

THE PENNSYLVANIA STATE UNIVERSITY

The Chemistry of Natural Waters

Chem. 111 Section 101

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4/6/2009

Lab portion performed on

3/16/09

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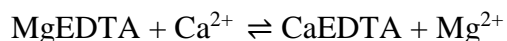
Introduction:

Water is arguably the most precious resource available on earth. It is essential for bodily function, used in industry, agriculture, and even entertainment. Natural occurring water must sometimes be treated before it can be used due to pollution, bacteria, or high or extremely low levels of dissolved minerals. Water hardness indicates the concentration of dissolved salts and minerals present in a given volume of water. Groundwater sources most commonly contain magnesium and calcium, minerals present in igneous rock formations reside above the water table. Although a water sample may contain a multitude of many different dissolved minerals, the hardness value is reported in parts per million (ppm) of calcium carbonate (CaCO_3), regardless of actual composition.

Water hardness can be important to know when installing plumbing systems in buildings. Very hard water can leave a mineral deposit inside pipes and coat heating elements in water heaters with a thick white residue. This residue can also clog pipes and create masses of white deposit around faucets and drains. Prior knowledge of hard water can allow for compensation for hard water, such as the installation of a water softening device. Water hardness can also be very important for wild life. Dissolved calcium in water is essential to the health process of marine organisms. Fish need dissolved minerals in water for many biological processes, including skeletal integrity and circulatory function. Fish farms need hard water in order to increase the size of fish faster. With very soft water containing no dissolved calcium, fish would not be able to survive (1).

Water hardness is determined by several methods, off of which are accurate to different degrees. One of the cheaper, but less accurate methods is known as ethylenediaminetetracetic acid titration (EDTA). A more expensive and consequently more accurate version is atomic absorption spectrophotometry (AA). Both of these methods were used to determine the hardness of the water sample in the lab portion of the assignment.

EDTA titration is done by a process using several chemicals which are added to the sample. A row of single drops of sample are placed in wells, and mixed with an equal amount of a chemical indicator, called black T (EBT). A buffer solution composed of $\text{NH}_3/\text{NH}_4\text{Cl}/\text{MgEDTA}$ is then added to each well. A pink color results in each well due to the indicator reacting with Mg^{2+} . From here, a serial titration is performed by added different known amounts of EDTA solution (1 drop, then 2 etc) to the different wells. When the wells begin to turn from pink to blue, the EDTA has reacted with the Ca^{2+} . When this has occurred, a calculation with a formula can be made. (2)



Atomic Absorption Spectrometry (AA) is a much more accurate, but more expensive alternative to the standard EDTA titration. A monochromatic light with the wavelength of the element that is being searched for (magnesium and Calcium) is passed through the flame of the sample being burned. The amount of absorbance of the light is directly correlated to the concentration of the element in the sample. From here, an “intensity value” is determined. Application of the Beer-Lambert law [$I_t = I_o(10^{-abc})$] allows for the determination of an absorbance value. Two separate reading must be made, one for magnesium, and another for calcium. The values of these two elements must then be compared to chart of made from known values. With these known data plots, a graph of a best fit line can be determined. The equation of

the best fit line then serves as an equation to calculate the hardness in parts per million of the raw data received from the spectrophotometer. (2) This method allows for a significantly more accurate value of hardness than EDTA titration.

Water can be softened through the use of a cation exchange resin. Divalent cations such as Ca^{2+} are replaced by monovalent cations such as Na^+ . This is done by passing hard water through a cation exchange resin. (2)

The sample was hypothesized to contain a relatively high hardness value. The sample was taken from State College, PA, where all of the public municipal water is drawn from 23 wells in 7 locations and from the Shingletown gap reservoir. (3) While it undergoes an expansive filtration system for microbial organisms, many minerals will get through. The geography of area contains large amounts of limestone, in which calcium is a main component. Since the water is drawn from the ground, it is expected that there will be a significant amount of these dissolved minerals present in the sample. (3)

