

Lesson 17

Title of the Experiment: Determination of water quality parameters such as pH, dissolved oxygen (DO) and electrical conductivity by chemical methods

(Activity number of the GCE Advanced Level practical Guide – 29)

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(A) Determination of pH

Introduction

pH affects most of the chemical reactions which take place in water and wastewater treatment plants, so it is important to test pH of the source and treated water frequently. Changes in pH of the source water may require the operator to change the feed rate of various chemicals. In contrast, changes in pH of the treated water may indicate that chemicals are not being fed properly, perhaps due to a chemical feeder running out of chemicals. The pH test explained in this lab exercise gives the knowledgeable operator one of the best indicators of the chemical balance of the plant's water.

pH is typically measured using a pH meter, so this is one of the simplest tests performed in the water and wastewater laboratory. Basically, measuring pH consists of calibrating the instrument, placing the electrodes in a well-mixed sample, and then reading the pH directly from the pH meter.

Despite the utility of this lab procedure, you should be aware of its shortcomings. Measuring the pH of a solution does not tell us which acids and bases are present, nor does it tell us their concentrations. Instead, pH is merely an indicator of the overall balance of hydrogen and hydroxide ions in the solution.

You should also note that the precision and accuracy of pH measurement depends on the type and condition of the instrument and on the care used in calibration and operation. Under normal conditions, ± 0.1 pH unit represents the limit of accuracy of the pH meter, so you should report pH values to the nearest 0.1 pH unit.

The **electrode** is the portion of the pH meter which senses the pH. It is a very sensitive and fragile instrument which is susceptible to scratches. If scratched, the electrode will result in erroneous pH readings, so always blot the electrode dry carefully when cleaning it. Light and temperature can also harm the electrode, so it should be stored in a buffer solution at 10-25°C and protected from light.

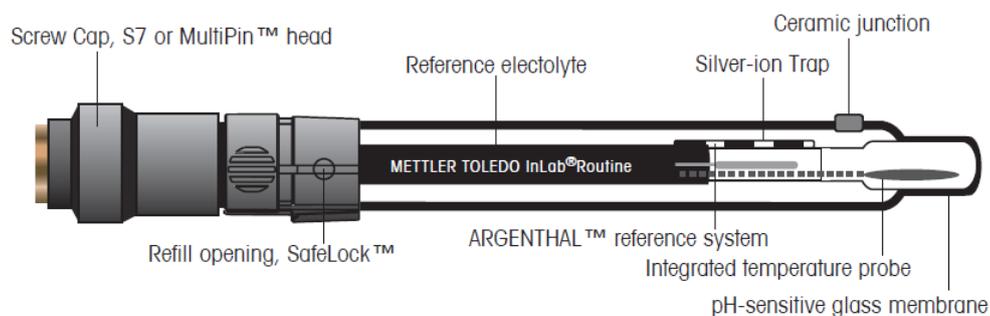


Figure 1: Typical combination pH electrode with inner pH sensor and outer reference element

The electrode is relatively free from interferences due to color, turbidity, colloidal matter, oxidants, reductants, or high salinity, except for a sodium error at high pH. This error at a pH above 10 may be reduced by using special "low sodium error" electrodes if your water is high in sodium and your pH is also high.

While using the pH meter, you should watch for erratic results arising from cracked electrodes, faulty connections, or fouling of electrodes with grease and/or solids residue. The two-point calibration explained in the procedure can help detect a faulty electrode. If a reasonably accurate value for the second buffer cannot be obtained after the meter has been standardized against the first buffer, then it is likely that one, if not both, of the electrodes is faulty and must be replaced.

The only reagents you will use in this lab are the buffer solutions used to calibrate and store the meter. The laboratory you visit will probably have these solutions on hand since they can be stored for at least a week and can often be bought commercially. If commercial solutions are available, the best practice is to use a fresh beaker of buffer solution for each calibration.

Learning out comes:

After completing this practical, students should be able to

- develop skills in water sampling
- calibrate pH meters
- develop ability in correct usage of pH meter
- measure pH of water samples

Materials / equipment:

- pH meter
- water sample/s
- wash bottle with de-ionized water
- soft tissue
- buffer solutions (pH = 4, 7 & 10)
- beakers (50 and 100 mL)

Procedure

1. Turn on the pH meter and allow the instrument to warm up.

Every brand of pH meter operates slightly differently, so we will not explain which buttons to push for every stage of the procedure. Instead, you can refer to the instrument's manual, if necessary.

2. Compensate for the temperature.

pH is slightly temperature-dependent, so we use the following steps to ensure that changes in temperature do not cause errors in readings. You will also notice that we record the temperature of the sample in a later step so that we will know at what temperature the pH was taken.

