



Massachusetts Water Watch Partnership

Standard Operating Procedure Rivers-2 For Dissolved Oxygen Revision 0

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Overview

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

1.0 Field Equipment List

- ___ 2 standardized, alcohol-filled thermometers
- ___ BOD bottles, 300 ml (1 per sample, take an extra in case of breakage)
- ___ Fresh Manganous Sulfate Powder pillows (pillow # 1) (1 per sample)
- ___ Fresh Alkaline Iodide-Azide Powder Pillows (pillow # 2) (1 per sample)
- ___ Fresh Sulfamic Acid Powder Pillows (pillow # 3) (1 per sample)
- ___ Fingernail clippers or scissors for cutting powder pillows
- ___ Eye dropper for topping off BOD bottle, if necessary
- ___ Marble (optional)
- ___ Field Sheets & pencils
- ___ Rubber gloves
- ___ Safety goggles
- ___ Cooler
- ___ Ice
- ___ Watch
- ___ Boots
- ___ Zip-loc bags (1 gallon size)

2.0 Sampling Protocol

ALWAYS TAKE TEMPERATURE AT SAME TIME YOU COLLECT DO SAMPLE for calculating % saturation later. See Protocol R-1.

Note: It is a good idea to wear safety goggles and rubber gloves during this procedure to avoid harmful contact with the chemicals.

- 2.1 Sample bottle:** use a 300 ml BOD sample bottle. For DO samples, an extension pole is not feasible.

- 2.2 Water depth at site:** The water must be deeper than the sample bottle and free of surface scum and debris. If the water is not deep enough at your regular sampling site, look for another location nearby which is equally representative of the site but deeper. If there is none, do not collect a sample and indicate on your field sheet that water level is too low.
- 2.3 Wading into stream:** Carefully wade into the stream, walking upstream and avoiding to stir up bottom sediments. Samples should be collected from relatively calm but flowing water, not in nor immediately downstream from a riffle. Stand so that you are facing one of the banks. Wait for pre-disturbance (from wading in) conditions to return before taking sample. If you are in a canoe, have your partner steady it and face one of the banks. Note that sampling from the streambank is discouraged, as it can result in non-representative samples.
- 2.4 Taking the sample:** Collect the sample so that you are not standing or floating upstream of the bottle. Remove the stopper of the BOD bottle. Point BOD bottle downstream and slowly lower it into the water until the lip is just submerged. Allow the water to fill the bottle very gradually, avoiding any turbulence or air bubbles (this will add oxygen to the sample and skew your results). Submerge completely and allow to overflow to ensure that air bubbles are not trapped in the sample or gently tap the bottle to allow bubbles to escape.
- 2.5 Cap the bottle:** Holding the bottle vertically, remove it from the river, leaving water around the cap at the flared mouth of the bottle. Cap the bottle by dropping the stopper directly into the bottle neck from 1/4 inch above. Check to make sure there are no air bubbles or space left at the top. If there are, you need to start over. Take your eyedropper and fill it with water from the stream. Go to the stream bank for step 2.6.
- 2.6 Fix the sample:** If there are no air bubbles present in the bottle, "fix" the sample immediately as described below:
- 2.6.1** Remove the stopper and add the contents of one Manganous Sulfate powder pillow (#1) and one Alkaline Iodide-Azide powder pillow (#2) to the 300 ml sample, using scissors or clippers to open packages. HINT: You may need to "roll" the pillow gently between your fingers to ensure delivery of all the powdered reagent into the sample bottle. Residual reagent powder around bottle neck can be washed into the bottle by swirling bottle gently.
- 2.6.2** Immediately insert the stopper so air is not trapped in the bottle. Holding the stopper in place, invert the bottle vigorously 50 times or until all reagents are dissolved. An orange-brown flocculent precipitate will form if oxygen is present.
- 2.6.3** Allow sample to sit undisturbed and wait until the flocculent in the solution has settled to the bottom half of the bottle. Have patience, this may take some time.
- 2.6.4** Remove the stopper and add the contents of one Sulfamic Acid powder pillow (#3). Immediately insert the stopper so air is not trapped and invert

several times to mix. The floc will dissolve and leave a yellow color if oxygen is present. HINT: If you have trouble avoiding introducing an air bubble in the sample at this step, put a marble in the sample bottle after adding pillow #3.

The oxygen in the sample is now "fixed" and ready to be transported to the laboratory for analysis.

- 2.7 Prepare bottle for transport:** Cap the bottle and seal by pouring a small amount of water into the flared lip area with the eyedropper of river water you collected in step 2.5.
- 2.8 Complete field data sheet:** Write the site # on the sample bottle, if it was not already done for you. Fill out the river field sheet completely and immediately. If air bubbles are noticed later (prior to lab titration), note it on the field sheet.
- 2.9 Trash:** Put all trash you have generated (pillow cases, broken bottles if any) in a zip-loc bag and take it back with you.

3.0 Troubleshooting

- 3.1 Air bubbles:** Air bubbles may get trapped in the bottle under the glass stopper. This is most likely to happen after pillows #1 and #2 have been added and the bottle has been inverted. Inverting the bottle may spill any water residing in the neck of the bottle.

TO FIX THIS: Ideally, learn how to drop the stopper from 1/4 inch above the bottle directly into the neck. This will form an airless seal. An alternative is to use an eyedropper filled with stream water from your site. After adding pillow #3 (sulfamic acid), dribble a bit of water into the bottle. This has the added advantage of rinsing into the solution any particles clinging to the bottle neck. Alternatively, drop a marble in the sample when you add pillow #3.

