

6. DISSOLVED OXYGEN MONITORING:

Using the Titration Method

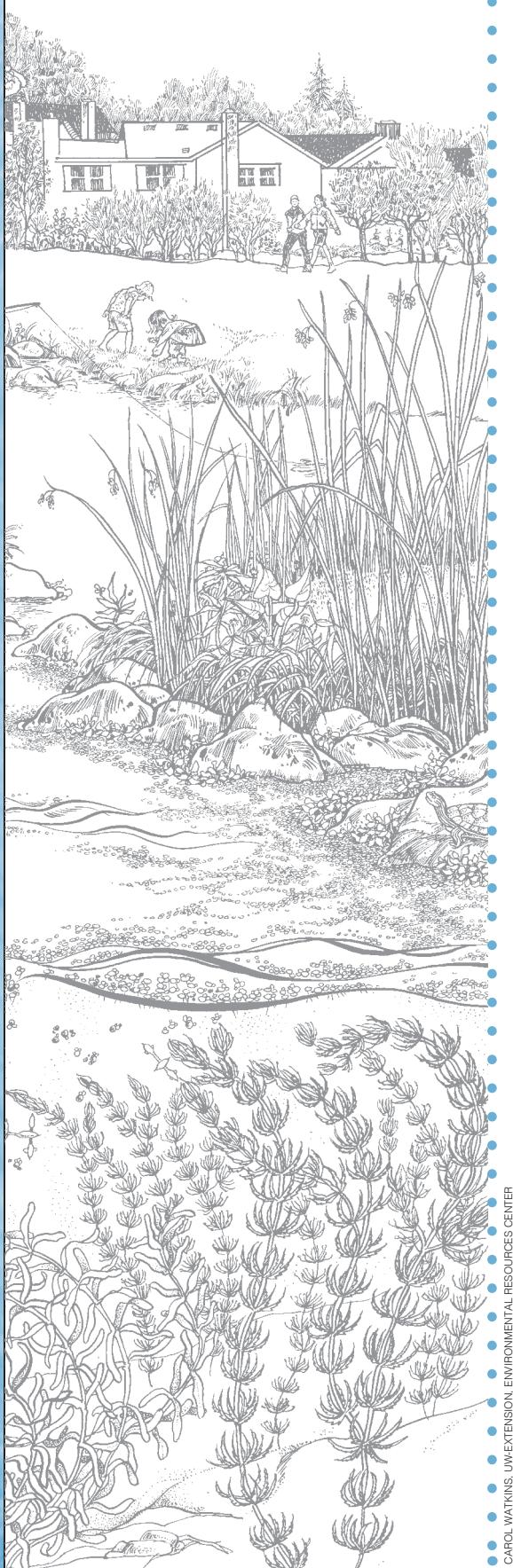
Before you start sampling, be sure to read the following pages to familiarize yourself with the equipment and the procedures that you will be using. All of the procedures that you will follow in sampling your lake are done for specific reasons. It is very important that you follow the sampling procedures exactly as they are laid out in the following pages to ensure good, consistent, high quality data. The following pages will provide you with sufficient background on the design of the equipment and proper procedures to use.



Please remember to keep all sampling equipment and chemicals out of the reach of children. Many of the chemicals you will be using are hazardous (see Appendix 1). After sampling, it is very important to rinse and thoroughly air dry all of the equipment that you used. As always keep paperwork and envelopes separate from equipment.

What Equipment Will You Need?

- At your training session, your CLMN regional coordinator will outline and provide all of the equipment that you will need to successfully monitor your lake.
 - Manual
 - Lake map with sampling sites marked
 - Life jackets (you provide)
 - Anchor and rope (you provide)
 - Field data sheets
 - Van Dorn sampling bottle
 - Safety gloves
 - Safety goggles
 - Chemicals and equipment in the LaMotte® titration kit (**note:** all chemicals should be replaced every year): manganese sulfate, alkaline potassium iodide azide, sulfuric acid, sodium thiosulfate, starch indicator solution, syringe, 25-ml graduated cylinder, eye dropper, dissolved oxygen sample bottles (labeled with appropriate depths) and rack, glass vial with plastic lid.



How Do You Prepare to Sample?

The Day You Sample

On the day you plan to sample, complete the top portion of your field data sheet by filling in the Waterbody # (or WBIC) and Station #. If you do not know what these numbers are contact your CLMN regional coordinator. If you are using the LaMotte® titration kit to measure dissolved oxygen, mark the bottles with appropriate pre-determined depths. Check to make sure all of your chemicals are fresh (they need to be replaced every year). Check your Van Dorn sampling bottle to make sure it is working properly. Once this is done, you can begin to load all of your sampling equipment into the boat. Before you launch, make sure you have an anchor, sufficient gas, and personal flotation devices in your boat.

