The Chemistry of Natural Waters

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Chemistry 111 Section 103

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Introduction

Water is such an omnipresent and universal compound, dominating the chemistry of all life on earth. Every species on earth needs water to survive, thus making it a very important resource for each of the seven billion humans on the planet. There exists approximately $1.5 \times 10^{21}$ L of water on earth. Nearly all of this water is not pure, but instead contains a variety of dissolved substances from all across the periodic table. For instance, the world’s oceans contain vast amounts of dissolved NaCl, acid rain contains dissolved H$_2$SO$_4$, and finally, most groundwater contains Ca$^{2+}$ and Mg$^{2+}$ cations.

It is the level of Ca$^{2+}$, Mg$^{2+}$, and other ions present in water that is used to measure water hardness. Water with a high level of these and other divalent cations is considered hard water, and similarly, water with low levels is said to be soft. The presence of cations like Ca$^{2+}$ and Mg$^{2+}$ in groundwater mainly comes from dissolved minerals that the water picks up as it flows. For example, the biggest sources of Ca$^{2+}$ are limestone (CaCO$_3$), dolomite (CaMg(CO$_3$)$_2$), and gypsum (CaSO$_4$ $\cdot$ 2H$_2$O).

Water hardness plays a very important role in everyday life and in industrial processes. For instance, soap works by weakening the bond between dirt and the surface being cleaned by using agents containing anions. If the water hardness level is relatively high, the anions in the soap will combine with the Ca$^{2+}$ and Mg$^{2+}$ cations and form soap scum. Also, water hardness can become a dilemma for industry. Industrial processes involving boiling and evaporation are especially problematic because minerals like calcite often precipitate out of the water and result in scale formation. This buildup on pipes is expensive to remove and can cause blockage.

The hardness of water varies around the United States considerably. New England, the South Atlantic-Gulf States, the Pacific Northwest, and Hawaii have the softest water. Relatively
speaking, areas near the coast have soft water. The hardest waters prevail in the northern part of the Midwest, beginning around Ohio, and dominate the west, before disappearing near the coast, again where soft water is found. Hard and very hard waters are found in some streams in most of the regions throughout the country.

Water hardness is measured in molarity (M), parts per million (ppm), and grains per gallon. The following table, taken from Fairfax County Water Authority, lists the classification of acceptable water hardnesses for tap water:

<table>
<thead>
<tr>
<th>Grains Per Gallon</th>
<th>Milligrams Per Liter (mg/L) or Parts Per Million (ppm)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>less than 1.0</td>
<td>less than 17.1</td>
<td>Soft</td>
</tr>
<tr>
<td>1.0 - 3.5</td>
<td>17.1 - 60</td>
<td>Slightly Hard</td>
</tr>
<tr>
<td>3.5 - 7.0</td>
<td>60 - 120</td>
<td>Moderately Hard</td>
</tr>
<tr>
<td>7.0 - 10.5</td>
<td>120 - 180</td>
<td>Hard</td>
</tr>
<tr>
<td>over 10.5</td>
<td>over 180</td>
<td>Very Hard</td>
</tr>
</tbody>
</table>

To determine the hardness of a water sample, a variety of testing methods can be used. One such method is analysis with ethylenediaminetetraacetic acid, or EDTA, by titration. An indicator, Eriochrome Black T, or EBT, is added first, along with an NH$_3$/NH$_4$ buffer to raise the pH. At this point the solution should be blue, but any Mg$^{2+}$ ions in the water sample will result in a wine red solution of EBT chelate because the Mg$^{2+}$ combines with the indicator. When EDTA is added, it combines with any Ca$^{2+}$ cations first and then with the Mg$^{2+}$ chelate, forming MgEDTA chelate. When all the Mg has been “used up” then the stopping point has been reached. A quantitative comparison of the moles of EDTA to the moles of divalent cations present in the water can then be performed.

Another method to determine the hardness of water is by atomic absorption spectrophotometry (AA). AA uses the fact that each element’s electrons have different levels of
energy in their relaxed and excited states, and promoting an electron from the relaxed state to the excited state takes a certain amount of energy for each element. To test for calcium and magnesium, energy in the form of certain wavelengths of light are passed through the sample. This sample has been turned into an aerosol at this point by a flame, so the sample is atomized. Any calcium will absorb light at 422.7 nm, and any magnesium will absorb light at 202.5 nm. The decrease in intensity in the light is measured by a computer in each machine, which uses the Beer-Lambert law to calculate the concentration of the metal being tested for.

