Experiment 4: Water Quality

CH3600: Environmental Chemistry, Plymouth State University


Introduction:
The quantification of a number of chemical species and related parameters are used to determine water quality, including pH (concentration of H$_3$O$^+$), conductivity and pE (ions and electron activities), water hardness (concentration of Ca$^{2+}$ and Mg$^{2+}$), alkalinity, and chloride concentration.

**pH**: pH is the measure of the concentration of H$^+$ (formally H$_3$O$^+$) ions in a solution—and is used to report the acid/base nature of a sample. pH values < 7 correspond to acidic solutions while pH values > 7 correspond to basic solutions. Natural waters may range from slightly acidic to slightly basic: acidity is usually from dissolved CO$_2$, while basicity is often from dissolved carbonates.

**Conductivity** is a measurement of the ability of an aqueous solution to carry an electrical current, largely as a result of dissolved anions (e.g. chloride, nitrate, sulfate, and phosphate) and cations (e.g., sodium, magnesium, calcium, iron, and aluminum). In reality, several factors determine the conductivity, including the concentrations, mobilities, and oxidation states of the ions and the temperature of the water. Temperature must always be measured concurrently to allow conversion into the reportable form at 25 °C. Note that conductivity is related to overall ionic strength and does not provide information about the presence or concentration of specific ions. Conductivity is the opposite of resistance (expressed in ohms) and is expressed in reciprocal ohms, known as mhos or siemens (S). The distance between the electrodes used in the measurement directly affects conductivity, and water samples tend to have low conductivity compared to the standard siemens, therefore the common unit in water chemistry is microsiemens per cm (μS/cm).

**pE** is defined as the negative log of the electron activity (pE = -log a$_e$), and is a way of reporting the electrochemical potential of a solution. Practically speaking, pE relays information about the oxidizing (large positive values) or reducing (large negative values) nature of the solution. Manipulation of the Nernst equation results in the following formula for determining pE:

\[
pE = \frac{E}{0.0591}
\]

where $E$ is the electrical potential measured versus the standard hydrogen electrode using a simple electrode setup such as that shown at left. Because a standard hydrogen electrode is impractical in most cases, a saturated Ag/AgCl electrode ($E^o = 0.200$ V) is usually the reference, and thus:

\[
E = E_{\text{measured}} + 0.200 \text{ V}
\]
**Water hardness** is caused by the presence of ions (Ca$^{2+}$, Mg$^{2+}$, and Fe$^{2+}$) and is so called due to these ions precipitating fatty acid carboxylates when mixed with soaps. Hardness is expressed in terms of mg/L (ppm) of CaCO$_3$ and is determined by titration with the chelating agent EDTA:

\[ M^{2+}(aq) + H_2EDTA^{2-}(aq) \leftrightarrow M-EDTA^{2-}(aq) + 2H^+(aq) \]

The indicator, Eriochrome Black T (designated HIn), used in this experiment requires at least some Mg$^{2+}$ in the sample to see the color change:

\[ Mg^{2+}(aq) + HIn^2-(blue) \leftrightarrow MgIn^{-1}(aq)\ (red) + H^{+}(aq) \]

At the end of the titration, the indicator complex reacts with the EDTA to give a blue endpoint:

\[ MgIn^{-1}(aq)\ (red) + H_2EDTA^{2-}(aq) \leftrightarrow MgEDTA^{2-}(aq) + HIn^2-(aq)\ (blue) + H^{+}(aq) \]

In this lab you will use a kit produced by the Hach Company to perform the analysis. This kit does not provide the same level of accuracy a buret-titration would, but it is a good example of the types of kits available for rapid field analysis.

**Chloride ions** are one of the most abundant anions present in wastewater, due to the constant intake and excretion of chloride ions by all animals as well as other anthropogenic activities (such as salting the streets in icy conditions). Therefore, it is a good indication of the presence of pollution in water samples. In this lab, you will use a standardized solution of silver nitrate (AgNO$_3$) to determine the concentration of Cl$^-$ via titration. Ag$^+$ combines with Cl$^-$ to form a white precipitate according to:

\[ Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \]

The endpoint of the titration is reached when all the chloride ions have reacted and the excess silver ion reacts with chromate (CrO$_4^{2-}$) to form an orange-red precipitate:

\[ 2Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4 \]

**Alkalinity** is a measure of the capacity of water to neutralize acids (see pH description). Alkaline compounds in the water (HCO$_3^-$, CO$_3^{2-}$, and OH$^-$) remove H$_3$O$^+$ ions, lowering the acidity (thus increasing pH). Without this acid-neutralizing capacity, acid added to a natural water source would cause an immediate and dramatic change in the pH. Measuring alkalinity is important in determining water's ability to neutralize acidic pollution from rainfall or wastewater.