Sampling Overview

Winkler Titration Method (LaMotte® Dissolved Oxygen Kit)

Sampling the dissolved oxygen in your lake can be tricky since oxygen in the air can easily contaminate your water sample. To create your dissolved oxygen profile, you will collect water samples at specified depths and measure the oxygen content of the water. Since you have no alternative but to bring your samples to the surface to measure the oxygen, you must take precautions to ensure that your samples do not get contaminated. When filling your collection bottles with your water samples, make sure that you allow the bottle to overflow at least 2 seconds before quickly capping the bottle. This will make certain that no air will get trapped in the bottle and contaminate your sample.

The LaMotte® kit uses the Winkler titration method for determining dissolved oxygen. With this method, reagents react with chemicals in your water sample causing a color change. The amount of reagent needed to create this color change helps you determine what your dissolved oxygen reading is. Use of the Van Dorn sampling bot-

tle is necessary for determining your dissolved oxygen profile since it retrieves water samples from the desired depth to be tested.

NOTE: If you are collecting water samples using a Van Dorn sampling bottle, see page 39. You must use a Van Dorn sampling bottle to collect samples for dissolved oxygen analysis.

ON LAKE PROCEDURES

Winkler Titration Method (LaMotte® Dissolved Oxygen Kit)

STEP 1. Your regional coordinator will assign to you 5 to 10 depths at which you should sample for dissolved oxygen and will help you mark your sample bottles accordingly. These depths will be the same as the ones you measure for water temperature.

STEP 2. Use the Van Dorn sampling bottle to collect samples at your pre-determined depths.

STEP 3. Remove the cap of the appropriate dissolved oxygen sample bottle. Place cap topside down to avoid contamination.

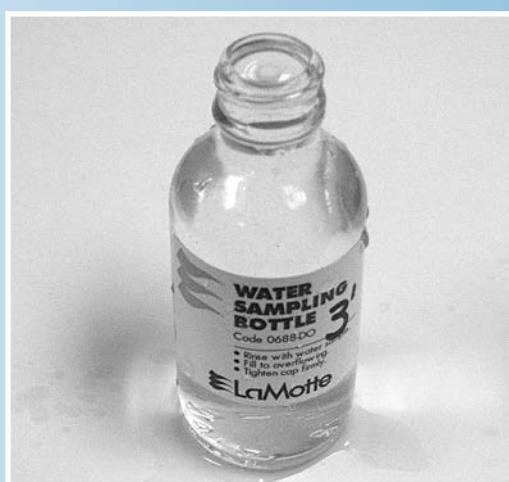
STEP 4. If you did not already record a temperature profile of your lake using a digital probe, now is the time to record the water temperature using the thermometer in the Van Dorn sampling bottle. After recording the water temperature of your first sample, let out a small amount of water from the sampler to rinse out the rubber tube. Then insert the rubber tube all the way to the bottom of your sample bottle. Open the hose clamp, release the vacuum and allow the water you collected to flow into your sample bottle overfilling the bottle for at least 2 seconds.



STEP 5. While the water is still flowing, slowly remove the tube allowing your sample bottle to overfill. Water will actually appear above the top of the bottle.

STEP 6. Quickly cap your sample bottle. There is a nipple in the cap. This nipple will displace water in the bottle making room for you to add chemicals for your analysis.

STEP 7. Put on your gloves and safety goggles.



DNR PHOTOS

ON LAKE PROCEDURES

Winkler Titration Method (LaMotte® Dissolved Oxygen Kit) (continued)

STEP 8. Remove the cap from the sample bottle you just filled with lake water and add eight drops of the manganous sulfate solution from the squeeze bottle. Make sure to hold the squeeze bottle completely vertical (i.e. not at an angle) for consistent drop size and to avoid splatter.

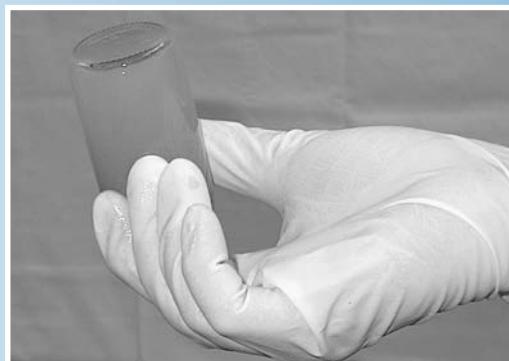
Note: Place cap topside down to avoid contamination.



