413.545.2936

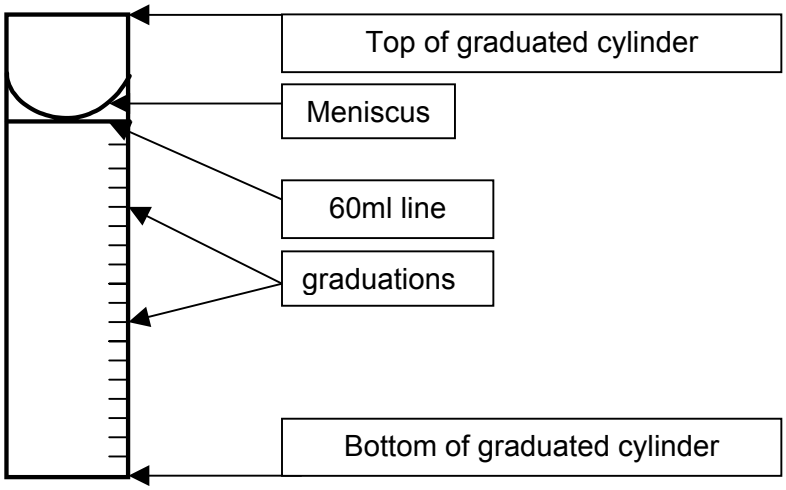
6.1 Remove QC sample from refrigerator, warm to room temperature before testing.

6.2 Rinse out a 100 milliliter graduated cylinder 3 times with distilled water.

6.3 Pour a few mls of the QC sample into it, swirling it around the cylinder, then pouring it down the drain.

[1] Inclusion of the trade manes does not constitute endorsement by the MA Water Watch Partnership, the University of Massachusetts, or the Commonwealth of Massachusetts not does it imply a comprehensive list of providers.
[2] EAL: University of Massachusetts Environmental Analysis Lab. QC samples may also be purchased from commercial laboratories

6.4 Measure 60 ml of the QC sample in the 100 ml graduated cylinder. When you measure a liquid quantity in a cylindrical container, a "meniscus", (a shallow U shape) forms on the liquid's surface. The bottom of the U should rest on the 60 ml line.



6.5 Pour the sample into a clean 60 ml BOD bottle.

6.6 Slowly empty the contents of an **alkaline iodide-azide** powder pillow (pillow # 2) into the bottle. (You don't use pillow # 1 in this QC test). Cap bottle so there is no air bubble, then invert several times. Let the solution settle, then invert several times again.

6.7 Empty the contents of a **sulfamic acid** powder pillow (pillow # 3) into the bottle. Swirl this around until the reagent is dissolved. The solution should turn yellow. This fixed sample is now ready to titrate.

7.0 Dissolved Oxygen Titration Protocol

7.1 Notes:

7.1.1 This method is valid for fixed QC samples and fixed lake samples.

7.1.2 Make sure you will use chemicals before their expiration date.

7.1.3 Always wear safety goggles. Rubber gloves are a good idea to avoid skin contact with chemicals.

7.2 Insert a **clean** delivery tube into a 0.2N sodium thiosulfate cartridge.

7.3 Attach the cartridge to the titrator body.

7.4 Over a sink, hold the titrator with the cartridge pointing straight up so any bubbles will drift to the top of the cartridge. Turn the delivery knob to eject air and a few

drops of titrant - until there are no more bubbles present in the delivery tube or the cartridge.

7.5 Gently rinse the delivery tube off with distilled water. Do not try to flick the rinse water off the tube!

7.6 Reset the digit counter to 0.

7.7 Rinse a clean 50 ml graduated cylinder with some of your sample from the 60 ml BOD bottle.

7.8 Carefully measure exactly 50 ml of the sample in the graduated cylinder.

7.9 Rinse a 100 ml erlenmeyer flask or beaker with distilled or deionized water.

7.10 Transfer sample from graduated cylinder to flask or beaker. Place the flask on a white surface because you will need to observe a color change.

7.11 Place the delivery tube tip into the solution and swirl gently the flask (or use a magnetic stirrer and stir bar) while turning the delivery knob. Carefully continue titrating until your sample turns a pale yellow color. If the sample abruptly turns clear, you've gone past the endpoint and selected the wrong sodium thiosulfate or sample size. Re-titrate using a larger sample volume or lower strength sodium thiosulfate.

7.12 Add a few drops of starch indicator solution and swirl to mix. This will turn your field sample dark blue.

7.13 Continue to titrate and swirl your sample, adding about 5 to 10 digits every few seconds. As the color turns to light blue, slow down, adding about 2 digits every few seconds until the blue just disappears.

