

Aquatic Chemistry Laboratory Report: Complexation Titrations

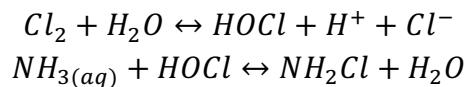
The following document is my final laboratory report for my Aquatic Chemistry course (Fall 2020). The report outlines the seven major processes performed at the Vernon Campbell Water Treatment Plant in Norman, OK and determines the hardness, calcium and magnesium concentrations, carbonate concentrations, alkalinity, and calcium carbonate equilibria from water samples from the Norman Water Treatment Plant using 0.01M EDTA titrations. The water samples include raw water, post-clarifier water, post-carbonation water, tap water, and ground water. This report displays my experience in drinking water treatment, complexation titrations, and writing full and professional lab reports.

Aquatic Chemistry Laboratory CEES 4114
Week 9 and 13: Complexation Titrations
Hannah Curtis

Introduction

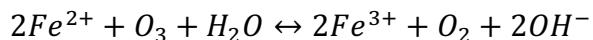
The Vernon Campbell Water Treatment Plant in Norman, Oklahoma was built in the 1960s to treat water from Lake Thunderbird. Today, the Vernon Campbell Water Treatment Plant receives 3 billion gallons of water a year from Lake Thunderbird and treats 17 million gallons of water a day to provide water for the majority of residents in Norman. The Norman Water Treatment Plant utilizes seven major processes in their water treatment: disinfection, coagulation, lime addition, flocculation, recarbonation, fluorine addition, and filtration. These processes work together to remove pathogens and other toxic chemicals that could harm Norman residents (“How Water Works,” 2018).

The first process of water treatment is disinfection. At the Norman Water Treatment Plant, water travels 8.5 miles from Lake Thunderbird to a 1-million-gallon storage container. The water then goes to a flow control vault where the water meter starts. At this point, the water is disinfected with chlorine gas and hydrous ammonia in order to form chloramines. These chloramines work to treat disease-causing bacteria and viruses. Additionally, the presence of chloramines reduces bromate formation from bromines which would interact unfavorably with ozone later in the treatment process. The chemical equations for the dissolution of chlorine gas into water and the reaction between aqueous ammonia and hypochlorous acid to form chloramines are shown below (National Research Council, 1980):

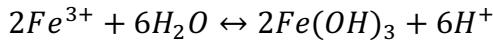


However, chlorine disinfection generates trihalomethanes which are regulated. Because of this, the Norman Water Treatment Plant decided to use ozone and ultraviolet (UV) light in their disinfection process instead. Construction for this “Phase II” plan began in 2017 and was implemented by May 2020. At the Norman Water Treatment Plant, UV is exposed to water in an enclosed pipe where the water is clearer. UV interacts with bacteria by degrading the DNA in the cells, thus prohibiting their ability to reproduce. This process is efficient, cost effective, and uses less energy than chlorine disinfection (City of Norman Water Treatment Plant, 2020). Ozone is added to the water to reduce adverse tastes and odors of the water. Ozone produces higher levels of disinfection with shorter contact time than both chlorine and UV disinfection. Ozone reverts to oxygen in water to remove hydrogen sulfide, bacteria, manganese, and iron through oxidation. However, ozone disinfection requires corrosive resistant materials and can be more costly than other types of disinfection. The chemical reactions between ozone with iron, manganese, and sulfide are shown below (Water Quality Association, 2020).