EDTA titration and AA analysis both give qualitative values for the hardness of water; however, they differ in that EDTA titration gives the hardness as a result of every dissolved cation in the sample, and AA analysis gives the concentration of only one metal. Consecutive AA tests are needed for each metal in question – in this case, calcium and magnesium. EDTA titration, however, does not give the concentrations of each cation, only the total hardness. These two separate methods are used because they both give different results leading to a greater understanding of the content that makes up the hardness of the sample. EDTA gives the total hardness of the sample, while AA will give values for each individual metal tested.

There exist various techniques to soften water. One method to reduce the hardness of water is by using chemicals such as lime (Ca(OH)_2), washing soda (Na_2CO_3), or baking soda (NaHCO_3). These agents precipitate out the Ca^{2+} and Mg^{2+} ions as insoluble salts. Another technique is to use an exchange resin. In such cation exchange resins, divalent cations such as Ca^{2+} and Mg^{2+} are replaced with monovalent Na^+, K^+, or H^+ cations. Exchange resins also purify water by removing other divalent cations such as the barium and radium cations. Although slightly more expensive than other techniques, exchange resins are highly effective and result in substantially reduced scale buildup in industrial processes and softer water for drinking.
In this experiment, the members of my group and I tested water samples from various places around the northeast and east United States. My sample is from Monroeville, PA; Brandon’s sample is from Charlotte, NC; Kierstin’s sample is from Conway, SC; Kristen’s sample is from River Edge, NJ. Lastly, Carly’s sample was taken from a creek in Springfield, PA. All samples except the sample from Springfield were taken from a tap in a residential home.

Our hypothesis was as follows: the hardest water will be the water from the Springfield, PA creek, in the “very hard” range. The next hardest water will be my water from Monroeville, also in the “very hard” range. After that will be the sample from River Edge, NJ, in the “hard” range. Next will be the sample from Charlotte, NC, at “moderately hard”. Finally, the sample from Conway, SC will be the softest water, in the “slightly hard” range. Our hypothesis for the hardness of each sample was based off of a number of sources. The rock types of each area was considered, and also a government-produced map of water hardness. My sample from Monroeville was taken from an area with a mixture of sandstone, siltstone, shale, claystone, limestone, and coal. The sample from the creek in Springfield comes from an area that contains a variety of rocks and minerals, such as limestone and dolomite. The area that the sample from River Edge, NJ was taken from contains the sedimentary rocks siltstone, shale, sandstone, and conglomerate. Concerning the samples from North and South Carolina, these samples are near the coast, and should have relatively low hardnesses, according to the U.S. Geological Survey map. Lastly, the water from the creek should be the hardest because it is natural groundwater that came from a creek near the bottom of a hill – water picks up cations that contribute to water hardness as it flows down hills and mountains.
Procedure

The members of my group used various methods of testing for water hardness, all of which were taken from *PSU Chemtrek.*

The first method used to test for water hardness was AA analysis. Two large pipettes were filled with the water sample and tested by the machines, which gave values for Ca\(^{2+}\) and Mg\(^{2+}\), each individually. To do this, the machines drew water up from the test tubes and turned it into an aerosol. The aerosol was rapidly heated in a 2300 °C flame, which atomized the sample. The light from the lamp passed through the sample and any calcium or magnesium absorbed the light at their given wavelengths. The amount of light absorbed was then determined by the machine by looking at the intensity of the light that made it through the sample. The values obtained for calcium and magnesium were then used to determine the hardness of the sample in ppm. My sample, the sample from Monroeville, PA, had an Mg\(^{2+}\) concentration that was too high for the machine to give an accurate reading. I diluted this sample in a 1:1 ratio by mixing 5 ml of my sample with 5 ml of distilled water.

Next, my group members and I observed the total dissolved solids (TDS) of our samples, and quantitatively compared them to the TDS of distilled water and 1x10\(^{-3}\) M Ca\(^{2+}\) water. This was done by placing a drop of each sample onto aluminum foil and evaporating all water, leaving behind the non-volatile salts.