- a. Bring all of the buffer solutions, the sample, and the pH meter to the same temperature. (The simplest method is to bring all to room temperature.)

- b. If the pH meter does not have automatic temperature compensation, measure the temperature of the buffer solutions and adjust the temperature compensation dial as necessary.
3. Use buffers to calibrate the meter.

To get the most accurate pH reading of our sample, we calibrate the meter before each use. During calibration, we place the electrodes in a series of buffer solutions with known pH values and set the meter to those values. Typically, we will use a buffer solution with a pH of 7.0, a buffer solution with a pH of 4.0, and a buffer solution with a pH of 10.0 for calibration, though we can use other buffers if necessary. In all cases, the second and third buffers should have pH values at least two pH units higher and lower than the first buffer solution. The following procedure is used to calibrate the meter to each buffer solution.

- a. Remove the electrode(s) from storage solution, rinse them with distilled water and carefully blot the electrode(s) dry with a high quality laboratory tissue.
 - b. Place the electrode(s) in a buffer solution and measure the pH of the buffer while gently stirring the solution.
 - c. Adjust the pH meter reading to the known pH value of the buffer solution, if necessary. Then place the instrument in standby mode.
 - d. Repeat this procedure with the next buffer solution.
4. Prepare the sample.

In order to get a good pH reading, you should ensure that the sample is not contaminated and that it is well-mixed. You can mix the sample using either a magnetic stirrer or a stir bar. In either case, the goal of stirring is to ensure that the sample is well mixed so that the pH reading is representative of the entire sample. Do not stir too vigorously or carbon dioxide will enter the water, forming carbonic acid and lowering the pH.

- a. Record the source of your sample water in the Data section.
 - b. To prevent contamination, rinse out a sample cup several times with sample water and fill it with the sample water to be tested.
 - c. If a magnetic stirrer is available, place a clean stir bar in the sample water and turn on the stirrer. If not, you will need to mix the sample with a stir bar at intervals.
5. Measure the pH of the sample.
 - a. Determine the sample's temperature and record the temperature in the Data section. Adjust the meter's temperature compensation dial if necessary.
 - b. Remove the electrode(s) from the storage solution, rinse it with distilled water and carefully blot the electrode(s) dry with a high quality laboratory tissue.
 - c. Place the electrode(s) in the sample. Continue stirring the sample as the pH is measured by the meter. Record the sample's pH in the Data section.
 - d. Place the instrument in standby mode and remove the electrode(s) from the sample. Rinse the electrode(s) thoroughly with distilled water and carefully blot dry.
6. When all samples have been tested, place the electrode(s) in tap water or pH 7.0 buffer solution for storage and shut off the meter.

Results:

| Source of Sample | Temperature | pH |
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(B) Determination of Dissolved Oxygen (DO)

Introduction

Dissolved Oxygen, or **D.O.**, is the amount of oxygen dissolved in a sample of water. This is the oxygen which is free to react with chemicals or to be used by organisms in the water.

Dissolved oxygen concentrations in water are dependent on a variety of factors. The temperature determines the saturation point of oxygen in the water, with colder waters typically holding more oxygen. Water which is agitated by running through a stream or a trickling filter typically has a higher concentration of D.O. than does stagnant water since the agitated water has a greater surface area coming in contact with the air. Aerators also increase the surface area of air to water and increase the D.O. concentrations. Aquatic plants release oxygen into the water during the day when they perform photosynthesis.

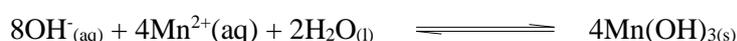
On the other hand, D.O. is removed from water by a variety of natural reactions. In the wastewater treatment plant, microorganisms use up oxygen in the water just as we use up oxygen in the air. Fish and other aquatic organisms also use up oxygen. At night, plants take in oxygen rather than releasing it, further lowering the D.O. levels. Finally, some compounds in the water react with, and use up, oxygen.

The D.O. content of water is very important in natural waters and in wastewater treatment plants because it determines which organisms are able to live in the water. Since wastewater treatment plants depend on bacteria to break down the organic compounds found in water, they must carefully monitor the D.O. content of the wastewater. If the amount of dissolved oxygen in the wastewater becomes too low, these bacteria will die and septic conditions will occur. Septic conditions can result in unpleasant odor and in fish kills.

A variety of methods can be used to test the D.O. content of water. D.O. meters are relatively accurate, and can usually obtain readings within 0.1 mg/L of the actual D.O. concentration of the water. However, this does not take into account interferences which can be caused by salts, sulfur-containing compounds, and chlorine. Nor does it consider improper readings which will result from air bubbles becoming dissolved in the sample water.