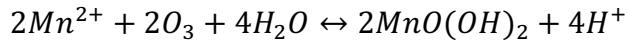
Iron Oxidation:



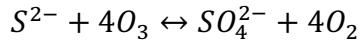
Iron Hydrolysis:



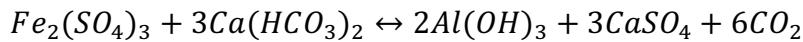
Manganese Oxidation and Hydrolysis:



Sulfide Oxidation:



The next process at the Norman Water Treatment Plant is coagulation. During this process, the water enters four clarifiers that have both an inner and outer chamber. Then, ferric sulfate is added in the inner core as the coagulation. This forces small dirt particles to stick together to form larger particles that are flocculated and settle at the bottom of the clarifier. This process consumes alkalinity in the water and removes turbidity. The chemical reaction for ferric sulfate coagulation is shown below (Davis, 2010):



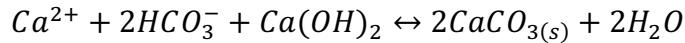
While in the inner chamber of the clarifier, lime is added to the water to remove hardness, adjust the pH, and coat the distribution lines. The lime addition process requires several chemical reactions. The first involves the formation of hydrated lime, $Ca(OH)_2$, from quick lime, CaO (Davis, 2010):



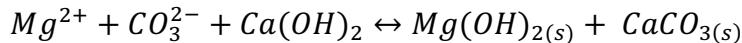
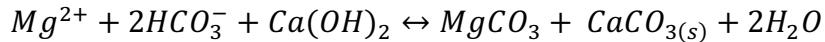
Next, the hydrated lime neutralizes carbonic acid in the water according to the following reaction:



Next, the carbonate hardness due to calcium precipitates according the following reaction:



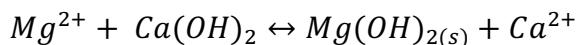
Next, the carbonate hardness due to magnesium precipitates according to the following reactions:



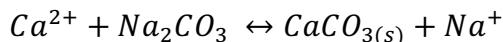
Next, the removal of noncarbonate hardness due to calcium occurs according to the following reaction:



Next, the removal of noncarbonate hardness due to magnesium occurs according to the following reaction:



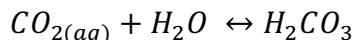
Last, soda ash is added according to the following reaction:



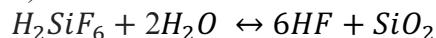
After the lime addition process occurs, the water is flocculated, or mixed, in the inner chamber of the clarifiers and settles in the outer layers. From there, clean water is decanted equally from each clarifier. The flocculation process works with the coagulation process to remove sediments and reduce turbidity.

Then, the water moves to the recarbonation basin where carbon dioxide, CO_2 , is added to form carbonic acid, H_2CO_3 . This process is necessary to lower the pH of the water which prevents

calcium carbonate, CaCO_3 , carryover into the filter. The chemical reaction between carbon dioxide and water to form carbonic acid is shown in the chemical reaction below (Davis, 2010):



In this same step, fluoride is added to the water in order to improve dental health. The fluoridation process typically uses hexafluorosilicic acid as the fluoride addition. The hexafluorosilicic acid hydrolysis to form hydrofluoric acid is shown in the chemical equation below (Haneke and Carson, 2001):



The last water treatment process at the Norman Water Treatment Plant is filtration. During this process, water enters the filter gallery which houses eight gravity filters. The water is filtered through a media, which consists of anthracite coal on top, torpedo sand below that, and four different sizes of gravel on the bottom, and stored in a 7.5-million-gallon underground clear well storage system. After this, the water is ready to be pumped into the distribution system as needed. When the filters fill with dirt, the system is backwashed, and the dirt is sent to a lagoon. Here, water is decanted off the top and sent back through the treatment process. The filtration process is performed to reduce turbidity. There is a turbidity meter after the water is filtered through the media—the turbidity readings must be under 0.3 turbidity 95% of the time (“The Water Treatment Process,” 2018).

The goal of this experiment is to determine the water hardness, calcium and magnesium concentrations, carbonate concentrations, alkalinity, and calcium carbonate equilibria from water samples from the Norman Water Treatment Plant. The water samples tested include three trials each of: raw water, post clarifier water, post carbonation water, tap water, and ground water. The total hardness, calcium concentration, and magnesium concentrations were determined using EDTA titrations; the carbonate concentration, alkalinity, and calcium carbonate equilibria were determined using sulfuric acid titrations. It is expected that the addition of lime and recarbonation processes will affect the water hardness. The addition of lime, which occurs in the primary clarifier, intentionally softens the water by precipitating solid $\text{CaCO}_{3(s)}$ and $\text{Mg(OH)}_{2(s)}$. These solids settle to the bottom of the clarifier during the flocculation stage. In the recarbonation process, the pH of the water is lowered. This increases the solubility of calcium carbonate. If more calcium carbonate is present in the water, the hardness will slightly increase during recarbonation.