Procedure:

The first test performed on the water sample was an evaporation to examine any residue left over. After being heated and evaporated over a hot plate on a piece of aluminum foil, the sample left behind a white crust powder composed of various dissolved salts. A control variable of distilled water was also vaporized, leaving no residue behind. This is because the distilled water has no dissolved minerals in it. Distilled water is soft water; the sample was obvious hard in comparison. A second control of $1 \times 10^{-3} \text{ M Ca}^{2+}$ was evaporated from the foil, also leaving a white residue behind. This however was not as easily noticed as the sample's, so it can be determined that the sample is harder than this very dilute Ca solution.

Next, ethylenediaminetetracetic acid (EDTA) titration was performed on the water sample. A strip of wells was filled with drops of sample and EBT indicator, along with a buffer solution. The wells were then titrated with a 2×10^{-4} M EDTA solution until a well changed in color from pink to blue, indicating a pH change from acidic to basic. After this experiment, a sample of water was softened using a “commercial conditioning product”. The same titration process was again performed except the sample was replaced with a softened version that resulted from the water conditioning agent.

The AA analysis was then performed on the sample. The AA machine was given a sample of the water through the aspirator and was configured to emit a wavelength of first 433.7 nm (for calcium) and then again for 202.5 nm (magnesium). These wavelengths correspond with the respective wavelengths of the ions. The ions present in a flame produced from the sample absorb the light of the specific wavelength, and an indicator within the machine measures the difference in intensity of the emitted light after it passes through the sample, allowing it to calculate the concentration. (4) The values determined for the sample were then compared to a line of best fit created from a table of known values. The magnesium concentration and the calcium concentration were used in a formula to convert the respective ppm of Ca^+ and Mg^{2+} into parts per million (ppm) of CaCO_3 .

Results:

Several values were provided for known concentrations of Mg and Ca. They were then used to create the graphs below. The equation shown on the graphs corresponds to the line of best fit for the given values. This equation is essential to the determination of hardness via Atomic Absorption spectrophotometry.