Winkler method is a frequently used chemical method for determination of dissolved oxygen in a water sample.

In an alkaline solution, dissolved oxygen will oxidize manganese(II) to the trivalent state.



The analysis is completed by titrating the iodine produced from potassium iodide by manganese(III) hydroxide.

Sodium thiosulphate is used as the titrant.



Success of the method is critically dependent upon the manner in which the sample is manipulated. At all stages, every method must be made to assure that oxygen is neither introduced to nor lost from the sample. Furthermore, the sample must be free of any solutes that will oxidize iodide or reduce iodine.

Learning outcomes:

After completing this practical, students should be able to

- develop skills in water sampling
- measure DO of water samples
- develop ability in correct usage of DO meter

Materials / equipment:

DO meter

water sample/s

wash bottle with de-ionized water

soft tissue

beakers (50 and 100 mL)

manganese (II) sulphate solution (prepared by dissolving 48 g of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in water to five 100 cm³ solution)

alkaline potassium iodide solution (prepared by dissolving 15 g of KI in about 25 cm³ of water, adding 66 cm³ of 50% NaOH, and diluting to 100 cm³)

concentrated sulphuric (VI) acid; (0.0125 M sodium thiosulphate solution)

starch solution (freshly prepared)

250 cm³ volumetric flask

250 cm³ conical flask

measuring cylinders

titration apparatus

magnetic stirrer

Procedure:

By DO meter

1. Turn on the D.O. meter and allow it to warm up for at least 15 minutes.

2. Clean the BOD bottles with chromic acid. Then rinse the bottles with tap water, followed by distilled water. Allow the containers to dry by draining upside-down on a rack.
3. Calibrate the D.O. meter. Here, we will describe the saturated air method of calibration, but you should keep in mind that there are other acceptable methods for calibrating the meter.
 - a. Place the probe in a BOD bottle filled halfway with distilled water. Do not turn on the probe stirrer. Be sure that the probe is dry and is not touching the distilled water.
 - b. Wait for five minutes.
 - c. Measure the air temperature.
 - d. Look up the calibration value which corresponds to the air temperature. Correct the calibration value as necessary for altitude or salinity of samples.
 - e. Calibrate the meter.
4. Collect a grab sample in the BOD bottle. To do so, fill the bottle so that it overflows two or three times its volume, and then replace the stopper so that the bottle is completely full and no bubbles are trapped under the stopper.

You should select a sampling location in which the wastewater is mixed thoroughly and is uniform in quality. If the testing is not done on an hourly basis, choose times when the samples best represent the wastewater's characteristics. Samples should be tested promptly after collection.

5. Measure the D.O. concentration of the sample water.
 - a. Place the probe in the sample water and turn on the probe stirrer.
 - b. Turn the meter switch to temperature and record the temperature in the Data section.
 - c. Turn the meter switch to D.O. and allow 10 seconds for the D.O. reading to stabilize. Then read the D.O. concentration and record in the Data section.
6. Clean the BOD container immediately after the test has been completed to prevent accumulation of residues in the container.

By Winkler method

1. Use a 250 cm³ volumetric flask to collect water sample. Fill the flask completely with water without trapping any air bubbles.
2. Add 1 cm³ of manganese(II) sulphate solution to the sample using a pipette. Discharge the solution well below the surface (some overflow will occur).
3. Similarly introduce 1 cm³ of alkaline potassium iodide solution. Be sure that no air becomes entrapped. Invert the bottle to distribute the precipitate uniformly. [Hazard Warning: Care should be taken to avoid exposure to any overflow, as the solution is quite alkaline.]
4. When the precipitate has settled at least 3 cm below the stopper, introduce 1 cm³ of concentrated sulphuric acid well below the surface. Replace the stopper and carefully mix until the precipitate disappears. A magnetic stirrer is helpful here.
5. Allow the mixture to stand for 5 minutes and then withdraw 100cm³ of the acidified sample into a 250 cm³ conical flask.
6. Titrate with 0.0125M sodium thiosulphate until the iodine colour becomes faint. Then add

1 cm³ of starch solution and continue adding the thiosulphate solution until the blue colour disappears.

- Record the volume of thiosulphate solution used and calculate the dissolved oxygen content in the sample in mg dm⁻³.

Remarks: If the water sample has a low DO value, it is recommended to withdraw 200 cm³ of the acidified sample into a 500 cm³ flask for the titration describe in step 5.