Methods and Materials

Materials

- buret
- ring stand
- buret clamp
- funnel
- pH meter
- wash bottle

- 2 25 mL pipettes
- 4 125 L erlenmeyer flasks
- 200 mL of each water sample
- 400 mL 0.01 M standard EDTA solution
- 50 mL buffer solution
- 5 mL Eriochrome Black T (EBT) indicator
- 5 mL HNB indicator
- 50 mL 1 M NaOH
- 5 mL Phenolphthalein indicator
- 5 mL Methyl Orange indicator
- 300 mL 0.02 N Na_2CO_3
- 300 mL 0.01 M sulfuric acid
- 1 L deionized water
- 1 L distilled water
- 1 L waste beaker

Standard Preparation

Total Hardness and Calcium Determination:

0.01 M EDTA solution:

Dissolve 3.723 g of disodium ethylenediaminetetraacetate dihydrate in distilled water and dilute until the total volume is 1.0 L. Standardize against standard calcium carbonate solution.

Buffer solution:

Dissolve 16.9 g ammonium chloride (NH_4Cl) in 143 mL concentrated ammonium hydroxide. Add 1.25 g of the di-magnesium salt of EDTA and dilute to 250 mL with DI water.

Eriochrome Black T (EBT) indicator:

Dissolve 0.5 g EBT and 4.5 g hydroxylamine hydrochloride in 100 mL 95% ethyl alcohol.

Alkalinity and Calcium Carbonate Equilibria Determination:

0.02 N Na_2CO_3 :

Dissolve 1.060 g anhydrous reagent grade Na_2CO_3 (dried at 140C for 24 hours) in distilled water.

0.01 M sulfuric acid:

Titrate three 20 mL samples of standard Na_2CO_3 solution with the acid using the pH meter and titrating to pH 4.3 (Jenkins et al., 1973).

Methods

Total Hardness Determination:

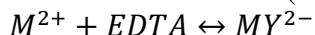
Decant 50.0 mL of the raw water sample with a 25 mL pipette into a 125 mL Erlenmeyer flask. Add 2.0 mL of the buffer solution to the same Erlenmeyer flask. At this point, the pH should be 10.0 ± 0.1 . Add 2 drops of EBT indicator and stir the flask. The color of the solution should be wine red. Thoroughly rinse buret with deionized water, then rinse buret with 0.01 M EDTA. If EDTA is clinging to the walls of the buret, repeat this process. Attach the buret to the ring stand and make sure the tap is in the closed position. Using the funnel, fill the buret with 0.01 M EDTA. Empty a few mL of EDTA into an Erlenmeyer flask until the bottom of the meniscus is at the 0 mL line. Place the first Erlenmeyer flask with the raw water solution under the buret. Begin dispensing the titrant into the flask with one hand while stirring the flask with the other hand. If any EDTA sticks to the top of the Erlenmeyer flask, rinse it into the solution with a wash bottle with deionized water. Using a pH meter, record the pH and volume of titrant dispensed at roughly every 0.5 mL of dispensed titrant. When the color begins to turn blue, record the pH and volume of titrant dispensed at roughly every 0.1 mL of dispensed titrant. When the color turns royal blue, record the volume of titrant dispensed. Repeat this process for the two other raw water sample trials.

Repeat this titration process for three trials each of: post clarifier water samples, post carbonation water samples, tap water samples, and ground water samples. Repeat this titration process with ten trials of distilled water samples to use as blanks.