After that, divalent cation analysis of the water samples was done by EDTA titration. Before the samples of our water were tested, water with known amounts of Ca\(^{2+}\) and Mg\(^{2+}\) were tested with this method. Using this method, a drop of the sample was added to each well in a 12-well strip, followed by a drop of EBT indicator and a drop of NH\(_3\)/NH\(_4\)Cl/MgEDTA buffer. Then, serial titration was done with the EDTA solution. The first blue well indicates when all of
the ions have reacted. The molarity (and subsequently, the hardness in ppm) of the Ca\(^{2+}\) and Mg\(^{2+}\) could then be determined by using the known molarity of EDTA and the number of drops of each in the first blue well.

After testing for the hardness of our water samples, the members of my group and I used two water softening processes, and then tested our softened water using EDTA titration to determine how much softer each method made the water. First, samples of our water were softened using a commercial water-conditioning agent, baking soda. Next, samples of our water were softened using divalent cation removal by ion exchange, which involves mixing the water with a cation exchange resin. By looking at where the first blue well appeared, the hardness of the softened water was determined.

**Results**

*for each sample calculation shown below, similar calculations were performed to obtain the remaining values for the other samples.*

<table>
<thead>
<tr>
<th>Table 1: AA Calibration for Calcium and Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calcium</strong></td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>Calcium</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Magnesium</strong></td>
</tr>
<tr>
<td>Magnesium</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Table 1 shows the calibration data for each AA machine. The machines were calibrated using waters of known concentrations. The check standard gives feedback as to how the machines vary from the accepted value. The check standard should ideally be the same as the known concentration. Figure 1 and 2 shows the data from Table 1 as a plot. A best fit line and equation was generated from the points, which was then used to convert the absorbance values from our samples to the concentration in ppm.
Table 2: Water Hardness as Determined by AA Spectrophotometry Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Code</th>
<th>Ca(^{2+}) Absorbance Value</th>
<th>Mg(^{2+}) Absorbance Value</th>
<th>Total Hardness (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monroeville, PA(^9)</td>
<td>Ca(^{2+})</td>
<td>0.4300</td>
<td>0.2217</td>
<td>240.1</td>
</tr>
<tr>
<td></td>
<td>Mg(^{2+})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charlotte, NC(^10)</td>
<td>Ca(^{2+})</td>
<td>0.1758</td>
<td></td>
<td>69.73</td>
</tr>
<tr>
<td></td>
<td>Mg(^{2+})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conway, SC(^11)</td>
<td>Ca(^{2+})</td>
<td>0.1514</td>
<td>0.0329</td>
<td>45.49</td>
</tr>
<tr>
<td></td>
<td>Mg(^{2+})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>River Edge, NJ(^12)</td>
<td>Ca(^{2+})</td>
<td>0.4453</td>
<td></td>
<td>159.01</td>
</tr>
<tr>
<td></td>
<td>Mg(^{2+})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Springfield, PA (creek)(^13)</td>
<td>Ca(^{2+})</td>
<td>0.3566</td>
<td></td>
<td>177.0</td>
</tr>
<tr>
<td></td>
<td>Mg(^{2+})</td>
<td></td>
<td></td>
<td>0.2882</td>
</tr>
</tbody>
</table>

*The sample from Monroeville was diluted in a 1:1 ratio before testing for Mg\(^{2+}\).*

Table 2 shows the absorbance values that the machines gave for each water sample. From these values, the total hardness in ppm was determined by using the equations below.

**Equation 1: Ca\(^{2+}\) Calibration Equation to Determine Ca\(^{2+}\) Concentration from Absorbance Value**

\[
y = 0.0093x + 0.0017
\]

Sample Calculation:

Charlotte, NC:

\[
0.1758 = 0.0093x + 0.0117
\]

\[
x = 17.65 \text{ ppm Ca}^{2+}
\]

**Equation 2: Mg\(^{2+}\) Calibration Equation to Determine Mg\(^{2+}\) Concentration from Absorbance Value**

\[
y = 0.0138x + 0.0063
\]

Sample Calculation:

Charlotte, NC:

\[
0.0921 = 0.0138x + 0.0063
\]

\[
x = 6.218 \text{ ppm Mg}^{2+}
\]

Equations 1 and 2 come right from the best fit line of Figure 1 and 2. Using these equations, the absorbance value for either Ca\(^{2+}\) or Mg\(^{2+}\) is used to calculate the corresponding
concentration of Ca\(^{2+}\) or Mg\(^{2+}\) in ppm. These concentrations were then converted into their equivalent concentrations of CaCO\(_3\), which are the units for water hardness.

