The Chemistry of Natural Waters

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Introduction:

The water we drink, the water that falls from the sky in the form of rain and the water our pools are filled with all have different degrees of hardness to them. Hardness doesn't refer to actually how solid the water is but rather the concentration of ions and salts in a given sample of water, more specifically the concentration of magnesium and calcium ions. The higher the amount of Mg^{+2} and Ca^{+2} cations the harder the water and visa versa the lower the amount the softer the water. The term "hard" has been used for a very long time; it arose from how hard it is to clean up the scum left behind when soap and hard water come in contact. The negative charges within soap molecules attract the positive cations found in hard water, the result of this combination is an insoluble scum. The scum that forms is then harder to clean up, so the harder the water the more scum and in turn the harder it is to clean it up. Mg^{+2} and Ca^{+2} ions aren't just found in water, they get picked up as the water travels through the ground, streams and other places where the water comes in contact with calcium and magnesium containing rocks and minerals. When water comes in contact with these different types of rocks they give off the various hardening ions (1). Hard water doesn't just taste a bit different it also causes many problems.

The hardness of water isn't a joke. In many industries and even in our own daily lives water hardness is a concern due to the many problems that it can create. Hard water in industrial equipment like evaporators and boilers is heated to temperatures where evaporation can occur. When hard water evaporates, it leaves behind crystals, mainly calcite crystals, which results in scale formation. Scale builds up in pipes, on evaporator surfaces and can even block hoses and jets. Especially when narrower pipes get clogged, it can be very expensive to remove and in some cases it is impossible to remove. Scale can also block heat being transferred in boilers, this leads to the loss of money because more work then has to be done in order to get the same energy quantity. These problems can generally be seen at any plant or area that requires a massive amount of water (2). Taking a shower, doing laundry and washing dishes all require water and with hard water all these day-to-day activities would eventually lead to problems. When bathing or taking a shower in hard water, soap mixes with the water and forms a film of soap curd, which can prevent removal of dirt and bacteria as well as can cause irritations of the skin. Clothing washed in hard water will be scratchy and discolored, as well as the life of the clothing will be shortened. This is due to the hardness minerals mixing with any soil and dirt on the clothing, this reaction creates, harder to clean, insoluble solids. The same principle of cleaning cloth applies to the cleaning of dishes, the detergent mixes with the harder water and in turn spotting occurs (3). Little changes in Mg^{+2} amounts in our bodies can also have a devastating affect; it can cause effects on vascular tone and cardiac excitability (3.5). Since the hardness of water cannot just be observed by looking at a sample, there are multiple ways of measuring and figuring out how hard a water sample is.

There are multiple ways of measuring and figuring out just how hard a sample of water is. A basic but not always accurate way of testing the hardness of water is to use a TDS determination. TDS stands for Total Dissolved Solids, it measures the amount of residue left behind when the water is evaporated. The reason that TDS isn't always efficient is because the residue left behind doesn't have to be Mg^{+2} and Ca^{+2} ions, for example the residue can be from salt (NaCl) and in that case the sample would leave residue but the hardness would be zero. TDS is used to get an idea of how hard a sample might be but there are multiple other ways to test hardness that are a lot more effective and give more accurate results (2).

One of these more effective methods includes Atomic Absorption Spectroscopy, or AA. The purpose of AA is to determine if a sample of a liquid contains any types of metal, these metals can include anything from calcium to zinc and many more. In the case of this lab the use of AA was to determine the concentration of Ca^{+2} and Mg^{+2} in the multiple water samples. AA works by burning the sample and sending a beam of UV light through the flame, a diagram of this cycle can be seen in Figure 1. The specific metals when heated absorb specific wavelengths of light, so when looking for if a specific metal is present in a sample the machine will send that specific wavelength through the flame and measure the intensity of the light that made it through the flame. The intensity measured is converted by the machine into the absorbance value of the metal and from the absorbance value the concentration of the metal in the sample can be determined (4). AA and TDS aren't the only ways to determine hardness there is also EDTA.

