Chapter 8 Electronic Measurement

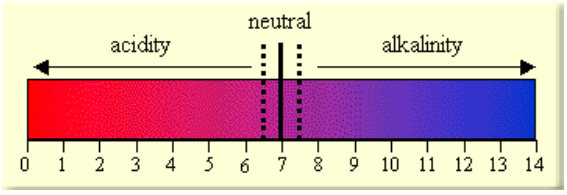
There are a number of sample analyses that can be performed using a meter and electrode. The three most common electronic measurements in wastewater are pH, conductivity, and dissolved oxygen. In electronic measurement, an electrochemical reaction occurs at the end of the electrode. This reaction creates an electrical millivolt current that is sent to the meter which interprets the current and compares it against a known millivolts value. The current is then translated to a value and displayed on the meter screen. All electronic meters must be calibrated -- they don't know anything until you tell them.

pH

pH is a measure of the acidity or basicity of a sample. Pure water dissociates into hydrogen ions and hydroxide ions.

$H_2O \rightarrow H^+ + OH^-$

Because there are equal concentrations of hydrogen ions and hydroxide ions, the water is considered neutral and the pH is 7.0. If another substance is added to pure water and adds more hydrogen ions there will be a higher concentration of hydrogen ions than hydroxide ions. This solution is called an acid. Likewise, if a sample has more hydroxide ions than hydrogen ions, the solution is called a base.



The pH scale goes from 0-14 with 7 being considered neutral. If the sample pH is below 7.0, the sample is acidic. If the sample pH is above 7.0, the sample pH is alkaline or basic. PH is directly related to the concentration of acids and bases. Each change of 1 pH unit represents a 10 fold change in concentration. For example, a sample with a pH of 2.0 is 1000 times more acidic than a sample with a pH of 5.0. Likewise an acid on the laboratory bench labeled 0.1 N Hydrochloric acid solution is 100 times more concentrated than a 0.001 N solution and may pose a safety hazard. If the pH of the 0.001 N acid is 3.0, what would the pH of the 0.1 N be? (pH =1.0) Be sure to wear appropriate gloves, goggles and apron when handling concentrated acids and bases.

pH Measurement

The pH meter is used to measure the hydrogen ion concentration of a sample. For routine work, the pH meter must be accurate and reproducible to the nearest 0.1 pH unit. pH is measured by an electrode that is sensitive only to hydrogen ions. For routine lab work, a sturdy combination electrode with either a plastic or glass body should be used. pH papers or pH indicator strips are unacceptable for laboratory pH measurement.

Electrode Preparation

A combination electrode contains both a measuring electrode and a reference electrode. The hydrogen ions in the sample create a potential difference which is compared to the reference electrode. This difference is translated into millivolt current and is displayed on the meter. As the electrode ages, potassium chloride inside the electrode is lost and must be periodically replenished. A glass combination electrode usually has a small hole on the side

which is used to fill the electrode with potassium chloride.

Gel filled combination electrodes cannot be refilled and must be discarded when they fail.

pH meters may also have an attachment port for an ATC (automatic temperature compensation) probe. This probe will correct for minor pH errors due to differences in temperature. The pH difference between a sample at 5°C and 20°C is about 0.1 pH unit. Some pocket pH meters are readily available that automatically compensate for temperature.

Electrode Storage

The electrode must **NOT** be stored dry. The best solution to store normal combination electrodes is saturated potassium chloride, (KCl) or if unavailable, use pH 7 buffer. Tap water or deionized water should not be used because the electrolyte within the electrode (KCl) will diffuse out and cause premature aging or additional maintenance. If the electrode is not going to be used for a long time, the electrode can be stored in a large test tube filled with KCl and covered with parafilm to prevent evaporation. Clean the electrode if a biofilm develops in the storage solution.

Daily pH meter Calibration

Modern digital pH meters are normally very stable and need to be calibrated only once or twice daily. Calibrate more frequently if meter is unstable or drifts. The pH meter should be calibrated with a minimum of 3 buffers. pH 7.0, pH 4.0 and pH 10.0 buffers are the standard buffers commonly used. It is best to select buffers that bracket the expected sample pH. For example, if the sample pH is usually 7.8, the lab technician should use at least pH 7.0 and pH 10.0 buffers. Sample pH and standard buffers should be measured at the same temperature, generally room temperature. There are many different manufacturers of pH meters and they all require calibration before use. Inexpensive meters may have only one calibration knob, while more expensive meters will have the capability of using multiple buffers.