**Equation 3: Conversion of Ca\(^{2+}\) Concentration to Equivalent Concentration of CaCO\(_3\) (hardness)**

\[
\frac{[(100 \text{ g CaCO}_3)/\text{mole}]}{[\text{ppm Ca}^{2+} \times [(40.0 \text{ g Ca}^{2+})/\text{mole}]} = \text{ppm CaCO}_3 = \text{ppm hardness}
\]

Sample Calculation:

Charlotte, NC:

\[
\frac{[(100 \text{ g CaCO}_3)/\text{mole}]}{17.65 \text{ ppm Ca}^{2+} \times [(40.0 \text{ g Ca}^{2+})/\text{mole}]} = 44.13 \text{ ppm CaCO}_3 = 44.13 \text{ ppm hardness}
\]

**Equation 4: Conversion of Mg\(^{2+}\) Concentration to Equivalent Concentration of CaCO\(_3\) (hardness)**

\[
\frac{[(100 \text{ g CaCO}_3)/\text{mole}]}{[\text{ppm Mg}^{2+} \times [(24.3 \text{ g Mg}^{2+})/\text{mole}]} = \text{ppm CaCO}_3 = \text{ppm hardness}
\]

Sample Calculation:

Charlotte, NC:

\[
\frac{[(100 \text{ g CaCO}_3)/\text{mole}]}{6.218 \text{ ppm Ca}^{2+} \times [(24.3 \text{ g Ca}^{2+})/\text{mole}]} = 25.59 \text{ ppm CaCO}_3 = 25.59 \text{ ppm hardness}
\]

Equations 3 and 4, taken from *PSU Chemtrek*\(^2\), show how the concentrations of Ca\(^{2+}\) and Mg\(^{2+}\) are converted into their equivalent concentrations of CaCO\(_3\). The concentrations are multiplied by the ratio of the molar mass of CaCO\(_3\) to the molar mass of either Ca\(^{2+}\) or Mg\(^{2+}\). The resulting concentration is the “hardness” of the water due to Ca\(^{2+}\) or Mg\(^{2+}\). For my sample from Monroeville, PA, it was at this point that I doubled the value for the hardness due to Mg\(^{2+}\), because it was originally diluted in a 1:1 ratio\(^9\). Finally, to get the total hardness of the sample, as shown in Table 2, the hardness due to Ca\(^{2+}\) is added to the hardness due to Mg\(^{2+}\).
Equation 5: Total Hardness of Water Sample

\[
\text{total ppm hardness} = \text{ppm hardness due to Ca}^{2+} + \text{ppm hardness due to Mg}^{2+}
\]

Sample Calculation:

Charlotte, NC:

\[
\text{total ppm hardness} = 44.13 \text{ ppm hardness} + 25.59 \text{ ppm hardness}
\]

\[
\text{total ppm hardness} = 69.72 \text{ ppm}
\]

Table 3: Observations for Total Dissolved Solids (TDS)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00 \times 10^{-3} M Ca^{2+} standard</td>
<td>Faint, but still visible white residue</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>Barely visible, if any, white residue</td>
</tr>
<tr>
<td>Monroeville, PA</td>
<td>Observation compared to 1.00 \times 10^{-3} M Ca^{2+}</td>
</tr>
<tr>
<td>Charlotte, NC</td>
<td>Much more visible white circle</td>
</tr>
<tr>
<td>Conway, SC</td>
<td>More visible white circle, but almost same as standard</td>
</tr>
<tr>
<td>River Edge, NJ</td>
<td>Visibly whiter</td>
</tr>
<tr>
<td>Springfield, PA (creek)</td>
<td>Much darker white ring</td>
</tr>
</tbody>
</table>

Table 3 lists the qualitative, visual observations of the non-volatile salt residue left behind (TDS) after drops of each sample were evaporated, including how the samples compared to a 1.00 \times 10^{-3} M Ca^{2+} standard.