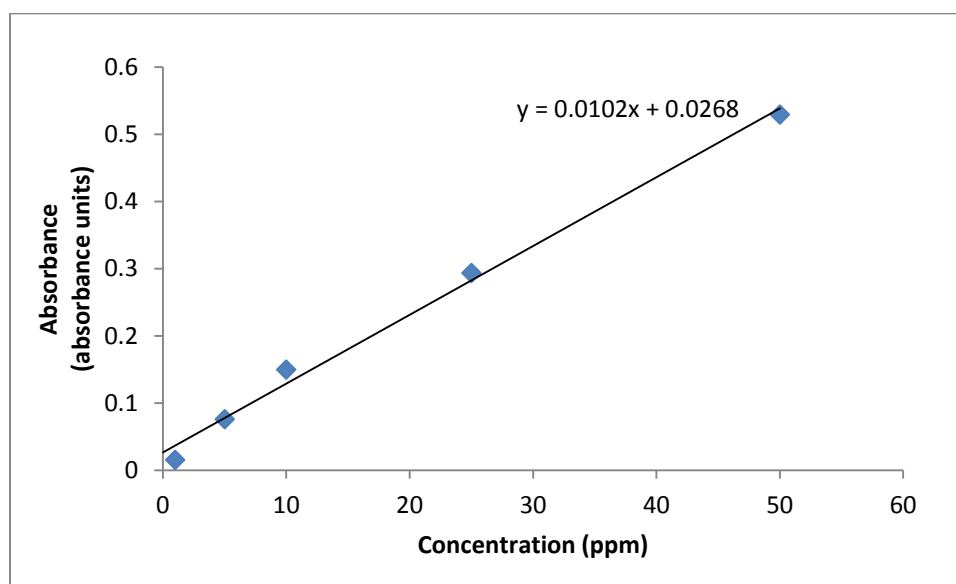


Figure 1 Light Absorbance Vs. Concentration of Ca^{2+}

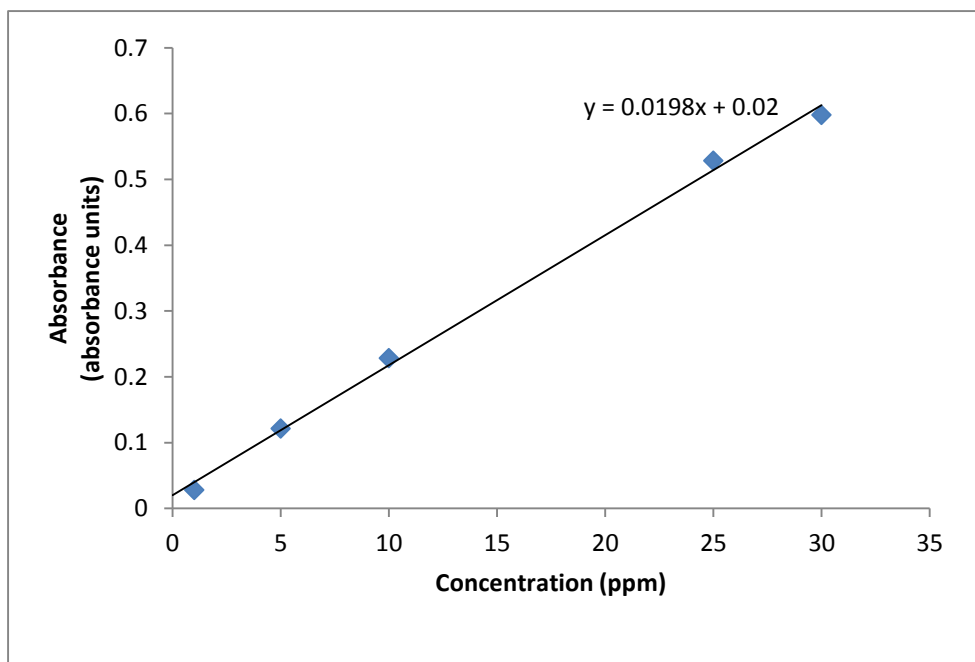


Figure 2 Light Absorbance Vs. Concentration of Mg^{2+}

By using the equation that was found by generating a line of best fit from the known values that given from spectrometer data, concentration of calcium (Ca^{+}) in parts per million was possible.

$$y = 0.0102x + 0.0268$$

$$.3385 = 0.0102x + 0.0268$$

$$x = 30.56$$

$$30.56 \text{ ppm } \text{Ca}^{2+}$$

The concentration of magnesium (Mg^{2+}) was determined using the line of best fit equation for the given values of its absorbency, and inputting the data from the sample as shown below.

$$y = 0.0198x + 0.02$$

$$.3535 = 0.0198x + 0.02$$

$$x = 16.84$$

$$16.84 \text{ ppm } \text{Mg}^{2+}$$

After these concentrations of both cations have been determined, they were then converted into hardness. To do this, the concentrations of the ions were treated as CaCO_3 . The formula below demonstrates.

$$\frac{(30.56 \text{ ppm } \text{Ca}^{2+})(100\text{g } \text{CaCO}_3/1 \text{ mole})}{(40\text{g } \text{Ca}^{2+}/1 \text{ mole})} = 76.4 \text{ ppm } \text{CaCO}_3$$

$$\frac{(16.84 \text{ ppm } \text{Mg}^{2+})(100\text{g } \text{CaCO}_3/1 \text{ mole})}{(24.3\text{g } \text{Mg}^{2+}/1 \text{ mole})} = 69.3 \text{ ppm } \text{CaCO}_3$$

The total hardness of the sample can then be found by adding these two values. The state college sample was found to contain 145.7 ppm CaCO_3 .

