Modified Winkler Method for Determining Dissolved O_2 in Aqueous Solutions

Reagents

A. Manganous sulfate solution **for 1L**

Dissolve one of the following in 1 L of distilled water:

480 g $MnSO_4 \bullet 4H_2O$ –or-

400 g $MnSO_4 \bullet 2H_2O$ –or-

364 g $MnSO_4 \bullet H_2O$

B. Alkali-iodide (add azide* if necessary) **for 1L**

Dissolve in 1 L of distilled water:

500 g NaOH –or- 700 g KOH -AND- 135 g NaI –or- 150 g KI

*Use azide for bacteria or nitrite laden samples:

Dissolve 10 g NaN_3 in 40 ml distilled water.

Add to 1 L of above solution.

C. Sulfuric acid (concentrated)

D. Starch **for 0.1L**

Dissolve 2 g soluble potato starch in 100 ml hot distilled water, stir.

(note: very important to add to hot water as starch may take some time to dissolve)

Salicylic acid (0.2 g) may be added as a preservative.(not necessary if starch is used on the same day it is dissolved)

E. Sodium thiosulfate **for 1L**

Dissolve in 1 L distilled water 6.25 g $Na_2S_2O_3 \bullet 5H_2O$ (note: this solution is perishable, and should be made up on the day it is used)

Materials

Test tubes of known volume or standard BOD water sampling bottles

Beral Pipets

Burets or 10 mL syringes

Erlenmeyer Flasks

Michael Kandianis, kandiani@uiuc.edu

Procedure

Collect sample: Using a test tube of known volume or a standard BOD bottle, immerse vessel into the sample water and fill to capacity. Cap the test tube or bottle immediately being careful not to agitate the water as this could cause a change in the dissolved oxygen concentration. Quickly proceed to Reagent addition step.

Reagent addition:

300mL standard BOD bottle sample (see parentheses below for 25mL)

1.) Add 1mL of $MnSO_4$ solution. (83µL or approx. 2 drops from beral pipet)
2.) Add 1mL of alkali-iodide-azide solution (same as #1)
3.) Invert several times to mix, thereby allowing a brown precipitate to form.
4.) Let the precipitate settle to at least half of the bottle/test tube volume.

*At this point the amount of dissolved oxygen in the sample is preserved and thus the samples will remain stable for a period up to 48 hours unless exposed to intense heat or direct sunlight.

5.) Add 1mL of concentrated sulfuric acid. This will dissolve the precipitate and will turn the sample a bright gold color. (83µL or approx. 2 drops from beral pipet)

6.) Transfer approximately 2/3 of the sample volume to a 250mL Erlenmeyer flask for titration. The amount of sample that is titrated should correspond to 200mL of the original sample after correction for displacement w/ reagents. i.e. for 2mL of $MnSO_4$ and KOH-KI/NaOH-NaI reagents combined, titrate 200*300/(300-2) = 201mL. (this calculation yields 16.78 mL for the 25mL sample)

7.) Slowly titrate the sample with the sodium-thiosulfate solution until a pale straw color is reached, being careful to record how much $Na_2S_2O3 \bullet 5H_2O$ was used.
8.) Add a few drops of starch solution and mix. The sample should now turn to a dark blue color.
9.) Continue titrating slowly, being careful to swirl the Erlenmeyer frequently ensuring that the **clear** endpoint is not overrun. (If using a small volume proceed at an excessively slow rate!!!)
10.) Once the endpoint is reached record the amount of $Na_2S_2O3 \bullet 5H_2O$ that was added. One mL is equal to 1 mg/L (or p.p.m.) dissolved oxygen in your sample. (Note: 1/12 mL or 83µL equals 1mg/L dissolved oxygen…thus 2/3 of a mL will be equal to 8 mg/L (water in equilibrium with atmospheric O_2) titrate carefully.

References

Standard Methods for the Examination of Water and Wastewater, 1995, New York, American Public Health Association.

Michael Kandianis, kandiani@uiuc.edu

Dynamics of Dissolved Oxygen in Natural Systems

Objective

To apply your chemical knowledge of dissolved oxygen analyses in order to observe how various organisms affect the dissolved oxygen concentration of natural waters.

Experimental Method

Materials:

- 4 glass tanks of equal size/water content
- 2 plants
- 2 goldfish

Procedure:

Using the aquariums provided in class, create four experimental systems comprised of one fish, one plant, one fish and one plant, and a vacant tank (control) respectively.

For each system…

- Obtain three water samples according to the method you practiced in class, and analyze each sample for its dissolved oxygen concentration. Record the average value of your three assays in the table below.

- Given your knowledge of dissolved oxygen from previous experiments, make a hypothesis on how the dissolved oxygen concentration will change over the course of one week (Increase/Decrease/Remains Constant). **Important:** Be sure to record your hypothesis for each system in the chart below.

- At the end of one week obtain three more water samples, and again, analyze each sample for dissolved oxygen. Record your average value of your results.

Results

SYSTEM	*Initial Dissolved O_2*	*HYPOTHESIS*	*Final Dissolved O_2*
Fish			
Plant			
fish and plant			
Control			

Data Analysis

On the back of this sheet, summarize your results by concluding how the dissolved oxygen concentration of each system changed over the course of the week. Also, determine whether your results did or did not support your hypotheses, and give reasons for the observed behavior of each system.

Michael Kandianis, kandiani@uiuc.edu