To calculate the total hardness of each sample, the moles of EDTA used in the titration must first be determined. To do this, the amount of EDTA used to reach the color change (V_e) must be converted to liters and multiplied by the molarity of EDTA:

$$\text{moles of EDTA} = \frac{V_e \text{ (mL)}}{1000} * 0.01 \left(\frac{\text{mol}}{L} \right)$$

Then, the moles of total hardness (M^{2+}) must be determined. The following chemical equation shows that the stoichiometric ratio of EDTA to M^{2+} is 1:1 (Harris, 2020):



In this case, the moles of M^{2+} will be equal to the moles of EDTA. Next, the concentration of M^{2+} must be found. This is found by dividing the moles of M^{2+} by the initial volume of the water sample (0.05 L). To convert this value to g CaCO₃/L, this value must be multiplied by the molecular weight of CaCO₃, or 100 g/mol. Finally, to determine the hardness in units of mg CaCO₃/L, this value must be multiplied by 1000 mg/g.

Total Calcium Determination:

Rough Titration:

Measure 50.0 mL of the raw water sample into a 125 mL Erlenmeyer flask. Add 3.0 mL of 1.0 M NaOH to the same Erlenmeyer flask. The pH at this point should be 12 ± 0.1 . If the pH is less than 12, add more NaOH to the solution. Add 0.1 g of HNB indicator. The color of the solution at this point should be wine red. Thoroughly rinse buret with deionized water, then rinse buret with 0.01 M EDTA. If EDTA is clinging to the walls of the buret, repeat this process. Attach the buret to the ring stand and make sure the tap is in the closed position. Using the

funnel, fill the buret with 0.01 M EDTA. Empty a few mL of EDTA into an Erlenmeyer flask until the bottom of the meniscus is at the 0 mL line. Place the first Erlenmeyer flask with the water solution under the buret. Begin dispensing the titrant into the flask with one hand while stirring the flask with the other hand. If any EDTA sticks to the top of the Erlenmeyer flask, rinse it into the solution with a wash bottle with deionized water. Using a pH meter, record the pH and volume of titrant dispensed at roughly every 0.5 mL of dispensed titrant. When the color begins to turn blue, record the pH and volume of titrant dispensed at roughly every 0.1 mL of dispensed titrant. When the color turns royal blue, record the volume of titrant dispensed.

Real Titration:

Measure 50.0 mL of the raw water sample into a 125 mL Erlenmeyer flask. Add 0.1 g of HNB indicator. The color of the solution at this point should be wine red. Titrate according to the method above with 0.01 M EDTA until right before the endpoint determined from the rough titration. At this point, add 3.0 mL of 1 M NaOH. When the color turns royal blue, record the volume of titrant dispensed. Repeat this process for the other raw water sample.

Repeat the rough and real titration processes for three trials each of: post clarifier water samples, post carbonation water samples, tap water samples, and ground water samples. Repeat this titration process with ten trials of distilled water samples to use as blanks.

To calculate the total calcium of each sample, the moles of EDTA used in the titration must first be determined. To do this, the amount of EDTA used to reach the color change (V_e) must be converted to liters and multiplied by the molarity of EDTA:

$$\text{moles of EDTA} = \frac{V_e (\text{mL})}{1000} * 0.01 \left(\frac{\text{mol}}{\text{L}} \right)$$

Then, the moles of total calcium (Ca^{2+}) must be determined. The following chemical equation shows that the stoichiometric ratio of EDTA to Ca^{2+} is 1:1 (Harris, 2020):



In this case, the moles of Ca^{2+} will be equal to the moles of EDTA. Next, the concentration of Ca^{2+} must be found. This is found by dividing the moles of Ca^{2+} by the initial volume of the water sample (0.05 L). To convert this value to g CaCO_3/L , this value must be multiplied by the molecular weight of CaCO_3 , or 100 g/mol. Finally, to determine the total calcium in units of mg CaCO_3/L , this value must be multiplied by 1000 mg/g.

Since the total hardness is the sum of all of the Ca^{2+} and Mg^{2+} in a water sample, the concentration of Mg^{2+} can be found by subtracting the total Ca^{2+} value from the total hardness value.