Cation	Absorption Given by AA Machine	Concentration (ppm)	Hardness ppm CaCO ₃
Ca ²⁺	0.3385	30.56	76.4
Mg ²⁺	0.3535	16.84	69.3
Total Hardness of the Sample (State College)			145.7

Table 3: State College Water Sample (AA)

EDTA titration yielded different results. To find the hardness using this method, the following formula was used.

$$(\text{Molarity}_{\text{EDTA}})(\text{Volume}_{\text{EDTA}}) = (\text{Molarity}_{\text{Sample}})(\text{Volume}_{\text{Sample}})$$

	Number of Drops of EDTA
Original Water Sample	9
Softened Water Sample	11 *

Table 4: Drops of EDTA to initiate color change

Original Sample:

$$(2 \times 10^{-4} \text{ M}_{\text{EDTA}})(9 \text{ drops}_{\text{EDTA}}) = (\text{M}_{\text{Sample}})(1 \text{ drop}_{\text{Sample}})$$

$$\text{M}_{\text{Sample}} = 1.8 \times 10^{-3} \text{ M}$$

Softened Sample:

$$(2 \times 10^{-4} \text{ M}_{\text{EDTA}})(11 \text{ drops}_{\text{EDTA}}) = (\text{M}_{\text{Sample}})(1 \text{ drop}_{\text{Sample}})$$

$$\text{M}_{\text{Sample}} = 2.2 \times 10^{-3} \text{ M}$$

After the molarity of the water samples was obtained for the original and the softened water (table 4), the hardness in parts per million of CaCO₃ was determined by a formula shown below.

Original Sample:

$$\frac{(1.8 \times 10^{-3} \text{ moles CaCO}_3)(100.0 \text{ g CaCO}_3)(1000 \text{ mg CaCO}_3)}{(1 \text{ Liter})(1 \text{ mol CaCO}_3)(1 \text{ g CaCO}_3)} = 180 \text{ ppm}$$

Softened Sample:

$$\frac{(2.2 \times 10^{-3} \text{ moles CaCO}_3)(100.0 \text{ g CaCO}_3)(1000 \text{ mg CaCO}_3)}{(\text{Liter})(1 \text{ mol CaCO}_3)(1 \text{ g CaCO}_3)} = 220 \text{ ppm}^*$$

* The results experienced and shown above aren't consistent with a water softening process. The value should have been lower, but these were the recorded results. Softening should have lowered the hardness value. (5)

The state college water sample was one of several in a group. The other samples data is tabulated below.

	Absorption Given by AA Machine	Hardness of Sample (ppm)
Audubon, NJ:		
Ca ²⁺	.2074	44.857
Mg ²⁺	.1238	5.50
Total Hardness of Sample		67.50
Pen Argyle, PA:		
Ca ²⁺	.3302	75.00
Mg ²⁺	.1539	63.40
Total Hardness of Sample		138.40
Frederick, MD:		
Ca ²⁺	.3276	≈34.33
Mg ²⁺	.1606	≈68.65
Total Hardness of Sample		102.98

Table 5: Atomic Absorption (AA) Hardness of all Water Samples (7) (8) (9)

Group data for EDTA Titration:

	Number of Drops of EDTA	Hardness of Sample (ppm)
Audubon, NJ:		
Original Sample:	7	140
Softened Sample:	3	60
Pen Argyle, PA:		
Original Sample:	5	100
Softened Sample:	No color change	Undetermined
Frederick, MD:		
Original Sample:	4.5	90
Softened Sample:	4.5	90

Table 6: EDTA Hardness of all Water Samples and respectful Softened Versions (7) (8) (9)

Discussion:

Group results show that water hardness can vary by geographic location. Samples from group came from four locations within Pennsylvania, Maryland, and New Jersey. State College tap water was the hardest (145.7 ppm) according to AA, followed by a sample from Pen Argyle, PA (138.4 ppm); Frederick, MD (102.98 ppm); and finally the softest was Audubon, NJ (67.50 ppm) (1). Frederick came in last this time with a reading of 90 ppm. Interestingly, the results derived from the EDTA titration yielded different results. While State College water still was found to have the hardest concentration of dissolved minerals (180 ppm), Audubon registered as 140 ppm (1), followed by Pen Argyle's 100 ppm.