Table 4: Water Hardness as Determined by EDTA Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of Ca^{2+} and Mg^{2+} (M)</th>
<th>Hardness (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monroeville, PA</td>
<td>1.9 \times 10^{-3}</td>
<td>190</td>
</tr>
<tr>
<td>Charlotte, NC</td>
<td>6.0 \times 10^{-4}</td>
<td>60</td>
</tr>
<tr>
<td>Conway, SC</td>
<td>6.0 \times 10^{-4}</td>
<td>60</td>
</tr>
<tr>
<td>River Edge, NJ</td>
<td>1.7 \times 10^{-3}</td>
<td>170</td>
</tr>
<tr>
<td>Springfield, PA (creek)</td>
<td>1.6 \times 10^{-3}</td>
<td>160</td>
</tr>
</tbody>
</table>

Table 4 gives the hardness of each sample in the group obtained by performing serial titration with EDTA.
Equation 6: Concentration of Ca$^{2+}$ and Mg$^{2+}$ in sample

Given: moles of EDTA = moles of Ca$^{2+}$ and Mg$^{2+}$ in sample

\[ M_{\text{EDTA}} \cdot V_{\text{EDTA}} = M_{\text{sample}} \cdot V_{\text{sample}} \]

Sample Calculation:

Charlotte, NC:

\[(2.0 \times 10^{-4} \text{ M}) \cdot (3 \text{ drops EDTA}) = (M_{\text{sample}}) \cdot (1 \text{ drop sample})\]

\[ M_{\text{sample}} = 6.0 \times 10^{-4} \text{ M} \]

Equation 7: Determining Hardness (ppm) from Concentration (M)

Given: molarity of Ca$^{2+}$ and Mg$^{2+}$ = molarity of CaCO$_3$

\[
\text{Hardness (ppm)} = \frac{M_{\text{sample}}}{1 \text{ L solution}} \times \frac{100 \text{ g CaCO}_3}{1 \text{ mole CaCO}_3} \times \frac{1000 \text{ mg}}{1 \text{ g CaCO}_3}
\]

Sample Calculation:

Charlotte, NC:

\[
\text{Hardness (ppm)} = \frac{6.0 \times 10^{-4} \text{ M}}{1 \text{ L solution}} \times \frac{100 \text{ g CaCO}_3}{1 \text{ mole CaCO}_3} \times \frac{1000 \text{ mg}}{1 \text{ g CaCO}_3}
\]

\[ \text{Hardness} = 60 \text{ ppm} \]

The number of the first blue well in the 12-well strip is equal to the number of drops of EDTA. This was noted, and then another trial was done, and the two numbers were averaged. The resulting number of drops was plugged into equations 6 to find concentration of Ca$^{2+}$ and Mg$^{2+}$. Then, the hardness in ppm was found with Equation 7.
Table 5: Water Hardness after Various Softening Techniques (Determined by EDTA Analysis)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness after Commercial Softening Agent (ppm)</th>
<th>Hardness after Cation Resin Exchange (ppm)</th>
<th>pH of Sample Before Resin</th>
<th>pH of Sample After Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monroeville, PA</td>
<td>160</td>
<td>&lt; 20</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>Charlotte, NC</td>
<td>80</td>
<td>40</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Conway, SC</td>
<td>N/A</td>
<td>N/A</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>River Edge, NJ</td>
<td>140</td>
<td>60</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>Springfield, PA (creek)</td>
<td>100</td>
<td>40</td>
<td>7</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 5 shows the hardness of the group’s water samples after being softened with 1) a commercial water conditioning agent, and 2) divalent cation removal by an ion exchange resin. The pH of the samples before and after the resin is shown to illustrate that the resin replaces the divalent cations with H\(^+\) cations. The sample from Conway, SC was not softened and tested because it was found to be too soft to use for this section of the experiment, as stated in the procedures in *PSU Chemtrek*.\(^2\)