Results

| Sample Location | Temperature | D.O. (mg/L) | D.O. (mg/L) |
|-----------------|-------------|-------------|-------------|
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(C) Determination of electrical conductivity

Introduction

Pure water does not conduct electricity, but any solvated ionic species would contribute to conduction of electricity. A substance can conduct an electrical current if it is made of positively and negatively charged particles that are free to move about and is called a **conductor**. When an electrical current is applied between two electrodes, the positively charged electrode, the anode, will attract negatively charged particles and the negatively charged electrode, the cathode, attracts positively charged particles. So to conduct electricity mobile charged particles must be present. A substance that does not conduct electricity is a **nonconductor**.

Metals are conductors. A metal can be viewed as an array of positive ions surrounded by a “sea” of mobile valence electrons. When an electrical current is applied to the metal, the electrons move away from the cathode and toward the anode, forming an electrical current in the metal. All ionic compounds are solids at room temperature. In the solid, the ions are not free to move, therefore the solid ionic compound does not conduct electricity. However, if the ionic compound is heated to its melting point, the ions in the molten (melted) ionic compound become mobile. Therefore the molten ionic compound does conduct electricity.

Molecular compounds do not conduct electricity as solids or as liquids. When a molecular solid is melted, the molecules do become mobile, but molecules are not charged and do not carry an electrical current.

Water is a good solvent for many compounds, both ionic and molecular, because it is polar.

Water dissolves many ionic compounds because its partially positive end is attracted to anions and its partially negative end is attracted to cations. This ion-dipole attraction allows water to pull the ions away from each other and surround them. Ionic compounds are not soluble in nonpolar solvents such as toluene. The “rule of thumb” for the solubility of molecular compounds is “like

dissolves like". This means that polar compounds dissolve in polar solvents and nonpolar compounds dissolve in nonpolar solvents. Water is a good solvent for polar compounds. (Toluene, a nonpolar solvent, is a good solvent for nonpolar compounds.) Water pulls the polar molecules away from each other and surrounds them.

A compound that dissolves in water to form an electrically conducting solution is called an **electrolyte**. A compound that dissolves in water to form a non-conducting solution is called a **nonelectrolyte**. A compound that dissolves in water to give a solution that conducts strongly is called a **strong electrolyte** and one that dissolves in water to give a solution that conduct weakly is called a **weak electrolyte**. When ionic compounds dissolve in water their ions dissociate (are separated from each other and then surrounded by water molecules). Solutions of ionic compounds conduct strongly, therefore soluble ionic compounds are strong electrolytes.

When molecular compounds dissolve in water their molecules dissociate (separated and surrounded by water). For example, sucrose (table sugar): The molecules in the solution do not conduct electricity, therefore most molecular compounds are nonelectrolytes. However, there are some molecular compounds whose solutions conduct electricity because the molecules chemically react with water to form ions. Many resistors and conductors have a uniform cross section with a uniform flow of electric current, and are made of one material. In this case, the **electrical resistivity** ρ is defined as:

$$R = \rho \frac{l}{A}$$

R – the electrical resistance of a uniform specimen of the material,

l – the length of the piece of material and

A – the cross-sectional area of the specimen.

Conductivity κ is defined as the inverse of resistivity and **Conductance** G is defined as the inverse of electrical resistance:

$$\kappa = \frac{1}{\rho} \quad \text{and} \quad G = \frac{1}{R}$$

Learning outcomes:

After completing this practical, students should be able to

- develop skills in water sampling
- calibrate conductivity meters
- develop in correct usage of conductivity meters
- measure electrical conductivity of water samples

Materials / equipment:

conductivity meter

water sample/s

wash bottle with de-ionized water

soft tissue

KCl

beakers (50 and 100 mL)

Procedure

1. Turn the conductivity meter on and allow the instrument to warm up.
Every brand of conductivity meter operates slightly differently, so we will not explain which buttons to push for every stage of the procedure. Instead, you can refer to the instrument's manual, if necessary.
2. Prepare a known concentration of KCl solution. Get a measurement from the instrument. Find are you measuring conductance or conductivity based on the display unit. Calculate the cell constant using this value (note: you can avoid this step if instrument display the cell constant).
3. Measure the conductance / conductivity of the water samples.
4. When all samples have been tested, clean the electrode(s) in tap water, wipe the water and place the cap on the electrode.

Results:

| Source of Sample | Conductivity | Conductance |
|------------------|--------------|-------------|
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References:

American Public Health Association, American Water Works Association, and Water Environment Federation. 1998. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington, D.C.

M. Hayashi, Temperature-Electrical Conductivity Relation of Water for Environmental Monitoring and Geophysical Data Inversion, *Environmental Monitoring and Assessment*, **96**, 119–128 (2004)

