Experiment #10

The Chemistry of Natural Waters

Lab Report

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Chemistry 111 Section 103

Introduction:

Water hardness is defined as a measure of the amount of calcium and magnesium salts dissolved in water[4]. Hard water is water that contains large amounts of dissolved calcium and magnesium cations, and soft water is water that little or none of the cations[10]. The hardness of water is important because it affects numerous aspects of our life. Water hardness has an effect on the way water tastes, it creates problems with plumbing and industries, and the water hardness has an effect on cleaning/washing[10]. The calcium and Magnesium that exist in the water do not taint it in any way. The hardness of water does, however, affect the way the water tastes, but different individuals have different opinions on which type tastes better. The problem of water hardness in the use of industrial water boilers/plumbing systems[10] is that the water evaporates leaving behind rocklike deposits consisting mostly of calcite crystals[10]. This is a problem because the calcite crystals build up and clogs pipes, blocks jet engines, etc. and is very expensive and difficult to remove, if removable at all[10]. Problems similar to these can be found everywhere that large volumes of natural waters are used to undergo the industry's processes[3]. In washing, when hard water is used to wash away soap the soap anions react with the calcium and magnesium cations to produce a greasy scum[3].

There are various methods in measuring water hardness. EDTA (ethylenediaminetetraacetic acid) titration is one method that is commonly used. EDTA titration is a chelating agent[3]. A chelating agent is a substance whose molecules can form several bonds

to a single cation[3]. An indicator is added to the sample to be tested that turns red if magnesium is present in the sample. EDTA is added after and first reacts with the calcium cations then the magnesium cations. After titration is complete, the water will turn blue. Where the titration starts can be used to determine the concentration of the calcium and magnesium cations[10]. One symptom of using EDTA titration is that the EDTA will reveal to just calcium and magnesium cations, but all +2 cations[10].

Another method to measure water hardness is Atomic Absorption Spectrophotometry (AA). Unlike EDTA titration, AA uses an instrument called an atomic absorption spectrophotometer that uses monochromatic light that has an energy corresponding to the element of interest (in this case calcium and magnesium tested separately) [10]. The atoms in the sample will absorb the light and the amount of absorbance is proportional to the concentration of the atoms in the sample[3]. As with EDTA titration, AA also has a drawback such that a very soft water (such as Aquafina) will not be measured correctly in the sense that negative amounts of an element are present in the reading. The fact that both methods have flaws in the measuring of calcium and magnesium cations is the reason why more than one method is used to measure hardness. By using one method, another method can then be used to confirm or disagree with the data.

I predict that the Aquafina water sample I am using for my sample to be extremely soft because it is purified water. When most water goes through a purification process, the goal of the company is to remove most of the minerals and other unwanted substances from the water. I predict that the water from the Brita water sample will be soft, but not as soft as

Aquafina because the Brita water is also put through a filtration system, but a less extensive one. I predict that the water taken from the Whitmore Building water fountain right outside the classroom to be hard water because public water typically isn't purified.

Procedure:

The procedure can be referenced in ChemTrek[10]. This is an overview of the in depth procedure:

The hardness of each of our water sample was tested using two different, accurate, techniques. The first accurate technique we used was Atomic Absorption Spectroscopy. We used two different AA instruments, one for calcium and one for magnesium. To determine the concentration of each element, we calibrated the instrument's reading using a controlled table of data. After graphing the data and determining the equation of the line, we used the absorbance values to calculate the concentration of each element.

The second accurate technique we used was EDTA titration. This part of the procedure differs from that of Chemtrek because my sample of Aquafina water was too soft to observe titration by following Chemtrek. The method I followed was to add 10 drops of my sample to a well of a 6x4 well tray. I then added 10 drops of eriochrome black T (EBT) indicator into the well with the sample as well as 10 drops of NH3/NH4Cl/MgEDTA buffer. Drops of 2 x 10^-4 Molar EDTA were added until the solution turned blue.

After the hardness of the sample, tests were run using various techniques in an attempt to make the water softer. Tests were conducted using commercial water softening agents, and

with cation exchange resin. These tests were run in order to explore how hardness can be removed from water.

Results:

Water samples: These names will be used to refer to the sample throughout the remaining report.