- 3.2 No floc settling:** There have been instances when no amount of waiting results in floc settling after adding the first two reagents. In that case, add pillow #3 anyway, but make a note on the field data sheet that the sampled should be flagged and why.

4.0 Transporting the Sample

- 4.1** Store the bottle upright in your cooler with ice.
- 4.2** 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 frozen koolit.

4.3 Deliver sample to the lab within 8 hours of collection.

5.0 Tips for volunteer coordinator

5.1 **Bottle exchange:** Some groups maintain a complete extra set of bottles, so volunteers can collect next month's bottles as they drop off their samples at the lab. If you follow this procedure, make sure your bottles are kept in Zip-loc bags and boxed, or in some other clean and secure container.

5.2 **Chemicals expiration:** Also make sure at the start of the season that the reagents supplied to samplers will not be used past their expiration date.

6.0 Lab Equipment List¹

- ___ Hach digital titrator
- ___ Hach sodium thiosulfate (0.2 N) titration cartridge with clean delivery tube
- ___ Starch indicator solution with drop dispenser
- ___ Clean 300 ml BOD bottle for QC sample
- ___ Fixed river water samples
- ___ Graduated cylinders, 100 and 500 ml
- ___ Erlenmeyer flask or beaker, 250 ml
- ___ Magnetic stirrer and stirring bar (optional)
- ___ Lab sheet and pencils
- ___ Safety goggles and gloves

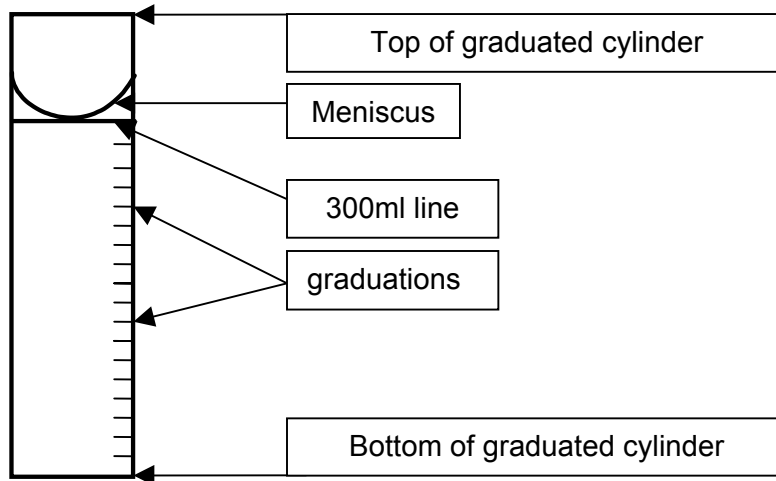
7.0 Quality Control Procedure using EAL² QC sample

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

¹ Inclusion of the trade names does not constitute endorsement by the MA Water Watch Partnership, the University of Massachusetts, or the Commonwealth of Massachusetts nor 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

- 7.1 Remove QC sample from refrigerator, warm to room temperature before testing.
- 7.2 Rinse out a 500 milliliter graduated cylinder by pouring a few mls of the QC sample into it, swirling it around the cylinder, then pouring it down the drain.
- 7.3 Carefully measure exactly 300 ml of the QC sample in the 500 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 300 ml line.



- 7.4 Pour the sample into a clean 300 ml BOD bottle.
- 7.5 Slowly empty the contents of an **alkaline iodide-azide** powder pillow (#2) into the bottle. (You don't use powder 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.
- 7.6 Empty the contents of a **sulfamic acid** powder 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. Since this will be a 100 ml sample, use the 0.2 N sodium thiosulfate cartridge.

8.0 Dissolved Oxygen Titration

8.1 Notes:

- 8.1.1 This method is valid for fixed QC samples and fixed river samples.
- 8.1.2 Make sure you will use chemicals before their expiration date.
- 8.1.3 Always wear safety goggles. Rubber gloves are a good idea to avoid skin contact with chemicals.

- 8.2 Insert a clean delivery tube into a 0.2N sodium thiosulfate cartridge.
- 8.3 Attach the cartridge to the titrator body.
- 8.4 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.
- 8.5 Gently rinse the delivery tube off with distilled water. Do not try to flick the rinse water off the tube!
- 8.6 Reset the digit counter to 0.
- 8.7 Rinse a 100 ml graduated cylinder with some of your sample from the 300 ml BOD bottle.
- 8.8 Measure 100 ml of the sample in the graduated cylinder.
- 8.9 Rinse a 250 ml erlenmeyer flask or beaker with distilled or deionized water.
- 8.10 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.
- 8.11 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.
- 8.12 Add a few drops of starch Indicator solution and swirl to mix. This will turn your sample dark blue.
- 8.13 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.
- 8.14 Record the number of digits on your lab sheet, 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.
- 8.15 Calculate mg/l of DO: $DO = \text{Digits Required} \times 0.02$.
- 8.16 Record your result on the lab sheet immediately.

9.0 Troubleshooting

- 9.1 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.

- 9.2 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).
- 9.3 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.
- 9.4 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.
- 9.5 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.

10.0 Figuring Percent Saturation of Dissolved Oxygen

- 10.1 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.

10.2
$$\frac{\text{Your DO Measurement}}{\text{Max. DO Concentration at Your Measured Temperature}} = \% \text{ DO Saturation}$$

For example, if you measured a DO concentration of 5 mg/l at 20°C (river 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	22	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