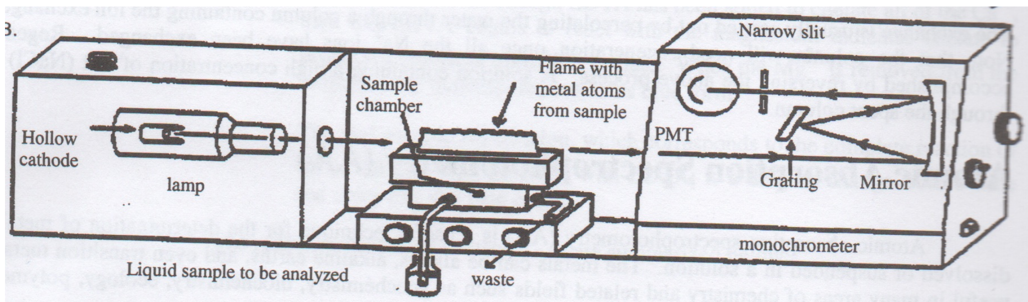

Figure 1: The inner workings of an atomic absorption spectrophotometer (2).

A ethylenediaminetetraacetic acid complexation titration or an EDTA titration is another way to determine the hardness of a water sample. The reaction can be seen below.

$$HD^{2-} + Mg^{2+} + Ca^{2+} \rightarrow MgD^{-} + H^{+} + Ca^{2+} \rightarrow CaEDTA + MgEDTA + HD^{2-}$$

Blue   Red   Blue

By adding various indicators and EDTA solutions, the hardness of the water can be determined. EBT indicator, originally a blue color, reacts with the Mg^{+2} ions in the sample and the combined mixture turns a reddish color. Since EBT only reacts with the Mg^{+2}, in order to find out if Ca^{+2} is present EDTA has to be used. The EDTA at first will only react with Ca^{+2} creating a colorless chelate, but once enough EDTA is added it will use up all the Ca^{+2} and will begin reacting with the Mg^{+2}. The Mg^{+2} will eventually be used all up and the EBT will go back to its original blue color. The less EDTA needed to turn blue, the softer the sample is (5). Both the AA and the EDTA analyses work in determining the hardness of water, but it is always more beneficial to use more then one method in order to show confirmedness and that the results are accurate. AA spectroscopy is more accurate but is also a lot more expensive than doing an EDTA titration (2).

Figuring out the hardness of water is beneficial but unless the hardness can be brought down to a softer level it means nothing. Hard water can be made softer in multiple ways, but in this lab baking soda and cation exchange resins were used. The baking soda contains sodium carbonate, the water utilizes the sodium within this compound and the divalent cations are broken off and replaced by Na^{+}. This process softens the water to a degree (2). Another method seen in this lab was the use of ion exchange resin as a softener. Ion exchange is a process that exchanges the hard ions of Mg^{+2} and Ca^{+2} for either Na^{+} or K^{+} ions. The resin is coated with Na^{+} and K^{+} ions, when the resin and the water come together the ions are exchanged. For every divalent cation taken from the water, two monovalent cations take its place. After the exchange is made the resin holds onto the Mg^{+2} and Ca^{+2} ions making the water softer (6).

The samples being tested in this experiment included tap water from the Brumbaugh in East Halls located on the Penn State University Park campus. That same tap water filtered through a Brita Water Filter once and then another sample filtered twice through a Brita Filter. The last two samples included rainwater and a DeePark bottled water sample, the DeerPark water was the sample I tested. The hypothesis that we formulated for this experiment is that the samples, which have been filtered and cleaned the most, will be the least hard and in turn will contain the least amount of Mg^{+2} and Ca^{+2} ions. The reason for this belief is that the more filtering the water goes through the more divalent cations are lost and as a result the water becomes softer. For example, Brita Filters contain some ion exchange resins, as the water is filtered it is also losing some Mg^{+2} and Ca^{+2} cations due to the resins. As the hard cations exchange with the monovalent cations, the water becomes softer (7).

Procedure:

In Section A water hardness was determined using Atomic Absorption Spectroscopy. AA is done by running a sample through two separate machines, one looking for the absorbance of Ca^{+2} and the other looking for the absorbance of Mg^{+2}. The absorbencies were later used in calibration graphs to find the concentration of each ion in the sample. In section B the technique used to determine hardness is Total Dissolved Solids or TDS. This was done by placing a drop of the water sample, a drop of distilled water and one of Ca^{+2} solution on a piece of aluminum foil a distance from one another. Once the three samples evaporated compare the residues left behind. Section C introduced how to use EDTA and what to look for when using it as a hard water tester. Part one used in this section showed what colors should be seen during EDTA and part two gave practice in how to use EDTA before actually testing our sample. EDTA works by using a solution and adding EBT indicator as well as a buffer. Once these are all mixed together, EDTA was added to the solutions until they turn blue. The amount of drops needed to turn it blue was put through a formula that gives the concentration. Section D used the same process but now the actual water sample was used instead of Ca^{+2} and Mg^{+2} solutions like used in Section C. The process of how baking soda softens water was observed in Section E. Another type of softening technique was seen in Section F, which was softening by the use of ion exchange resin. Since my sample was already pretty soft, I used a Ca^{+2} solution instead. Then the final section, Section G, showed multiple ways of expressing the hardness of water like ppm and grains per gallon (2).