Total alkalinity is measured by measuring the amount of acid needed to bring the sample to a pH of 4.2. At this pH all the alkaline compounds in the sample are "used up." The result is reported as mg/L (ppm) of calcium carbonate according to the reaction:

\[ CO_3^{2-} + 2H_3O^+ \rightarrow H_2CO_3 \]

In this lab you will measure total alkalinity via titration with HCl using an indicator for the endpoint.

**Total Dissolved Solids.** Total dissolved solids (TDS) are dissolved non-volatile chemical species plus suspended and settleable solids in water. In natural waters, this typically consists of calcium, chlorides, nitrate, phosphorus, iron, sulfur, and other particles that will pass through a 2 micron filter. Suspended solids include silt and clay particles, plankton, algae, fine organic debris, and other particulate matter. Dissolved ions affect the water balance in the cells of aquatic organisms, suspended particles may serve as carriers of toxics, a high concentration of total solids will make drinking water unpalatable.
In water with low amounts of organic matter, ions make up the vast majority of total dissolved solids, and thus conductivity may be used as a way of measuring TDS. In this lab, you will measure TDS using both conductivity as well as the more complete method of evaporating a sample of water. Total solids are measured in milligrams per liter (mg/L).

Safety Considerations:
Eye goggles should be worn at all times during this lab. Any material containing chromate or silver must be collected in a properly labeled waste container. The NaCl solutions can be poured down the drain if no other chemicals have been added to them.

Procedure and Analysis:

Station 1: pH, conductivity, pE

pH
1. If the pH meter is not already calibrated, follow your instructor's directions to calibrate it using standardized buffer solutions.
2. Rinse out a 100 mL beaker twice with a small amount of your sample. There is no need to dry the beaker.
3. Dispense about 50 mL of water (enough to cover the tip of the pH probe) into the beaker.
4. Remove the pH probe from the buffer solution and rinse thoroughly with distilled water into the provided waste beaker.
5. Wipe the excess distilled water from the tip of the probe with a Kim wipe.
6. Submerge the probe in your water sample and swirl gently a few times.
7. Wait for the pH meter to stabilize (may take a minute or two) and record the pH.
8. Remove the probe, rinse it with distilled water, and return it to the storage solution.

Conductivity and Total Dissolved Solids 1
9. Remove the probe from the storage solution and rinse thoroughly with distilled water into the provided waste beaker.
10. Wipe the excess distilled water from the tip of the probe with a Kim wipe.
11. Submerge the probe in your water sample.
12. Be sure the meter is in Conductivity mode. Wait until the meter stabilizes (may take a minute or two) and record the conductivity. Also record the temperature, but notice that the meter automatically converts to conductivity at 25 °C.
13. Push the TDS button on the meter. Record the amount of Total Dissolved Solids.
14. Remove the probe, rinse it with distilled water, and return it to the storage solution.

pE
15. Place the two electrodes into the solution.
16. Record the potential of the solution ($E_{measured}$) in mV.
17. Remove the probes, rinse them with distilled water, and return them to the storage solution.
18. Dispose of the sample in the beaker down the drain and rinse the beaker with distilled water.

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Station 2: Water Hardness via Hach kit

1. Use a graduated cylinder to add 100 mL of your water sample to an Erlenmeyer flask
2. Insert a clean, hooked delivery tube into the titration cartridge
3. Attach the titration cartridge to the Digital Titrator
4. Turn the knob to fill the delivery tube and eject a few drops of titrant
5. Reset the counter to 0
6. Add 2 mL of Hardness 1 Buffer
7. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow and swirl to dissolve
8. Place the delivery tube into the water.
9. Titrate to the endpoint, signaled by a color change from red to blue. Swirl the delivery tube in the sample constantly during the titration.
10. Check the tube of titrant for the concentration of EDTA. The calculation of total hardness as mg/L of CaCO$_3$ depends upon this concentration:
   a) If concentration is 0.800, total hardness is equal to the number read directly from the Digital Titrator.
   b) If concentration is 0.0800, total hardness is equal to the number on Digital Titrator divided by 10.