Always follow the manufacturer's instructions. The following is an example of a typical calibration procedure.

pH Meter Calibration Procedure

1a Connect the pH electrode to the pH meter. Remove the electrode from the KCl or pH 7 buffer storage solution; rinse with deionized water and blot dry. TIP: The bulb of the pH electrode must be below the water level. If the meter reading is erratic, check the water depth.

1b. Select the pH mode.

1c. Clear any previous calibration data. Press the **STANDARDIZE** button. Calibrate with at least 3 buffers. Select pH buffers that will bracket the typical sample pH. A third buffer can be used to validate the electrode response. Normal buffers are 4, 7, 10. Purchasing color coded buffers is recommended.

1d Place the electrode in pH 7 buffer. Press the **STANDARDIZE** button and **ENTER** the standardization value. A small 7.0 should appear; indicating the calibration point has been entered.

1e Rinse the electrode with deionized water and blot dry.

1f Place the electrode in pH 10 buffer. Press the **STANDARDIZE** button and **ENTER** the standardization value. A small 10.0 should appear; indicating the calibration point has been entered.

1g Rinse the electrode with deionized water and blot dry.

1h. Place the electrode in pH 4 buffer. Press the **STANDARDIZE** button and **ENTER** the standardization value. A small 4.01 should appear; indicating the calibration point has been entered. .

1i Press the SLOPE button. The slope should be 56 ± 3 mv or (>95% efficient) **QC: Record the slope on the pH Meter Calibration Log.** Press the slope button again to get back to the original pH display.

Corrective Action: If the slope is not within tolerance, recalibrate. If the meter does not calibrate properly, replace the buffers or electrode and try again.

Automatic Temperature Compensation
If using an ATC probe, the probe should be placed in the buffers and sample at the time of calibration.

Troubleshooting pH Meter
1. Disconnect the electrode and attach the shorting strap.

2. Press the millivolt button. The display should show zero. If the display does not change, the meter needs repair.

3. Gel electrodes generally require no maintenance if kept moist. However gel electrodes have a shelf life of around 3 years. Recording the date the electrode was placed in service helps with troubleshooting. If the electrode response is sluggish or does not adjust to the correct pH, the electrode is about to fail and should be replaced.

4. Glass electrodes fail because of scratches, deterioration, and accumulation of debris on the glass bulb. Rejuvenate the electrodes by cleaning in 0.1 M HCl and 0.1 M NaOH.

Corrective action: If the pH responds slowly or drifts after rejuvenation, replace the electrode.
5. Reference electrodes fail because of clogged liquid junctions. The liquid junction must remain open to avoid slow response and meter drift. If the liquid junction becomes clogged, place in warm deionized water for several hours. Some combination electrodes can be refilled with saturated KCl.
6. If the pH meter does not respond to different buffers (remains at pH 7 all the time), replace the electrode.

pH Sample Handling
1. Clean plastic or glass containers can be used
2. Samples should be collected and analyzed within 15 minutes. No sample preservation is permitted. On site analysis is preferred.
3. Minimum sample volume should be 50 ml.

SAFETY: Use latex gloves when collecting and handling all wastewater samples

Sample pH Measurement
1. Use a calibrated pH meter. The meter should be in "pH" mode.
2. Carefully pour the sample into a 100 ml beaker. If the temperature is significantly different from room temperature, use the Automatic Temperature Compensating (ATC) Electrode if available or adjust the meter manually.
3. Immerse the pH electrode into the solution. Be careful not to break the glass bulb.
4. Swirl the sample gently until the meter reading stabilizes. For poorly buffered samples such as deionized water, immerse in three or four consecutive portions of sample, and then immediately measure the pH in a fresh sample.
5. Report the answer to the nearest 0.1 pH units on the bench sheet.

Data Management and Records Management
1. All records must be maintained in three ring binders or bound laboratory notebook.
2. Maintain all calibration records for a minimum of 5 years.

pH Quality Control
Decisions on the accuracy of the reported data will be based on the quality control information.

 Sample holding time less than 15 minutes.
Corrective Action: Reject samples and request a resample. Measure on site.
 Record sample date, time, type, sampler, date and time of analysis, analyst.
 Record method used
 Samples must be mixed well, poured quickly, and swirled constantly when measuring the pH
 Calibrate against a minimum of 3 buffers.
 Record slope
 Buffers should bracket the expected sample pH.
 Buffers should be used within the expiration date. Record date of purchase, lot number, and expiration date of buffers used.

Corrective Action: Expired buffers should be discarded. Replace with fresh buffers. Purchase a 6 month supply and rotate stock frequently.

