The Hach dissolved oxygen kit

Equipment List

Chemicals
1) One bottle, Sodium Thiosulfate (0.0108N)
2) Dissolved oxygen reagent packet 1 (Manganous Sulfate>
3) Dissolved oxygen reagent packet 2 (LiOH, KI, Na-Azide)
4) Dissolved oxygen reagent packet 3 (Sulfamic Acid)
Glassware
1) One Hach Sampling bottle
2) One Hach mixing bottle
3) One Hach plastic measuring tube

The Chemistry

Step 1.

Fill the Dissolved Oxygen bottle with the water to be tested by allowing the water to overflow the bottle for two or three minutes. This is to clear out the bottle and to make the sampling as uncontaminated as possible. To avoid trapping air bubbles in the bottle, incline the bottle slightly and insert the stopper with a quick thrust. Note the cone-shaped top which aides in forcing air bubbles out. If the bubbles become trapped in the bottle in Steps 2 or 4, the sample should be discarded before repeating the test.
This means... When you take a sample from your water source and cap it up, you begin the process of measuring the oxygen in your water by closing your sample off from the atmosphere. Inserting the stopper rapidly into your bottle forces air bubbles (containing oxygen) out. If these bubbles remain in the bottle, they may cause the test kit to indicate more oxygen is present than may actually be there.

Step 2.

Use the clippers to open one Dissolved Oxygen 1 Reagent Powder Pillow and one Dissolved Oxygen 2 Reagent Powder Pillow. Add the contents of each of the pillows to the bottle. Stopper the bottle carefully to exclude air bubbles. Grip the bottle and stopper firmly; shake to mix. A side to side shaking motion works best. A flocculant (floc) precipitate will be formed. If oxygen is present in the sample, the precipitate will be brownish orange in color. A small amount of powdered reagent may remain stuck to the bottom of the bottle. This will not affect test results.
What is going on in this step:

- **Reagent Powder Pillow #1 (Manganous Sulfate)** $MnSO_4$
  This powder packet contains a powdered chemical called Manganous Sulfate which reacts with the oxygen present in the water. During the reaction, the oxygen is bound to the manganese (chemical element Mn), forming a brownish solid which settles to the bottom of the bottle (MnO_2). This process is called ***fixing*** the oxygen. In order for this

fixation process to work however, the solution must be at high pH, so we need another reagent to make this occur...

- **Reagent Powder Pillow #2 (LiOH, KI, Na-azide)**
  If the Manganous Sulfate *fixes* the oxygen dissolved in the water, why do we need more chemicals? There are three specific chemicals present in packet #2 which are important to the *fixation* of the oxygen.
    - **LiOH (Lithium Hydroxide)** is a base, which means that in water it breaks up to form the OH^- ion, and the Li^+ ion. In this reaction, LiOH basically just functions as a catalyst to activate the binding process. The binding process involved with Manganous Sulfate requires a high pH to proceed. The addition of LiOH does just that.
    - **KI (Potassium Iodide)** is added to function as a dye, and will react with the sulfamic acid added, as explained below.
    - **NaN_3 (Sodium Azide)** is an agent added which will not come into play until later in the reaction sequence. Because we will not come back to it, a quick explanation is appropriate. (For a more in-depth explanation, see the Winkler method titration page.) Basically during the final titration, Sodium Thiosulfate produces some nitrite (NO_2^-) which conflicts with the intended reaction. The addition of Sodium Azide prevents this conflictual reaction from occuring.

Step 3.

Allow the sample to stand until the floc has settled halfway in the bottle, leaving the upper half of the sample clear. Shake the bottle again. Again let it stand until the upper half of the sample is clear.

What is the story?

Allowing the floc time to settle in the bottle basically ensures that the chemical reaction occuring in the bottle has time to reach completion. If we proceded to step 4 before settling was complete, we might not get an accurate measurement of how much oxygen is actually dissolved in the water.

Step 4.

Use the clippers to open one Dissolved Oxygen 3 Reagent Powder Pillow. Remove the stopper from the bottle and add the contents of the pillow. Carefully restopper the bottle and shake to mix. The floc will dissolve and a yellow color will appear if oxygen is present.

What is this mysterious reagent number 3?

- **Reagent Powder Pillow #3 (Sulfamic Acid $C_6H_{13}O_3NS$)** Upon addition of the Sulfamic Acid, the MnO_2 from above is reduced to Mn^{2+}, and the Iodine from the Potassium Iodide above is oxidized by the MnO_2 from I^- to I_2. This reaction step effectively causes the solution to take on a yellow-ish brown color proportional to the number of I_2 molecules present which in turn is proportional to the original amount of O_2 molecules in the water.

  $$MnO_2 + 4H^+ + 2I^- = Mn^{2+} + I_2 + 2H_2O$$

  We say at this point, that the oxygen is ***fixed***. This means that all of the oxygen from the original sample which was in solution has now been chemically modified to a form which won't change when exposed to the air. It is now in a stable form, and can be transported back to a classroom for analysis if necessary.

Step 5.

Fill the plastic measuring tube level full of the sample prepared in Steps 1 through 4. Pour the sample into the square mixing bottle.

Step 6.

Add Sodium Thiosulfate Standard Solution drop by drop to the mixing bottle, swirling to mix after each drop. Hold the dropper vertically above the bottle and count each drop as it is added. Continue to add drops until the sample changes from yellow to colorless.

What does this do?

- **Sodium Thiosulfate Standard Solution**
  As drops of this chemical enter the solution, the Sodium separates from the thiosulfate ion. The thiosulfate then reacts with any Iodine (I_2) molecules available in the water. When the Iodine molecules react, they break up into I^- ions which are colorless.

$$2S_2O_3^{2-} + I_2 = 2S_4O_6^{2-} + 2I^-$$

What does this all tell us about the amount of oxygen in the water?

Stoichiometry (a fancy word meaning the chemical book keeping of the amount and concentration of chemicals in a reaction) tells us that 4 molecules of the Sodium Thiosulfate are required to change the color resulting from one molecule of O_2 in the original water. This clear definition allows us to get a very accurate estimate of the number of O_2 molecules in the original solution.

I hope that this brief report has helped to answer questions you may have had about how our dissolved oxygen kit works. Feel free to send email to us (roger@hwr.arizona.edu) or (martha@hwr.arizona.edu) or to our assistant, Chris Gutmann (cgutmann@hwr.arizona.edu).

Sincerely,

Roger Bales & Martha Conklin

University of Arizona