Alkalinity Determination:

Measure 50.0 mL of the raw water sample into a 125 mL Erlenmeyer flask. Measure the initial pH of the water with a pH meter. Add 5 drops of Phenolphthalein indicator. The color of the solution should be pink at this point. Titrate with 0.01 M sulfuric acid according to the method above. Record the volume of the titrant added when the solution becomes colorless. This is the V_p value. Record the volume of titrant added when the pH reaches 8.3. This is the $V_{8.3}$ value. If, after the addition of 5 drops of Phenolphthalein, the solution is still colorless, skip this titration and move to the next step.

Add 5 drops of Methyl Orange indicator. The color of the solution should be orange at this point. Titrate with 0.01 M sulfuric acid according to the method above. Record the volume of the titrant added when the solution becomes dark red. This is the V_{mo} value. Record the volume of titrant added when the pH reaches 4.3. This is the $V_{4.3}$ value. Titrate past the endpoint to a pH around 3 to 3.5.

There are three different types of alkalinity: caustic, carbonate, and total. Caustic alkalinity is the amount of strong acid required to lower the pH of a sample to $pH_{CO_3^{2-}} = 10.3$. Carbonate alkalinity is the amount of strong acid required to lower the pH of a sample to $pH_{HCO_3^-} = 8.3$. Total alkalinity is the amount of strong acid required to lower the pH of a sample to $pH_{CO_2} = 4.3$. These alkalinities can be calculated using V_p , which is the amount of acid in mL to reach the Phenolphthalein endpoint, and V_{mo} , which is the amount of acid in mL from the Phenolphthalein endpoint to the Methyl Orange endpoint. These two volumes can be determined graphically using Gran Plots, which plot the amount of titrant added, V_a , vs $V_a * 10^{eq} + pH$. These plots are created using the points from $0.8V_e$ through V_e . In this case, $V_p = V_{8.3}$, $V_p + V_{mo} = V_{4.3}$, and V is the sample volume (0.05 L). Once these values are determined, the types of alkalinity can be determined using the following equations (Hernández-Santana, 2020):

$$\text{Total Alkalinity } \left(\frac{eq}{L}\right) = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] - [H^+] = (V_{4.3} * N)/V$$

$$\text{Carbonate Alkalinity } \left(\frac{eq}{L}\right) = [CO_3^{2-}] + [OH^-] - [H^+] - [H_2CO_3^*] = (V_{8.3} * N)/V$$

$$\text{Caustic Alkalinity } \left(\frac{eq}{L}\right) = [OH^-] - [H^+] - [HCO_3^-] - 2[H_2CO_3^*] = (V_{10.3} * N)/V$$

Additionally, the concentration of certain carbonate and hydroxide species can be determined using V_p and V_{mo} . The following table gives the predominant form of alkalinity and equations for determining the concentration of this species for various conditions.

Table 1: Alkalinity Approximations

Condition	Predominant form of Alkalinity	Species, moles/L
$V_p = V_{mo}$	CO_3^{2-}	$[CO_3^{2-}] = V_p * N * V^{-1}$
$V_p = 0$	HCO_3^-	$[HCO_3^-] = V_{mo} * N * V^{-1}$
$V_{mo} = 0$	OH^-	$[OH^-] = V_p * N * V^{-1}$
$V_{mo} > V_p$	CO_3^{2-} and HCO_3^-	$[CO_3^{2-}] = V_p * N * V^{-1}$ $[HCO_3^-] = (V_{mo} - V_p) * N * V^{-1}$
$V_p > V_{mo}$	OH^- and CO_3^{2-}	$[CO_3^{2-}] = V_{mo} * N * V^{-1}$ $[OH^-] = (V_p - V_{mo}) * N * V^{-1}$

Calcium Carbonate Equilibria Determination:

Measure the initial pH of each water sample with a pH meter. If there are visible amounts of $CaCO_3(s)$, filter the samples through fine filter paper. To determine the total Ca^{2+} concentration, follow the procedures and calculations from the “*Total Calcium Determination*” methods. To

determine the alkalinity, follow the procedures and calculations from the “*Alkalinity Determination*” methods.