 Store buffers in the dark, at room temperature, and in the chemical supply cabinet.
 Performance evaluation samples should be run at least annually.
 Split samples can be run with a second lab or second lab technician.
 Duplicate sample pH results should be within 0.1 pH units.

Conductivity

Conductivity or electrical conductance (EC) is a measure of the ability of a solution to conduct an electrical current. Current is conducted by the presence of ionic compounds in the water. The more ions present, the easier it is to conduct the current and therefore the higher the conductivity. Conductivity in wastewater analysis provides a quick estimate of the Total Dissolved Solids of the solution. Conductivity is also used as part of the laboratory QC program indicating the quality of reagent grade deionized or distilled water.

The conductivity cell consists of two platimum electrodes coated with platinum black. The distance between these two wires is called the cell constant. The most important requirement in conductivity measurement is a clean cell. A dirty cell will contaminate the solution and cause the conductivity to be incorrectly measured.

Conductivity Units
Conductivity is customarily reported in units of micromhos per centimeter (umhos/cm) or the international units of microsiemans/cm (uS).
1 umhos/cm = 1 uS/cm

Ions
Ions are atoms or groups of atoms that have an unbalanced number of electrons and protons. The most common example of an ion is sodium. Sodium in its atomic form has 11 protons and 11 electrons. Unfortunately, the #11 electron is a long way from the nucleus of the atom and is easily lost; leaving only 10 electrons. Because sodium now has 11 protons and 10 electrons, it has a +1 charge. This is the most stable form of sodium and is the only form found in water. There are a large number of minerals in water that are commonly in ionic form; ie. Ca^{+2}, Mg^{+2}, Cl^{-1}, SO_4^{-2}, HCO_3^{-1}, Fe^{+2}, PO_4^{-3}, NO_3^{-1}

Non-ions
There are other compounds in water that do not have a charge. These compounds are usually classified as molecules. Molecules share electrons and don't conduct electrical current well. Two common non-ionic compounds are silica and organic molecules.

Meter Calibration
To measure conductivity, the conductivity meter and electrodes must be calibrated.

The conductivity meter is calibrated against a 0.01 N potassium chloride (KCl) solution. This solution is easy to make and will have a reference conductivity of 1412 umhos at 25°C. There are many conductivity meter manufacturers so follow the manufacturers recommended calibration procedure.

Calibration Procedure

The following is a universal calibration procedure.

1. Clean the conductivity cell with DI water if needed.
2. Adjust the temperature of the standard to 25°C. An ATC (automatic temperature compensating electrode) can be used instead.
2. Rinse the electrode with deionized water to remove any cleaning solution.
3. Pour the 0.01 N standard KCl solution into 3 labeled 100 ml beakers.
4. Dip the conductivity cell into beaker #1, swirl slowly. Be sure to immerse the electrode below the hole in the side of the electrode.
5. Dip the conductivity cell into beaker #2, swirl slowly. Do not rinse the electrode with DI water between beakers.
6. Finally dip the conductivity cell into beaker #3. Avoid touching the conductivity cell to the sides or bottom of the container as the standard is swirled slowly.
7. Press the standardize knob/button to adjust/enter the standard value of 1412 umhos.

Conductivity Sample Handling

1. Clean plastic or glass containers can be used
2. Samples should be collected and analyzed as soon as possible. The sample may be preserved by refrigeration up to 28 days.
3. Sample volume should be at least 500 ml.

Conductivity Measurement

Once the conductivity cell has been calibrated, the sample is measure by following the same procedure as the standard.

1. Rinse the electrode with deionized water
2. Adjust the temperature of the sample to 25°C. An ATC (automatic temperature compensating electrode) can be used instead.
3. Pour the sample into 3 labeled 100 ml beakers.
4. Dip the conductivity cell into beaker #1, swirl. Avoid touching the conductivity cell to the sides or bottom of the container.
5. Dip the conductivity cell into beaker #2, swirl.
6. Finally dip the conductivity cell into beaker #3.
7. Record the conductivity value displayed on the meter.

Low Conductivity Samples

One of the controls performed on laboratory reagent water is conductivity. Because the conductivity is so low, it may be significantly influenced by temperature, measurement time, mixing, atmospheric gases (CO_2). Ideally the conductivity should be measured in a flowing stream of DI water to reduce the holding time errors created by dissolving CO_2.