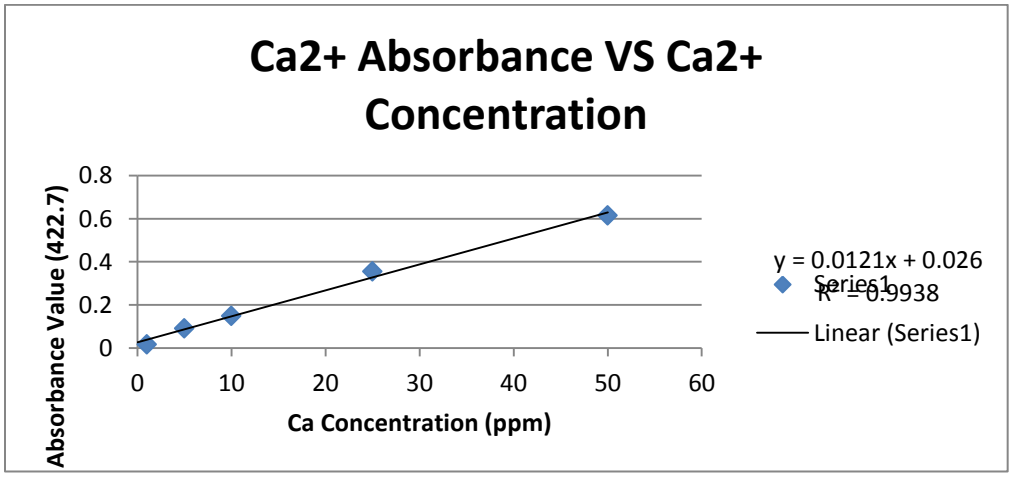
Sample 1: Jake Shoemaker's water sample was taken from Aquafina bottled water[8]

Sample 2: Sam Silverberg's water sample was taken from the water fountain outside room 111 in Whitmore Laboratory[9]

Sample 3: Alex Schneider's water sample was taken from a sample of Brita filtered water[7]

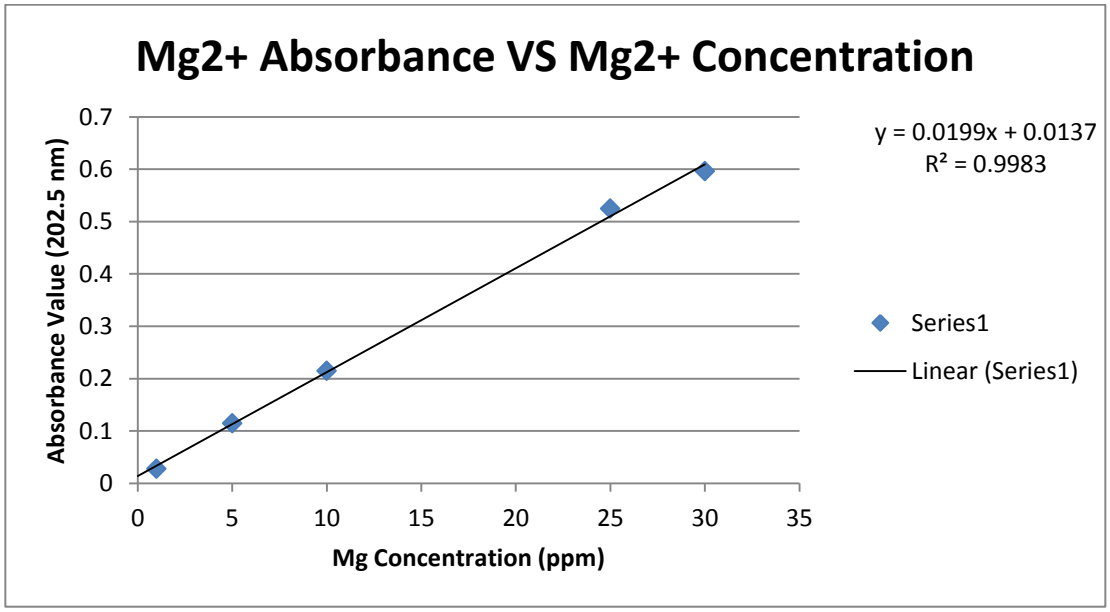
The graphs below were calibrated using data points and were used to convert the absorbance values from the AA into the concentrations of each element:

Graph 1: Calcium Calibration Graph



Graph 1 displays the points of data that were used to calibrate the concentration of calcium cations in the samples.

Graph 2: Magnesium Calibration Graph



Graph 2 displays the points of data that were used to calibrate the concentration of Magnesium cations in the sample.

Table 1: This table shows absorbance values, concentrations, and hardness of Ca2+ according to AA.

Water Sample	Absorbance Value (Ca2+)	Ca2+ Concentration (ppm)	Ca2+ Hardness (ppm CaCO3)
Sample 1[8]	0*	0*	0*
Sample 2[9]	.4	31.01	77.39
Sample 3[7]	.0982	5.67	14.918

*The Ca2+ absorbance value of sample 1 was a negative value showing that the water is too soft to be measure by the AA spectrometer, therefore a value of 0 is used.

Table 2: This table shows absorbance values, concentrations, and hardness of Ca2+ according to AA.

Absorbance Value (Mg2+)	Mg2+ Concentration (ppm)	Mg2+ Hardness (ppm CaCO3)
.2389	11.3	46.5
.3025	14.6	60.1
.3045	14.61	60.123

Table 3: Table 3 shows total hardness determined by AA.

Water Sample	Total Hardness (ppm)
Sample 1[8]	46.5
Sample 2[9]	137.49
Sample 3[7]	75.041

A sample calculation to calculate the Ca2+ concentration of my sample is shown as follows and was conducted for each sample's absorbance value.

