Introduction

The chemical components (hardness, dissolved oxygen, nitrates (NO$_3^-$), phosphates (PO$_4^{3-}$), heavy metals, pollutants etc.) of water can be measured by a variety of experimental techniques. We will explore one such technique, Titrations, to measure water hardness in several different samples.

Discussion

Water Hardness

Hard water water that has high mineral content and a common problem, affecting water in more than 85% of the country. It is a result of the dissolved minerals (ions in chemistry!) calcium (Ca$^{+2}$), magnesium (Mg$^{+2}$). Hard water forms when water percolates through deposits of limestone and chalk which are largely made up of calcium and magnesium carbonates and the metals are dissolved in the water.

![Concentration of Water Hardness in Grains Per Gallon](image)

Hard water can be a health benefit to humans (in moderation) but often has deleterious effects such as:

1. Soap scum in sinks and bathtubs forming rings
2. Spots on dishes or shower doors
3. Reduced foaming and cleaning abilities of soaps and detergents
4. Dingy and yellowed clothes with soapy residues that require extra rinsing to remove
5. Clogged pipes from buildup of minerals
6. Increased water heating costs from buildup of minerals, reducing efficiency of water heaters
Laboratory 8: Water Hardness

Chemistry

Water hardness can be determined by titration with a chelating agent (Greek for 'claw') that will bind the Ca$^{+2}$ and Mg$^{+2}$ ions. We will use EDTA (ethylenediaminetetraacetic acid) which is a weak acid that can lose 4 H$^+$ ions (bold) to when it binds the ions.

\[
\begin{align*}
\text{HOC-CH}_2\text{N-CH}_2\text{CH}_2\text{N-HOC} & \quad + \text{Ca}^{+2} \\
\text{HOC-O} & \quad \rightarrow \\
\text{H}_2\text{C-COH} & \quad \text{N-HOC-CH}_2\text{N-CH}_2\text{CH}_2\text{N-HOC} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

Titrations

Titrations are a standard technique used to determine the concentration of an unknown solution (a water sample) by chemically reacting it with a known solution (your EDTA solution). There are a variety of techniques for doing this, we will focus on the most basic technique realizing that we can apply it to more complicated problems if required.

If the reaction goes to completion, and the yield is 100%, then the concentration of the unknown solution can be determined through the stoichiometry (fancy chemistry term for the concentration or amount) of the chemical reaction. The completion of the reaction is determined by a variety of methods including color changes, pH, and electrical conductivity. Concentration is generally measured in terms of **Molarity** (M), which has units of (moles of solute/L of solution), or (mol/L) but since this is ENV 101, we will measure it in parts-per-million (ppm).

The **end point** of a reaction is the point at which the reaction is neutralized (the concentration of the reactants are equal) or 100% complete and is determined by using an **indicator**. Most indicators signal the end point of a reaction by changing colors, though other changes are possible. The indicator chosen for this reaction is Erichrome Black T, an organic dye, that is wine-red but turns to a blue color when the reaction is complete.

The standard instrument used in titrations is the **Buret** which is a piece of calibrated glassware used to accurately measure volumes of liquids. Figure 1 shows a typical example. The buret is filled with the solution (water sample) to be titrated and is often referred to as the titrant.

Volume measurements are made by reading the point on the graduated scale that coincides with the bottom of the curved surface called the **meniscus** of the liquid as shown in Figure 1. A discussion of why a meniscus is formed can be found in Hein Ch. 13.4, Chang Ch. 11.3, or McMurry Ch. 10.4.

![Figure 1: Typical schematic of a buret.](Image)
Laboratory 8: Water Hardness

Do not waste your time trying to fill the buret to the zero line or some other round number, because the exact volume to which the buret is filled is unimportant because we are measuring the difference in volume ($\Delta v$).

Titrant is added until just one drop changes the solution from wine-red to a blue color. The exact process will be demonstrated in class by your instructor. The final volume of liquid is then measured.

Using the volume of your water sample, the volume of EDTA used and the stoichiometry (don’t worry it’s easy) of the reaction it is then possible to determine the concentration of the Ca$^{2+}$ and Mg$^{2+}$ ions (or hardness).