STEP 9. Then add eight drops of the alkaline potassium iodide azide solution. Once again, make sure to hold the squeeze bottle completely vertical (i.e. not at an angle) for consistent drop size and to avoid splattering.



STEP 10. Cap your dissolved oxygen bottle and mix your sample by inverting the bottle 10 to 20 times. Put the bottle in the sample tray and allow the precipitate (e.g. the solid substance that is forming in your bottle due to a chemical reaction) to settle. This process may take a few minutes.



DNR PHOTOS

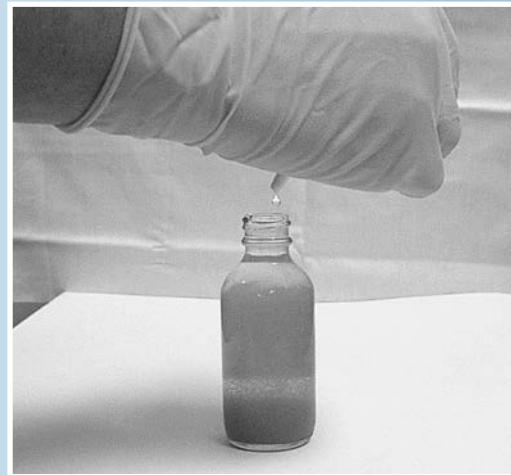
ON LAKE PROCEDURES

Winkler Titration Method (LaMotte® Dissolved Oxygen Kit) (continued)

STEP 11. Once the precipitate has settled, re-mix your sample by inverting the sample bottle another 10 to 20 times. Put the bottle in the sample tray and allow the precipitate to settle again.



STEP 12. Once the precipitate has settled for a second time, add eight drops of sulfuric acid (H_2SO_4) from the squeeze bottle. Cap your sample bottle and invert to mix. Continue mixing the bottle for several minutes until all the precipitate has dissolved. The sample is now "fixed", meaning that the dissolved oxygen concentration cannot change.



DNR PHOTOS

STEP 13. Repeat steps 1-12 for each pre-determined depth that you are collecting a water sample.



NOTE: Your fixed D.O. sample will retain its dissolved oxygen level for up to 8 hours if the sample is refrigerated and kept in the dark. However, for best results, the sample should be titrated as soon as you return to shore.

Before you continue processing your dissolved oxygen samples, be sure to read the following pages to familiarize yourself with the equipment and the procedures that you will be using. All of the procedures that you will follow in sampling your lake are done for specific reasons. It is very important that you follow the sampling procedures exactly as they are laid out in the following pages to ensure good, consistent, high quality data. The following pages will provide you with sufficient background on the design of the equipment and proper procedures to use.



- **MENISCUS** • The curved upper surface of a still liquid in a tube caused by surface tension; concave if the liquid wets the walls of the container, convex if it does not.

ON SHORE PROCEDURES

Winkler Titration Analysis (LaMotte® Dissolved Oxygen Kit)

Before you begin analyzing your samples on shore, here is a quick checklist to make sure that you have everything you will need.

- Manual
 - Field Data Sheets
 - Pencil
 - Safety gloves
 - Safety goggles
 - LaMotte® titration kit

Note: All chemicals should be replaced every year.

Set up your LaMotte® dissolved oxygen kit in a place that has plenty of room and is convenient place to work. You should have already added eight drops of the manganese sulfate solution and eight drops of the alkaline potassium iodide azide solution to each of you samples in the field.



NOTE: If you did not "fix" your samples in the field (as outlined in step 12 on page 65), **make sure that you do it now** by adding the eight drops of sulfuric acid (H_2SO_4) to each of the dissolved oxygen samples you took. Invert the bottles enough to mix the acid and dissolve the precipitate.

ON SHORE PROCEDURES

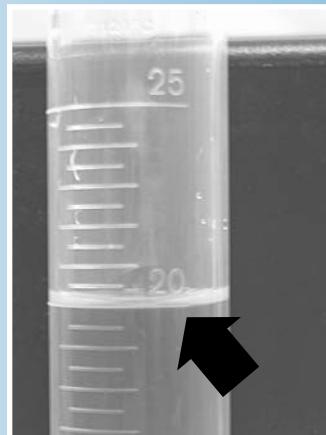
Winkler Titration Analysis (LaMotte® Dissolved Oxygen Kit)

STEP 1. Rinse the 25 ml graduated cylinder and the small glass vial with the center-hole plastic lid with distilled water.