**Discussion**

The results of the AA analysis, TDS observation, and EDTA titration all support each other when comparing each sample. My sample, from Monroeville, PA, was clearly the hardest out of all the samples, yielding a hardness of 240.1 ppm by AA analysis, 190 ppm by EDTA analysis, and leaving the most visible circle of residue in the TDS observation. These results give my sample a classification as “very hard”. The data indicates that the next hardest water after the Monroeville sample was either Carly’s creek sample from Springfield, PA, or Kristen’s sample from River Edge, NJ. On the AA machines, the Springfield sample triumphed over the River Edge sample, with 177.0 ppm to 159.01 ppm. However, after EDTA analysis, the River Edge sample was actually found to be harder, at 170 ppm, compared to 160 ppm for the Springfield sample. As for TDS, both samples looked about the same, and both were less visible than my sample, although still very visible. As a result of this discrepancy in the data, the
samples from Springfield and River Edge can, for all intents and purposes, be considered to have the same level of hardness, at a “hard” level classification. Next, Brandon’s sample from Charlotte, NC was the second softest water sample acquiring a “moderately hard” rating, with a value of 69.73 ppm by AA analysis, 60 ppm by EDTA titration, and a TDS observation that was more visible than the CaCl\(_2\) standard. Lastly, Kierstin’s sample from Conway, SC was found to be the softest water in the group, receiving a “slightly hard” rating, with AA analysis giving a value of 45.49 ppm, EDTA titration giving a value of 60 ppm, and a TDS observation that looked similar to the standard and less visible than all samples in the group.

The obtained results agree with the hypothesis to a considerable degree; the only discrepancy between the hypothesis and the results is that instead of the Springfield creek sample being the hardest, my sample from Monroeville was found to be the hardest. Also, the River Edge and Springfield sample were found to be roughly the same hardness. Other than that, the prediction that the softest water would be from Conway, followed by Charlotte, and then by Springfield, was supported by the results of the experiment. Also, the classification predictions all were supported by the results with the exception being that the Springfield sample had a classification of “hard” instead of “very hard”.

The water softening methods had varying degrees of effectiveness on the water samples. In general, the exchange resin softener outperformed the baking soda commercial softener. My water went from 190 ppm to <20 ppm using the resin exchange, but only went from 190 ppm to 160 ppm using baking soda. Others in my group reported similar results, with the exception of Brandon and his Charlotte, NC sample, which increased in hardness by 20 ppm after the baking soda and decreased by 20 ppm with the resin exchange. This increase in hardness may just be a result of the error associated with EDTA analysis, as discussed below. The decrease in pH of the
samples from about 7 or 8 to about 2 or 3 is a result of the divalent cations \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) being replaced with \( \text{H}^{+} \) ions.

Every sample had some type of error between the AA results and the EDTA results. Three of the five samples were found to be harder when tested with the AA machines as opposed to EDTA titration. Possible sources of error include slight contamination with distilled water when transferring the samples, although good-transfer technique was used so little, if any error can be attributed to this. Also, variations in the drop size of the pipette when performing EDTA titration may have contributed to most of the error. Although the same pipette was used, slightly different sizes of drops may have occurred. Finally, the AA machines are not perfect, and may have given some error, although most likely this error would be small. Between the two methods, AA is far more accurate than EDTA titration. With regards to EDTA titration, if the first well to turn blue happened to do so one well later, then the corresponding increase in hardness would be 20 ppm. This is what happened when analyzing my sample during between trial 1 and trial 2, thus giving me an average of 190 ppm. This severely limits the accuracy of this method. The AA machines have a much smaller error, as evidenced by the check standard values. The check standard values should ideally be the same as the actual known concentrations. As shown above in the check standards, they are close to the known concentrations at a magnitude that would definitely give a more precise error than 20 ppm.

**Conclusions**

Water hardness varies around the eastern United States considerably, as predicted by the rock types and elevations of the areas in question and by the maps provided by the US Geological Survey. My water sample from Pittsburgh, PA was found to be the hardest, at 240.1 ppm. The next hardest sample, at 177.0 ppm, came from a creek in Springfield, PA. After that
were the sample from River Edge at 159.01 ppm, and the sample from Charlotte, at 69.73 ppm. The softest water sample came from Conway, SC, at 45.49 ppm. The values obtained from AA analysis were listed here because, as discussed above, it is a more accurate method to determine water hardness. The results of this experiment agree with the expected hardnesses of water found in each area that the samples were taken from, when considering the rock types, elevation, and any maps provided by the USGS.

References


11. Hughes, Kierstin. Chem 111 Laboratory Notebook. 41-47.