Station 3: Chloride concentration via titration

1. Fill a buret with AgNO$_3$ solution. Note the concentration of the solution
2. Using a graduated cylinder, dispense 25 mL of Ultra-pure water into an Erlenmeyer flask.
3. Accurately add 0.5 mL of the potassium chromate indicator solution. Add 2-3 drops of NaOH
4. Record the initial volume of AgNO$_3$ solution contained in the buret.
5. Titrate your water sample with the AgNO$_3$ solution to the end point of the titration, signaled by the persistence of an orange-red precipitate.
6. Once the endpoint is reached, record the final volume of AgNO$_3$ solution contained in the buret. This is the Blank Volume, which should be subtracted from all further titrations.
7. Using a graduated cylinder, dispense 25 mL of your water sample into an Erlenmeyer flask.
8. Using a graduated disposable pipette, add 0.5 mL of the potassium chromate indicator solution.
9. Record the color of the solution.
10. Add 2-3 drops of NaOH. Use a clean stirring rod to get a drop of the solution onto a strip of pH paper. If the solution is acidic, repeat.
11. If less than 40 mL are in the buret, refill it. Record the initial volume of AgNO$_3$ solution.
12. Titrate your water sample with the AgNO$_3$ solution to the end point of the titration. The end point occurs when the orange precipitate persists for at least 10 seconds.
13. Once the endpoint is reached, record the final volume of AgNO$_3$ solution contained in the buret.

Station 4: Alkalinity

1. Using a graduated cylinder, dispense 100 mL of your water sample into an Erlenmeyer flask.
2. Add 3 drops of methyl orange indicator solution. (If the starting color is orange-red, the alkalinity of your sample is 0, and you may skip the remaining steps).
3. Record the color of the solution.
4. Fill a buret with HCl solution. Record the concentration (should be roughly 0.02M).
5. Record the initial volume of the HCl solution contained in the buret.
6. Titrate your water sample with the HCl solution to the end point of the titration, signaled by the change from yellow to orange-red.
7. Once the endpoint is reached, record the final volume of HCl solution contained in the buret.
Station 5: *Total Dissolved Solids 2*

1. Label two 250 mL beakers
2. Place a watch glass on each beaker. Weigh each beaker/watch glass and record the masses.
3. Use a graduated cylinder to dispense 100 mL of your water sample into EACH beaker.
4. With the watch glasses in place, use a hot plate to *slowly* heat the beakers to a gentle boil.
5. Continue heating the beakers until all of the water has almost completely evaporated.
6. Use tongs to remove the beakers from the hot plate and transfer them to an oven set at 95 °C for 10 minutes so they will dry completely.
7. Use tongs to remove the beakers from the oven and allow them to cool completely.
8. Weigh each beaker with its watch glass and record the mass.

**Analysis**

*The following should be done in your notebook. You may choose to do this after the lab, but your lab will not be signed off, and your duplicate pages will not be accepted, until it is completed. This analysis should also appear in your formal lab report.*

1. **pE**: Convert the measured potential into volts (V) and calculate pE using the formulas from the Introduction.
2. **Chloride**: Calculate the Cl⁻ concentration in mol/L and ppm using the stoichiometric equations given in the Introduction.
3. **Alkalinity**: Calculate the alkalinity of the sample in ppm (mg/L) of CaCO₃ by finding the moles of HCl, converting to moles of CaCO₃, and then converting to mass of CaCO₃. Be sure to consult the stoichiometric equations given in the Introduction.
4. **TDS 2**: Calculate the Total Dissolved Solids as mg / L by the difference in mass of the beakers before and after evaporating.
5. Provide a table with the values for pH, pE, conductivity, hardness, chloride concentration, alkalinity, and total dissolved solids by both conductivity and evaporation. You will need to provide calculations for pE, chloride, alkalinity, and total dissolved solids.

**Conclusions**

*Answers to these questions must be included as part of your Conclusions in your written lab report. Include them in your Conclusions narrative, not as numbered list of questions and answers.*

1. Do a little research via the Internet to find typical ranges in natural waters for pH, conductivity, hardness, alkalinity, chloride concentration, and total dissolved solids. Present these values in table form in your report.
2. Comment on the overall quality of your water sample. Were any of your measurements particularly notable for being outside of the normal ranges for natural waters?