Results:

Table 1: The absorbance values from AA Spectroscopy.

Magnesium and Calcium Absorption Values from AA

Water Sample	Calcium Absorption	Magnesium Absorption
DeerPark Bottled Water (8)	0.0610	0.0612
Tap Water(9)	0.3469	0.2931
Tap Water Brita Filtered Once(10)	0.0901	0.2579
Rainwater(11)	0.0149	0.0112
Tap Water Brita Filtered Twice(12)	0.0306	0.1479

The values were obtained from two AA machines and were the values used to determine concentration of metals.

Table 2: The checked standards for Calcium.

AA Checked Standards for Ca^{+2}

Ca^{+2} Concentration (ppm)	Ca^{+2} Absorbance Value(at 422.7nm)	Check Standard (ppm)
1.000	0.01396	0.97
5.00	0.06464	4.67
10.00	0.11952	9.30
25.0	0.27555	24.41
50.0	0.49527	49.76

This table was used to create the calibration graph for Calcium.

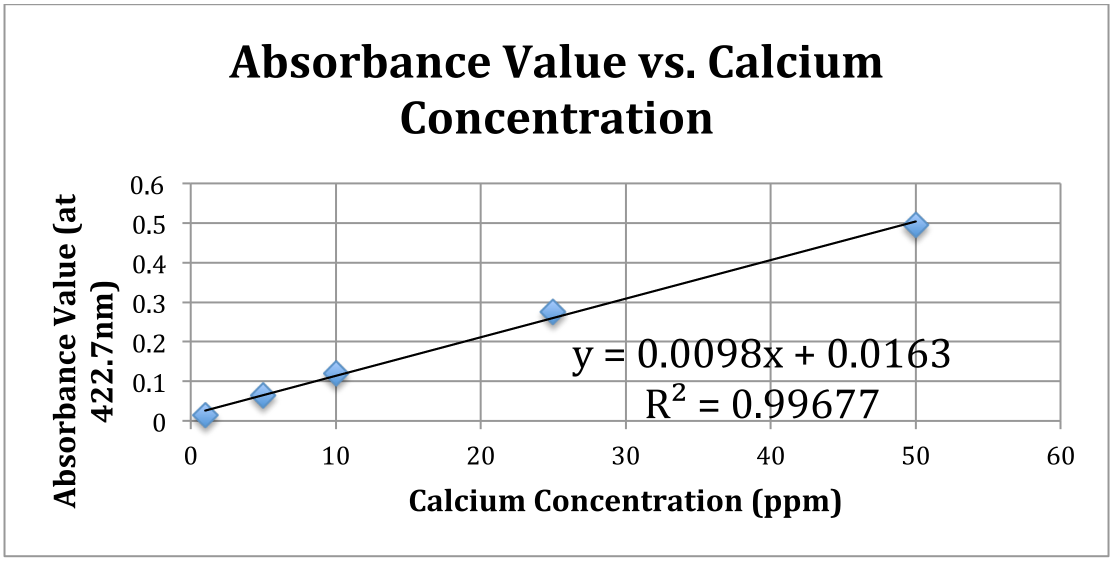

Figure 2: This calibration graph gives the curve that will allow me to get the hardness of calcium in samples by plugging in absorbance values.

Table 3: The check standards for Magnesium.

AA Checked Standards for Mg^{+2}

Mg Concentration (ppm)	Mg Absorbance Value (at 202.5nm)	Check Standard (ppm)
1.000	0.01370	0.81
5.00	0.09067	5.06
10.00	0.19378	10.75
25.0	0.41642	24.87
30.0	0.48433	30.68

By using these check standards I was able to create the calibration graph for Magnesium.