Mg2+ Concentration:

y = 0.0199x + 0.0137 y (absorbance value) = 0.2389 x (concentration) = ?

0.2389 = 0.0199 x +0.0137 =====> x = 11.3 ppm

11.3ppm x [(100g $CaCO_3$/ 1 mole) / (24.3g Mg^{2+}/ 1 mole)] = 46.5ppm $CaCO_3$

46.5ppm $CaCO_3$ = water hardness for Mg^{2+}

Total Hardness = (hardness of Ca^{2+}) + (hardness of Mg^{2+})

Total Hardness = (0ppm) + (46.5ppm)

Total Hardness = 46.5ppm

Table 4: Shows hardness of water by EDTA titration

Sample	EDTA Titration (ppm)
Sample 1[8]	40
Sample 2[9]	400
Sample 3[7]	100

The following is an example as to how concentration was determined using the EDTA titration:

M1 V1 = M2 V2

(Molarity EDTA) x (Volume EDTA) = (Molarity of Ca^{2+}) x (Volume of Ca^{2+})

(2 x 10^-4M) x (2 drops) = (Molarity of Ca^{2+}) x (10 drops)

Molarity of Ca^{2+} = (4 x 10^-4M) x (1/10)

Molarity of Ca2+ = 4 x 10^-5 M

Table 5: This date shows the evaporation and determination of TDS

Sample	Observation
Sample 1[8]	Little to No White Ring
Sample 2[9]	Thick, White Ring
Sample 3[7]	Faint, Barely Visible White Ring

Table 6: This table shows the effects a commercial softening agent and cation ion exchange resin affects the hardness of water.

Water Sample	Original Hardness(EDTA Titration, ppm))	Commercial Softening Agent (ppm)	Cation Exchange Resin (ppm)
Sample 1[8]	40	4	2
Sample 2[9]	400	240	80
Sample 3[7]	100	60	30

Discussion:

The analysis of the water hardness provided results that I had expected for all three samples. Sample 1 was expected to be extremely soft because Aquafina bottled water undergoes an intensive purification process and the Brita water (sample 3) was also found to be soft as expected because it also goes through a filtration process[5]. Sample 2 was found to be relatively hard as predicted because it undergoes no purification process, therefore, the

calcium and magnesium cations absorbed into the water from sources such as limestone are able to remain in the water[3].

Each method used resulted in different results. EDTA titration analyzes the solution in order to measure total dissolved solids (TDS) [10]. EDTA titration is measured by observing how much EDTA is required to result in the solution turning blue[11]. An error to this method of determining the amount of solid in a solution is that more EDTA is used than is actually required to turn the solution blue. AA was also used in order to measure the amount of calcium and magnesium cations reside in the water, but other solids are not taken into account[10]. The fact that AA was unable to determine a calcium cation absorbance value in sample 1 is also a source of error because the instrument cannot measure an absorbance value if the water is too soft. Various amounts of human may exist as well such as adding different drop sizes during the EDTA titration or making a mathematical error when calculating the concentration using the absorbance value. The method that works the best and is more accurate in measuring water hardness is the AA spectrometer because it measures the total amount of solid dissolved in water instead of looking at the acids/bases.

Drinking water sources in the United States tend to have high concentrations of calcium and magnesium cations, therefore being hard[12]. Drinking water has typical values 100 mg of calcium per liter, but more than 200 mg of calcium per liter is considered rare[12]. Magnesium concentration is much lower, usually, and contains typically 10 mg per liter and over 100 mg per liter is considered rare[12]. Calcium hardness is usually is more highly concentrated than magnesium[6]. This observation agrees with the data that was found in sample 2 such that

magnesium is usually much less concentrated than calcium[12]. When comparing sample 1 to other bottled water values found, it is very much in accordance with the findings of other scientists[2]. It was found that nearly no trace of calcium or magnesium exists in many bottled water brands that are bottled around Pennsylvania[1]. Sample three's hardness values also relate very closely those of found hardness by others. Brita filters water using ion exchange ions, which have been proven to remove hardness. Brita water also has a similar pH of almost 7 in comparison to other water analyses[5].

Conclusions:

Water hardness is defined as a measure of the amount of calcium and magnesium salts dissolved in water. Hard water is water that contains large amounts of dissolved calcium and magnesium cations, and soft water is water that little or none of the cations. Water samples with a moderately high hardness rating leaves behind a white ring when the water is evaporated because the solids are left behind. EDTA and AA are useful ways in order to measure water hardness, but neither are perfect, nor is one necessarily more accurate than another. There are also methods that can be used to soften water such as using a commercial water-conditioning agent and cation exchange resin. Though the cation exchange resin is more effective, both work very well. The results that were expected to be found, such as Aquafina and Brita water to be soft and water from a water fountain to be hard, held true and the hypothesis was proven correct.

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