Procedure

The following steps (as demonstrated by your instructor) should be performed at least 3 times (at least once by each student). When you have 3 good trials you may move on to the results section.

Preparing your water sample

1. Use a volumetric pipet to dispense 25.00 mL of your water sample into a 250 mL erlenmeyer flask.
2. Using a volumetric pipet, add 5.00 mL of pH 10 buffer solution to the 250 mL erlenmeyer flask.
3. Add 2 drops of Eriochrome Black T indicator to the 250 mL erlenmeyer flask.
4. Add 15 drops of 0.03 M MgCl$_2$ (Magnesium Chloride) to the 250 mL erlenmeyer flask.

Preparing your buret

1. Obtain a buret from your instructor. Check to see that the knob on the side turns.
2. Place your buret in the ring stand and clamp it in place.
3. Make sure the knob is in the off (horizontal position).
4. Using a funnel fill the buret with the EDTA solution to somewhere between 0-5 mL. The exact value does not matter as you will write it down.
5. Drain a small amount of EDTA from the buret to dispel any air bubbles that might be in the tip.
6. Using a funnel fill the buret with the EDTA solution to somewhere between 0-5 mL.
7. You are now ready to start a titration - make sure you record the initial volume of the buret in your data table.

Figure 2: How to read the volume of liquids using the meniscus.

Figure 3: Using a card to help read the meniscus.

Figure 4: Remove air bubbles from your buret.
Performing a titration

1. You are now ready to start a titration - make sure you record the initial volume of the buret in your data table.

2. For your first trial add the EDTA solution in the Buret 1 mL at a time. If you notice you are close to the color change, you may add the EDTA solution slower.

3. For your second (and all other) trials you should be able to add a large amount of EDTA quickly (about 90%) and then add it drop by drop near the end.

4. A successful titration should turn from wine-red to blue in 1-2 drops!

5. When the color change occurs, note the final volume of EDTA in the Buret.

6. You will need at least 3 'good' trials before you can analyze your data.

Good Techniques

The two figures below illustrate some good techniques to use when performing a titration. First to be super-duper accurate and precise you can add a half-drop instead of a full-drop at the end of the titration as shown in Figure 5. You can then rinse the drop into the flask as shown in Figure 6.

![Figure 5: Good Technique - Dispensing a half drop.](image1.png)  
![Figure 6: Good Technique - Rinsing the half drop into the flask.](image2.png)

Not that you can print the labs in color (we are too cheap for that), but if you look on the internet you can see the color change for the titrations.

![Figure 7: Color Change](image3.png)
Results

Titration Data

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
<th>Trial 5</th>
<th>Trial 6</th>
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</thead>
<tbody>
<tr>
<td>1. Volume of Water Sample::</td>
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<td>2. Initial buret reading:</td>
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<td>3. Final buret reading:</td>
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<td>4. Volume of EDTA delivered (show calculation):</td>
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<td>5. Hardness of Water (ppm) (show calculation):</td>
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Calculating Hardness

The following formula takes into account the stoichiometry of the chemical reaction (because this is not CHE 101/111) The Molarity of the EDTA is fancy-smancy chemistry lingo for strength. Your instructor will tell you the strength of the EDTA during the lab (assuming he is not senile and forgets).

\[
ppm \, Ca^{+2} = \frac{Volume \, EDTA}{Volume \, of \, Sample} \times Molarity \, EDTA \times 100,000
\]

Figure 8
Individual Results

Show all calculations in the space below the table.

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<th>Students:</th>
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<tbody>
<tr>
<td>Sample ID:</td>
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<tr>
<td>Trials Averaged:</td>
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<td>Average Hardness:</td>
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### Class Results

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### Questions

1. There are none! Jay got tired and went to bed. Maybe next year.
Hello. Make sure you keep reading and do the pre-lab assignment!
Prelab Questions

1. Define each of the following terms as they relate to the experiment:
   (a) Titration

   (b) End point

   (c) Indicator

   (d) EDTA

   (e) Hardness

   (f) Meniscus
<subliminal message>Doesn’t it feel wonderful to have read the lab?</subliminal message>