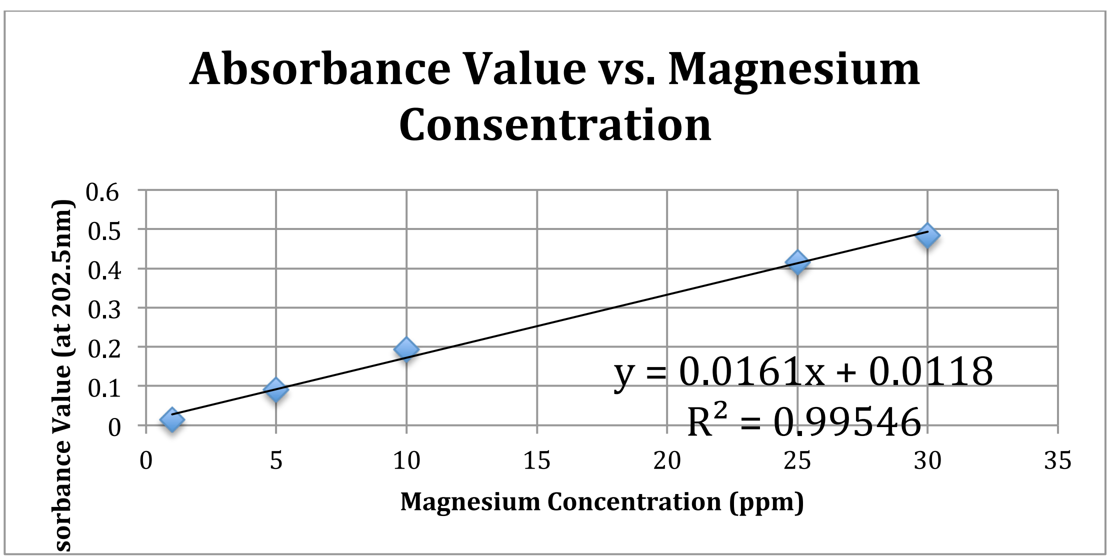

Figure 3: This calibration graph shows the curve that will let me get the hardness of Magnesium in the samples based on their absorbance values.

Table 4: Concentrations calculated using the absorbencies from Table 1 and the formulas of the best fit line from Figures 2 and 3.

Concentration of Calcium and Magnesium from Calibration Graphs

Water Sample	Concentration of Calcium (ppm)	Concentration of Magnesium (ppm)	Total Concentration (ppm)
DeerPark Bottled Water (8)	11.25	12.63	23.88
Tap Water(9)	169.36	144.94	314.30
Tap Water Brita Filtered Once(10)	18.80	63.00	81.80
Rainwater(11)	0	0	0
Tap Water Brita Filtered Twice(12)	3.65	34.79	38.44

The formula and an example of how I got these values can be seen below.

Formula for concentration of Calcium and DeerPark bottled water sample calculation:

Formula: y=0.0098x+0.0163

Sample calculation: 0.0610=0.0098x+0.0163 : x=4.56Ca^{+2} ppm

$$1ppm\ Ca^{+2} \times \left[\frac{\frac{100g\ CaCO_3}{1mole}}{\frac{40.0g\ Ca^{+2}}{1\ mole}}\right] = 2.5ppm\ CaCO_3\ = 2.5ppm\ hardness$$

$$4.56ppm\ Ca^{+2} \times \left[\frac{\frac{100g\ CaCO_3}{1mole}}{\underline{40.0g\ Ca^{+2}}}\right] = 11.25ppm\ CaCO_3\ = 11.25ppm\ hardness$$

Formula for concentration of Magnesium and DeerPark bottled water sample calculation:

Formula: y=0.0161x+0.0118

Sample calculation: 0.0612=0.0161x+0.0118: x=3.07Mg^{+2} ppm

$$1ppm\ Mg^{+2} \times \left[\frac{\frac{100g\ CaCO_3}{1mole}}{\frac{24.3g\ Mg^{+2}}{1\ mole}}\right] = 4.12ppm\ CaCO_3\ = 4.12ppm\ hardness$$

$$3.07ppm\ Ca^{+2} \times \left[\frac{\frac{100g\ CaCO_3}{1mole}}{\frac{24.3g\ Mg^{+2}}{1\ mole}}\right] = 12.63ppm\ CaCO_3\ = 12.63ppm\ hardness$$

Table 5: Hardness values from EDTA Titration results.

EDTA Value results

Water Sample	EDTA Value for Sample (ppm)
DeerPark Bottled Water (8)	60
Tap Water(9)	320
Tap Water Brita Filtered Once(10)	100
Rainwater(11)	40
Tap Water Brita Filtered Twice(12)	100

The formulas for the values above can be seen below.