STEP 2. Take out your first "fixed" dissolved oxygen sample. Uncap your sample bottle and fill the graduated cylinder with 20 ml of your "fixed" sample.

Due to the adhesive nature of water molecules, when you look at the water level from the side, the liquid in the graduated cylinder will not be flat. Instead the liquid will sag downward. This curved surface is called the meniscus. Always read from the bottom of the meniscus when measuring the volume of liquid that you want. In this case you want the bottom of the meniscus to line up with the 20 ml mark on the graduated cylinder.



STEP 3. Pour the 20 ml sample that you just measured from the graduated cylinder into the small glass vial. Cap the glass vial with the center-hole plastic lid. Please note that even though the glass vial may have volume measurement markings on it, the graduated cylinder is a more accurate measure of volume than pouring your "fixed" sample directly into the small glass vial.



STEP 4. Insert the tip of the syringe into the sodium thiosulfate solution. Turn the bottle and syringe upside down and slowly draw the solution into the syringe past the line marked "0". Remove any air trapped in the syringe by pushing liquid back into the bottle until the bubbles are expelled. You may need to tap the syringe while it is upside down to move the bubbles towards the tip. Remove the syringe. Store the sodium thiosulfate solution in a cool, dry place.

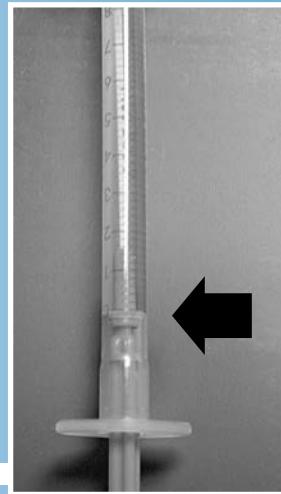


DNR PHOTOS

ON SHORE PROCEDURES

Winkler Titration Analysis (LaMotte® Dissolved Oxygen Kit) (continued)

STEP 5. Pushing the plunger of the syringe and expelling any extra solution onto the ground, match up the top of the plunger with the line on the syringe marked "0" (see "Reading the Syringe" on page 71).



STEP 6. Insert the syringe into the hole in the cap of your glass vial containing your "fixed" sample. Very slowly, add the sodium thiosulfate solution drop by drop by pushing on the plunger of the syringe. Gently swirl your sample after each drop. It is possible to add as little as 0.1 units (half the distance between the lines on the syringe) with each addition.



STEP 7. Add the sodium thiosulfate solution until the color of your water sample has changed to a very faint straw yellow. To clearly see the color, it may be helpful to hold a sheet of white paper behind your sample vial after each addition. The exact color is not that important. The object is to add drops to lighten the color, but to stop before the sample becomes clear. The amount of sodium thiosulfate that you add will vary between your samples depending on the amount of dissolved oxygen that is in each sample.

Note: If the dissolved oxygen content of your sample is very high, it may not become a faint yellow color even after you have added the entire contents of the syringe! In this case, you will need to refill the syringe with the sodium thiosulfate solution by repeating steps 4 and 5. Make sure you note this on your data sheet!



DNR PHOTOS

ON SHORE PROCEDURES

Winkler Titration Analysis (LaMotte® Dissolved Oxygen Kit) (continued)

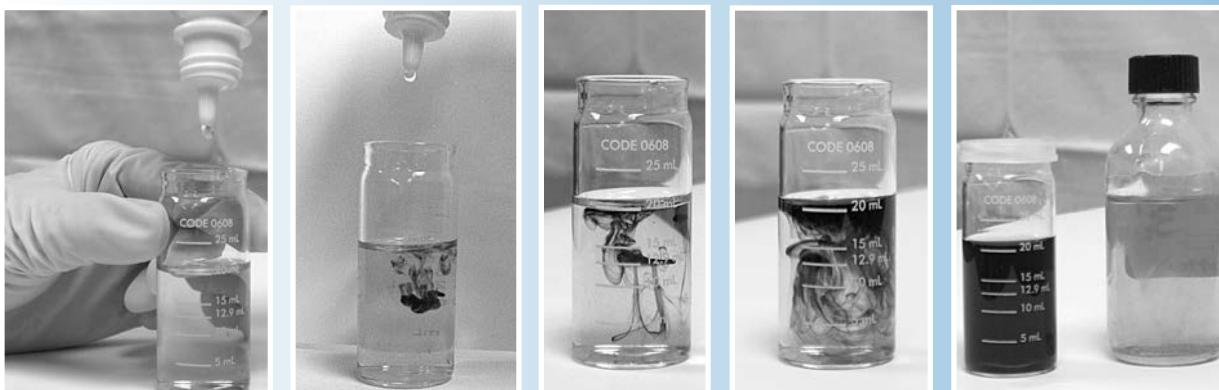
STEP 8. When you have achieved the straw yellow color, carefully remove the syringe from the vial and set the syringe aside. Do not empty the contents of the syringe as you will need it for step 11.