From there, the Q value, ΔG value, and Langelier Index value can be determined. The Q value, or reaction quotient, can be calculated using the following equation:

$$Q = \frac{[HCO_3^-][Ca^{2+}]}{[H^+]}$$

If the Q value is larger than the K value, the reaction will proceed to the left. If the Q value is smaller than the K value, the reaction will proceed to the right. Next, the ΔG value, or free energy change, can be determined using the following equation:

$$\Delta G = RT * \ln \frac{[HCO_3^-][Ca^{2+}]}{[H^+] * K}$$

If ΔG is equal to 0, the reaction is at equilibrium. If ΔG is less than zero, the reaction will proceed to the right. If ΔG is greater than zero, the reaction will proceed to the left and precipitation will tend to occur. The Langelier Index is another method to determine whether the solution is at equilibrium. The Langelier Index is determined using pH_a , which is the analytical pH, and pH_s , which is the saturation pH. The pH_a value is determined during the laboratory with a pH meter. The pH_s is determined using the measured values for bicarbonate and Ca^{2+} , along with the equilibrium constant, K. The pH_s can be calculated with the following equation

$$pH_s = -\log \frac{[HCO_3^-][Ca^{2+}]}{K}$$

Then, the Langelier Index can be calculated with the following equation:

$$L.I. = pH_a - pH_s$$

If the Langelier Index is equal to 0, the solution is at equilibrium with respect to $CaCO_{3(s)}$. If the Langelier Index is greater than 0, the solution is supersaturated with respect to $CaCO_{3(s)}$. If the Langelier Index is less than 0, the solution is undersaturated with respect to $CaCO_{3(s)}$, and dissolution tends to occur (Jenkins et al., 1973).

Results

The raw titration data for the hardness and Ca^{2+} determination experiments are shown in Table 2 below, along with average and standard deviation values for the multiple trials. For each sample, three titrations were performed. Ten titrations were performed for blanks.

Table 2: Raw Titration Data

Initial pH												
Trial Number	1	2	3	4	5	6	7	8	9	10	Average	Standard Deviation
Raw Water	8.50	8.25	8.59	-	-	-	-	-	-	-	8.45	0.18
Post Clarifier	10.57	10.39	10.39	-	-	-	-	-	-	-	10.45	0.10
Post Carbonation	10.49	9.45	9.38	-	-	-	-	-	-	-	9.77	0.62
Tap Water	10.81	8.76	10.47	-	-	-	-	-	-	-	10.01	1.10
Ground Water	10.35	9.21	10.43	-	-	-	-	-	-	-	10.00	0.68
Blank	7.48	6.95	10.46	9.48	8.70	9.48	7.02	8.20	8.77	9.52	8.61	1.18
EDTA added to color change for calcium determination (mL)												
Trial Number	1	2	3	4	5	6	7	8	9	10	Average	Standard Deviation
Raw Water	3.2	2.8	4.0	-	-	-	-	-	-	-	3.3	0.6
Post Clarifier	1.7	1.7	3.4	-	-	-	-	-	-	-	2.3	1.0
Post Carbonation	2.0	2.5	3.8	-	-	-	-	-	-	-	2.8	0.9
Tap Water	3.0	3.4	2.9	-	-	-	-	-	-	-	3.1	0.3
Ground Water	0.5	0.4	0.2	-	-	-	-	-	-	-	0.4	0.2
Blank	0.0	0.0	0.3	0.2	0.0	0.1	0.1	0.0	0.0	0.0	0.1	0.1
EDTA added to color change for total hardness determination (mL)												
Trial Number	1	2	3	4	5	6	7	8	9	10	Average	Standard Deviation
Raw Water	8.5	10.2	7.5	-	-	-	-	-	-	-	8.7	1.4
Post Clarifier	3.5	3.6	4.3	-	-	-	-	-	-	-	3.8	0.4
Post Carbonation	4.2	4.4	4.5	-	-	-	-	-	-	-	4.4	0.2
Tap Water	3.5	4.0	6.0	-	-	-	-	-	-	-	4.5	1.3
Ground Water	0.4	0.9	1.5	-	-	-	-	-	-	-	0.9	0.6
Blank	0.0	0.1	0.1	0.2	0.4	0.2	0.1	0.1	0.0	0.6	0.2	0.2

The average and standard deviation values of hardness, calcium concentration, and magnesium concentration for each type of water sample are shown in Table 3 below. These values were determined using the calculations from the “Methods and Materials” section.