7.14 Record the number of digits, but then continue titrating by adding one more digit as you look carefully for a blue swirl. Keep doing this every few seconds, one digit at a time until your last digit causes no visible change. Record the previous digit as the correct amount.

7.15 Calculate mg/l of DO: DO = Digits Required x 0.04.
For example, if you saw a change at 194 digits, but none at 195, write down 194 as the units of titrant used and calculate as follows:
194 x 0.04 = 7.76mg/l DO or 7.76 parts per million

7.16 Record your result on the lab data sheet immediately.

8.0 Troubleshooting

8.1 Some brown particles may remain when the sample is ready for titration. This can cause variable results because the chemicals in the sample are now unevenly concentrated.

TO AVOID THIS: Carefully observe the BOD bottle after adding all three reagents. If particles are visible, or if there is a deposit on the bottom of the bottle, try shaking the bottle to dissolve any remaining solid matter. If this doesn't work, use a plastic, teflon, stainless steel or glass stirring rod or spatula to stir up the bottom sediments. This should allow the acid in the solution to fully dissolve the particles.

NOTE: Make sure you rinse the stirring rod well after trying this, to avoid corrosion of your utensil.

In case you are still unable to fully dissolve the particles, proceed with the analysis but flag the results on the lab data sheet.

8.2 If your results seem wildly inaccurate, check to see you are using the sodium thiosulfate cartridge. Some folks have been known to use a sulfuric acid cartridge by mistake (that cartridge is used for pH and alkalinity analysis).

8.3 If you have titrated a quality control sample received from UMass and your value seems very high (remember, DO almost never goes above 14 mg/l in natural settings), it may be because you added powder pillow #1 to the sample before titrating. The QC test only uses pillows # 2 and # 3.

8.4 If your result is too high, you may have air bubbles in the cartridge: to avoid bubbles, advance the plunger manually or with the delivery knob until titrant is forced out of the delivery tip and the delivery tube is filled with solution. Do this as you would a hypodermic syringe, with the delivery tip nearly straight up to remove all bubbles.

8.5 Sometimes an old cartridge can give an inaccurate reading, particularly if it has been left uncapped and allowed to evaporate somewhat. If you suspect the cartridge, try using a new one.

9.0 Figuring Percent Saturation of Dissolved Oxygen

9.1 Water can hold a limited amount of dissolved oxygen. When it holds the maximum amount it can, a water body is said to be at saturation, or 100% saturated. The dissolved oxygen (in mg/l) of water at saturation changes with temperature: the higher the temperature, the less oxygen water holds. Massachusetts Surface Water Quality Standards express minimum criteria for dissolved oxygen in both mg/l and % saturation. To calculate % saturation of the sample, you divide the measured dissolved oxygen content of your sample by

the maximum oxygen content at the temperature of your sample. The maximum oxygen content of water at various temperatures is given in Table 1 below.

9.2 $\frac{\text{Your DO Measurement}}{\text{Max. DO Concentration at Your Measured Temperature}}$ = % DO Saturation

For example, if you measured a DO concentration of 5 mg/l at 20°C (lake temperature) you would divide 5 mg/l by 9.1, the maximum concentration at 20° C. The percent saturation would be 55%.

Table 1. Saturation Dissolved Oxygen Concentration according to temperature

Temp °C	DO(mg/l)	Temp °C	DO(mg/l)	Temp °C	DO(mg/l)	Temp °C	DO(mg/l)
0	14.6	9.5	11.4	19	9.3	28.5	7.7
0.5	14.4	10	11.3	19.5	9.2	29	7.7
1	14.2	10.5	11.1	20	9.1	29.5	7.6
1.5	14.0	11	11.0	20.5	9.0	30	7.5
2	13.8	11.5	10.9	21	8.9	30.5	7.5
2.5	13.6	12	10.8	21.5	8.8	31	7.4
3	13.4	12.5	10.6	12	8.7	31.5	7.3
3.5	13.3	13	10.5	22.5	8.6	32	7.3
4	13.1	13.5	10.4	23	8.6	32.5	7.2
4.5	12.9	14	10.3	23.5	8.5	33	7.2
5	12.7	14.5	10.2	24	8.4	33.5	7.1
5.5	12.6	15	10.1	24.5	8.3	34	7.0
6	12.4	15.5	10.0	25	8.2	34.5	7.0
6.5	12.3	16	9.8	25.5	8.2	35	6.9
7	12.1	16.5	9.7	26	8.1	35.5	6.9
7.5	12.0	17	9.6	26.5	8.0	36	6.8
8	11.8	17.5	9.5	27	7.9	36.5	6.8
8.5	11.7	18	9.4	27.5	7.9	37	6.7
9	11.5	18.5	9.3	28	7.8	37.5	6.7