Sample problem for how the EDTA value was found:

Formula: $M_{EDTA} \cdot V_{EDTA} = M_{water} + V_{water}$

$2.00\times10^{-4} \cdot 3_{drops} = M_{water} + 1_{drops}$: $M_{water} = 6.00\times 10^{-4}M$

$$\frac{6.00\times10^{-4} moles}{1\ Liters\ of\ Solution}\times\frac{100.0g}{1\ mole}\times\frac{1000mg}{1g} = 60ppm$$

Side note:
V-Volumes are measured in drops
M-concentration

Table 6: Total Dissolved Solids (TDS) results.

TDS Titration Results

Water Sample	TDS analysis results
DeerPark Bottled Water (8)	Faint residue line around outer edge of drop, fainter residue than Ca^{+2} solution.
Tap Water(9)	Darker and much heavier ring of residue than Ca^{+2} solution.
Tap Water Brita Filtered Once(10)	Darker and heavier ring of residue than Ca^{+2} solution.
Rainwater(11)	Extremely faint, the lightest residue rings.
Tap Water Brita Filtered Twice(12)	Residue line about the same as the Ca^{+2} solution.

The Ca^{+2} solution is a base that the other results were compared to, the heavier the sample the more residue left behind.

Table 7: The softening results from my sample.

Softening Results from Baking Soda and Resin

Water Sample	Original Molarity	Baking Soda	Resin
DeerPark Bottled Water (8)	6.0x10^-4	6.0x10^-4	N/A

Only my values were included because no exchange of the others took place, my resin didn't apply since I used the Ca^{+2} solution instead of my sample since it was already soft.

Discussion:

My hypothesis for this lab states that the water sample that has gone through the most filtrations and cleaning will be the least hard and will contain the least amount of Mg^{+2} and Ca^{+2} ions. DeerPark water, tap water, BRITA filtered once water, BRITA filtered twice water and rainwater were the five samples that we tested. The results from the tests done in this experiment agree with our hypothesis and the reasons why can be seen below.

The first sample in question in determining the water hardness was the DeerPark water sample. The atomic absorption spectroscopy results, seen in Table 1, for Calcium absorption were 0.0610 and for Magnesium 0.0612. These absorptions were plugged into the best-fit lines of Figure 2 and 3; the results received from this can be seen in Table 4. The results showed the total concentration of hardness ions to be 23.88ppm. The results from this test correlate closely with the results seen in the EDTA titration values, which are shown in Table 5. The EDTA value for this sample was 60ppm. Which is a little higher than the AA value found, the reason for this will be explained later (8). The results found from these tests agree with what I found online on the DeerPark website. The company website stated that the range of Calcium can go from 0.86 – 44.1ppm and the range of Magnesium can go from ND-9.1ppm (13). The results I found and the actual results found from the DeerPark company website agree with one another, my results fit within the range given on the website. Since the TDS result gave a faint line of residue, compared to the residue left behind by the Ca^{+2} solution, when evaporated, the DeerPark sample has some type of hardness but a very low amount. This is due to that DeerPark collects water from springs high up in the mountains. The water is softer at the top of the mountain since it hasn't had time to pick up any minerals as it would if it continued downstream (8).

The next sample that was tested was the tap water sample, which was suspected to be the hardest of our water samples. Since this sample was extremely hard to begin with, it was diluted to a 1:1 ratio of distilled water to tap water. The AA spectroscopy results for the absorption value of Calcium and Magnesium from Table 1 are 0.3469 and 0.2931. The results were then sent to Figure 2 and 3 to be plugged into the best-fit line formulas, which gave the results seen in Table 4. The total concentration of hardness ions in tap water was calculated to be 314.30 ppm (9). 314.30ppm is a lot higher than the value found on the State College water website that stated the hardness to be between 120-190ppm (14). The reason for theses results could either be due to that the dilution wasn't correctly done or the information provided by my teammate was wrong. The EDTA value calculated is very precise when compared to the AA value. Table 5 provided this EDTA hardness value, which was concluded to be 320ppm. Another result that contributed to the degree of hardness of the tap water was the TDS result. Tap water gave a heavier and much darker residue when compared to the Ca^{+2} solution, the darkest out of all the water samples, this was found from Table 6 (9). The water from State College comes from groundwater that comes from wells that naturally picks up minerals that cause hardness. This is why the tap water is the hardest of our water samples (14).