STEP 9. Remove the center-hole plastic lid from the glass vial.

STEP 10. Add eight drops of the starch indicator solution to your 20 ml sample in the glass vial.

Put the lid back on. Gently mix your sample by swirling the vial. Your sample will turn dark blue or black.



STEP 11. Reinsert the syringe that you set aside in step 8 into your sample vial. The syringe should still contain the sodium thiosulfate from steps 4 through 8.



DNR PHOTOS

ON SHORE PROCEDURES

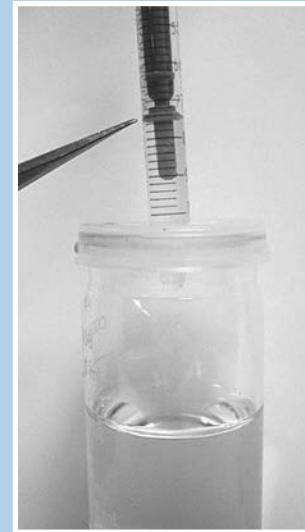
Winkler Titration Analysis (LaMotte® Dissolved Oxygen Kit) (continued)

STEP 12. Very slowly, add the sodium thiosulfate solution to your sample one drop at a time. Take care to swirl the contents of the glass vial between drops. Add the sodium thiosulfate solution drop by drop until the blue or black color of your sample disappears when you swirl it. Swirling the contents of your sample vial allows time for the color to change between drops! Every drop counts so proceed slowly.



STEP 13. When your sample has turned clear, remove the syringe. Before expelling the remainder of the sodium thiosulfate solution in the syringe, read and record the volume of solution that you used (see “Reading the Syringe” on the next page).

This step is very important, as it is the “answer” to the dissolved oxygen content of your water sample! Once you have recorded the volume of solution that you used, you can discard the remaining solution by flushing it down a drain with lots of water. Do not return it to the sodium thiosulfate bottle!



DNR PHOTOS

STEP 14. Rinse the syringe with distilled water and wipe it off before repeating steps 1 through 13 for your next sample. Remember, since this analysis only uses 20 ml of your “fixed” sample, if at any time you feel that you made a mistake, you should have enough “fixed” sample water remaining to repeat the analysis.

Note: all chemicals should be stored out of the reach of children. Chemicals should be replaced every year.

STEP 15. Be sure to rinse all of your equipment with distilled water when you are finished.

READING THE SYRINGE

Once your sample in the glass vial has changed from blue to clear (steps 12 to 13), the dissolved oxygen titration is complete. To determine the amount of dissolved oxygen in your sample, record the position of the plunger in your syringe. The syringe is marked in 0.2 (two-tenths) intervals.

Example 1: The tip of the plunger is flush with the number 6.0 after step 12 (page 70). Since you started adding the solution when the plunger was flush with the number 0, your sample contains 6 **parts per million (ppm)** of dissolved oxygen.

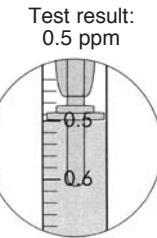
Example 2: Suppose you had to refill the syringe once with the sodium thiosulfate solution before your sample changed color to a faint straw yellow. After adding the sodium thiosulfate solution for a second time, the color of your sample changes from blue to clear. At this point the plunger is flush with the number 3.2. Therefore, the dissolved oxygen content of your sample is 13.2 ppm (10 ppm from the first syringe of sodium thiosulfate solution when the entire contents were added, plus 3.2 ppm from the second syringe of sodium thiosulfate solution).



PARTS PER MILLION (ppm) • An expression of concentration indicating weight of a substance in a volume of one liter. Milligrams per liter (mg/l) is an equivalent unit.

Reading the syringe.

Read the test result directly from the scale where the large ring on the Titrator meets the Titrator barrel. If the Titrator was refilled to reach the final color change, add the total amounts of titrant used to determine the final test result.



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