The differences in AA and EDTA hardness determination methods can result from a number of factors. Firstly, and EDTA titration is significantly less precise than a AA. Each well of the EDTA experiment corresponds to 20 ppm, so the values always increase (or decrease) in increments of 20 ppm. Precision down to the decimal level as such as in AA is not possible with EDTA. Secondly, the EDTA reacts with not only Mg and Ca, but also with everything else in the water. AA strictly detects the Mg and Ca (or any other desired element), everything else in the water is not counted. This allows for the actual hardness, not a value inflated by other impurities. This is why EDTA can yield on average higher values. AA however isn't perfect. The check standards provided on the data chart show that AA doesn't provide the same value over and over. The values recorded are simply averages. The EDTA however has very good reproduction of data (same value will be determined each time), but lacks the ability to measure past increments of 20 ppm. (6)

It was hypothesized that State College Tap water would have a relatively high hardness. Water described as hard contains a hardness of over 120 ppm, and at 145 ppm, State College

easily makes that mark. (3) It was surprising though to find that it was higher than all of the other samples. While they ranged from a wide geographic area, they were expected to be relatively similar. However, State College's mountainous terrain and vast deposits of limestone in and around the well sites creates a substantial amount of dissolved minerals in the ground water, which is then directed to the tap.

Conclusion:

State college water is harder than the average public water. A value of 145.7 ppm CaCO_3 makes sense due to the geographical location of the city, and the fact that the water supply is derived from ground sources. The ground water is naturally filtered through large deposits of limestone throughout the region, which contain substantial amounts of calcium and other minerals. Water that is this hard needs to be taken into account when building and designing plumbing and water infrastructure, due to the fact that the risk of damage due to mineral buildup is very high. Water softeners would be advisable for structures that use water has a primary heating source and the resulting softer water will reduce the white crusty buildup around sinks and faucets.

Works Cited

- 1) Wurts, William A. "Understanding Water Hardness." World Aquaculture 1.24: 18. 26 Mar. 2009
<<http://www.ca.uky.edu/wkrec/HARDNESS.htm>>.
- 2) Thompson, Stephen. "The Chemistry of Natural Waters." PSU Chemtrek. 1990. Ed. Joseph T
Keiser. 15th ed. Plymouth: Hayden-McNeil Publishing, 2009. 22 pp.
- 3) State College Borough. Water Authority. 2007 Water Quality Report. SCBWA.org. 2008. 29 Mar.
2009 <<http://www.scbwa.org/pdf/wqr4.pdf>>.
- 4) "Perkin Elmer 30303B Atomic Absorption Spectrophotometer." Colgate Geography. 2003.
Colgate University. 3 Apr. 2009 <<http://departments.colgate.edu/geology/instruments/aa.htm>>.
- 5) NebGuide. Oct. 2008. University of Nebraska. 5 Apr. 2009 <<http://www.ianrpubs.unl.edu/epublic/live/g1491/build/g1491.pdf>>.
- 6) Perone, Samuel P. "Determination Calcium-Magnesium by EDTA Titration." Quantitative
Analysis Laboratory. 1998. San Jose State University. 3 Apr. 2009 <<http://www.sjsu.edu/faculty/chem55/55mgca.htm>>.
- 7) Anthony, Vincent. The Chemistry of Natural Waters. Chapter 10 40-48. N.p.: n.p., 2009.
- 8) Barbabas, Bryan. The Chemistry of Natural Waters. Chapter 10 31-36. N.p.: n.p., 2009.
- 9) Barnett, Genevieve. The Chemistry of Natural Waters. Chapter 10 38-41. N.p.: n.p., n.d.