Tap water that was filtered once through a BRITA Water Filter was the next sample to be tested. 0.0901 and 0.2579 are the absorbance values, from Table 1, for Calcium and Magnesium. These values were plugged into the best-fit lines of the calibration graphs, Figure 2 and 3, in order to find the total concentration of hardness ions, which for the once filtered tap water was 81.80ppm. The EDTA value, from Table 5, for the once filtered water sample was 100ppm. This is once again a little higher than the AA value, but not by much

(10). The BRITA water cartridges, that are responsible for the filtering of the water, filters out some of the minerals that cause water hardness. The cartridge contains cation ion exchange resin; its job is to get rid of the hardness causing minerals by exchanging them with ions that don't cause hardness. This cycle is why the water filtered through the BRITA filter is a lot softer than the straight, unfiltered tap water (7). The TDS results agree with other tests, as shown in Table 6, the amount of residue left behind by the BRITA filtered once water was a lot lighter in color than the tap water but still darker than the Ca^{+2} solution (10).

Rainwater collected from a spout, which never touched the ground was the next sample to be tested. The absorbance values found for rainwater by using AA are located in Table 1, the absorbance value for Calcium was 0.0149 and the absorbance value for Magnesium was 0.0112. These values were then plugged into the equations found from figure 2 and 3 these equations gave the concentration of hardness causing minerals, totally at 0.0ppm. The reason that rainwater had a value of 0.0ppm was because the absorbance values were so low that when plugged into the formulas, a negative answer was given. This means that rainwater is so soft that there is basically no hardness causing minerals in the sample (11). The reason rainwater has practically no hardness because hardness is the measure of Ca^{+2} and Mg^{+2} ions and since water vapor loses all impurities as it evaporates, all the minerals are left here on earth. Rainwater is so soft because none of these minerals are carried up into the sky when the water evaporates (15). The EDTA value from Table 5, came out to be 40ppm, this is still the lowest value for hardness out of our samples. The reason that any hardness was found was because EDTA is usually high and this would correlate with our data. The TDS results as shown in Table 6, also agree with the other two tests. Rainwater left behind an extremely light residue line, very close to the distilled water (11).

The last sample to be tested was the twice BRITA filtered water sample. The AA absorbance values for Ca^{+2} and Mg^{+2} from Table 1 were 0.0306 and 0.1479. The absorbance values found were then plugged into the calibration graph curves, Figure 2 and 3 these results were displayed in Table 4. The total concentration found from AA was 38.44ppm, which correlates somewhat with the results found from EDTA from Table 5. The results from EDTA were higher than AA at 100ppm, which still isn't to far off of what was found in AA. TDS testing showed that twice-filtered water left behind a residue that was almost the same as the Ca^{+2} solution (12). The hardness concentration as suspected was lower for double filtered tap water compared to only once filtered water, because the water was exposed to more of the ion exchange resin. The more exposure to the resin, the softer the water sample will be (7).

Our hypothesis was supported by our data; the more filtered water was proven to be softer than less filtered water. The results from AA went in this order from lowest concentration to highest; rainwater, DeerPark bottled water, twice BRITA filtered water, once BRITA filtered water and tap water. This trend follows our hypothesis because rainwater is the most filtered and cleaned water and tap water is the least filtered and dirtiest water. The same trend was seen in EDTA and in TDS results, except for EDTA of once and twice filtered but that is due to the uncertainty of EDTA.

There was plenty of room during this lab for error. Starting with the check standards from the AA testing. Even though the atomic absorption spectroscope is very expensive, it still has sources of error. The check standards were a little off for when we tested our samples, which shows that our data won't be exact. Another source of error could be seen when conducting EDTA titrations. The results from EDTA are increments of 20ppm, so anything that may fall between two 20's will be rounded off. This can be seen between the EDTAs of twice and once filtered water samples, they came out the same using EDTA but obviously aren't the same, which could be seen in the results from AA testing. AA is definitely the most accurate but not the most convenient. AA machines are very accurate but they are costly and not something someone could take on the go, unlike EDTA, which is a cost effective way of testing water hardness. TDS is more of a reinforcer of the other two tests, it doesn't tell you how much Mg^{+2} or Ca^{+2} are in a sample but rather the amount of dissolved solids can range from NaCl to any other soluble salt.

Conclusion:

My hypothesis that more filtered and cleaned water will be softer and will contain the least amount of Ca^{+2} and Mg^{+2} ions was correct. All the trends seen in my data correlate with my hypothesis. For example the AA total concentrations, in ppm, from lowest to highest are rainwater, DeerPark bottled water, twice BRITA filtered water, once BRITA filtered water and tap water. This trend along with the other trends agrees with my hypothesis, so my original hypothesis stands.

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