Electrode Storage/Replatinization

The platimum black coating on the electrodes of the conductivity cells is extremely important to the cell operation. If the cell constant begins to change, inspect the electrodes for wear or flaking of the platinum black. To help reduce flaking of the electrodes, store the electrodes in deionized water. If the electrode shows wearing or flaking, it can be re-platinized. The re-

platinizing solution is expensive but can be reused many times.

Quality Control
Decisions on the accuracy of the reported data will be based on the quality control information.

Sample QC
 Record sample date, time, type, sampler, date and time of analysis, analyst and method used
 Samples must be mixed well, poured quickly, and swirled as soon as possible for best results.
 Record the sample temperature and adjusted temperature ($25^{o}C \pm 0.1$)

Equipment QC
 Calibrate against a conductivity standard. 0.01 N KCL is the most common standard. Record the date the standard was prepared or purchased, lot number, and expiration date
 Record the cell constant.
A good meter will have the ability to display the cell constant. Record the cell constant. It is normally around 1.0. Record the value in the calibration log book.

Corrective Action:
Replace or replatinize cells that do not show the expected cell constant.

 The conductivity standard used should be within the expiration date. Record date of purchase, lot number, and expiration date.

Corrective Action: Replace expired standards

 Use an automatic temperature compensation electrode.
 Performance evaluation samples should be run at least annually.
 Split samples can be run with a second lab or second lab technician.

Dissolved Oxygen

Dissolved oxygen is often measured to determine the oxygen level in receiving streams, in the aeration basin, and in the BOD test. The DO meter and electrode work in similar fashion to other electronic meters but unlike the others, this meter must be continually "on" to remain polarized. To be "on" the electrode must be continuously attached to the meter and the meter must be either plugged into an AC outlet or if battery operated, the battery must be good. If the battery fails, or the meter is unplugged, the DO electrode must be repolarized for an hour before being used to measure a sample.

Selecting a DO meter
ASK! There are a number of DO meter manufacturers and a lot of headaches associated with DO meters. Talk to a number of other laboratories to find out about membrane replacement, manufacturer support, ease of calibration, and reliability. Purchasing a $1000 meter, then finding out the manufacturer will not support the electrode after a few years is a tough pill to swallow. Are accessories for BOD measurement available, fragile, expensive? When running the BOD test, how many parts will have to be cleaned between samples? Lots of parts will mean lots of potential sources of error.

Calibrating the DO meter
DO meters must be calibrated following the manufacturer's instructions. Since oxygen is a gas, it is influenced by the barometric pressure (altitude) and temperature. The manufacturer provides a table that can be used to determine the saturated DO level at different elevations and temperatures. Meters are commonly calibrated against a saturated air solution. The saturated air can be a saturated sponge in the storage sleeve (Orion) or in a BOD with about 1" of water (YSI).

Figure: Laboratory calibration of DO meter with BOD probe

It is recommended that the DO meter calibration be periodically validated using the Winkler Titration Method.

Membrane replacement

A functioning membrane is essential to good DO measurement. The membrane allows oxygen to permeate to the electrode where it creates a millivolts current directly proportional to the DO concentration. One of the major advantages of the electrode method is that it can be used continuously. The DO electrode can be submerged in the stream to different depths or in an aeration basin and the DO monitored continuously. However, the membrane does not last indefinitely and must be changed frequently.

Figure: DO electrode, the membrane at the end of the probe requires periodic replacement.

Erratic calibrations or readings are usually indicative of either a bad membrane or bad battery. Maintaining a maintenance log will help the lab technician predict when failure is likely to occur.

Replacing the membrane should only take a couple of minutes. Follow the manufacturer's instructions and be sure to use the manufacturers recommended filling solution. The filling solution is not the same as the KCl used for the pH meter. The electrode should be disconnected from the meter when the membrane is replaced. If the membrane has been replaced properly there should be no air bubbles beneath the membrane and the membrane surface should not be wrinkled.

Sample Measurement

The DO should be measured at a representative point. Remember dissolved oxygen is a gas and is affected by turbulence and temperature. Measuring a DO sample at a point of high turbulence will not be representative. Likewise, measuring DO in shallow or quiet areas of a river will be different than in deeper and faster moving areas. A sampling plan will help define what information is needed and where the most appropriate location will be.

Using the DO meter for BODs will be discussed in the BOD chapter.

Specific Ion Electrodes

Specific ion electrodes are used in wastewater for such parameters as Total Chlorine Residual or Ammonia. They follow the same rational and techniques as a pH meter which is a specific ion electrode measuring hydrogen ions. These electrodes must be calibrated using prepared standards with each run and the calibration information recorded just like pH.