Table 3: Total Hardness and Calcium and Magnesium Concentrations

Total Hardness	Average (mg CaCO₃ / L)	Standard Deviation
Raw Water	175	27
Post Clarifier	76	9
Post Carbonation	87	3
Tap Water	90	26
Ground Water	19	11
Blank	4	4
Calcium Concentration	Average (mg CaCO₃ / L)	Standard Deviation
Raw Water	67	12
Post Clarifier	45	20
Post Carbonation	55	19
Tap Water	62	5
Ground Water	7	3
Blank	1	2
Magnesium Concentration	Average (mg CaCO₃ / L)	Standard Deviation
Raw Water	108	39
Post Clarifier	31	11
Post Carbonation	32	16
Tap Water	28	29
Ground Water	11	14
Blank	2	5

The total carbonate concentration, bicarbonate concentration, carbonate concentration, proton concentration, total alkalinity, carbonate alkalinity, and caustic alkalinity, along with the average and standard deviation values across the three trials are shown in Table 4 below.

Table 4: Carbonate Species Concentrations and Alkalinity

Trial Number	1	2	3	Average	Standard Deviation
Total Carbonate Concentration (mM)					
Raw Water	2.79	2.79	2.70	3.76	0.05
Post Clarifier	0.68	0.53	0.46	0.56	0.11
Post Carbonation	2.27	0.67	1.03	1.32	0.84
Tap Water	1.27	1.02	0.97	1.09	0.16
Ground Water	4.25	4.24	4.34	4.27	0.05
Bicarbonate Concentration (mM)					
Raw Water	2.73	2.73	2.63	2.69	0.06
Post Clarifier	0.29	0.15	0.11	0.18	0.09
Post Carbonation	0.52	0.47	0.91	0.63	0.24
Tap Water	1.25	1.00	0.95	1.02	0.16
Ground Water	4.15	4.02	4.20	4.12	0.09
Carbonate Concentration (mM)					
Raw Water	0.01	0.02	0.01	0.01	0.00
Post Clarifier	0.40	0.38	0.35	0.38	0.03
Post Carbonation	1.75	0.20	0.12	0.70	0.92
Tap Water	0.02	0.01	0.01	0.01	0.00
Ground Water	0.08	0.20	0.12	0.13	0.06
Proton Concentration (mM)					
Raw Water	9.33E-6	8.91E-6	1.17E-5	9.92E-6	1.53E-6
Post Clarifier	3.63E-8	1.91E-8	1.62E-8	2.39E-8	1.09E-8
Post Carbonation	3.31E-7	4.17E-7	3.80E-7	3.76E-7	4.30E-8
Tap Water	3.31E-6	3.98E-6	3.98E-6	3.76E-6	3.87E-7
Ground Water	2.69E-6	2.88E-6	2.09E-6	2.55E-6	4.15E-7
Total Alkalinity (mg CaCO₃/L)					
Raw Water	158	159	151	156	4
Post Clarifier	47	52	51	50	3
Post Carbonation	45	45	60	50	9
Tap Water	67	53	50	56	9
Ground Water	273	277	282	277	5
Carbonate Alkalinity (mg CaCO₃/L)					
Post Clarifier	27	32	33	30	3
Post Carbonation	9	10	6	8	2
Ground Water	4	10	6	7	3
Caustic Alkalinity (mg CaCO₃/L)					
Post Clarifier	6	15	12	11	5

The bicarbonate concentration, carbonate concentration, total alkalinity, carbonate alkalinity, and caustic alkalinity were calculated according to the steps outlined in the “Methods and Materials” section. For the carbonate and bicarbonate concentrations, Table 1 was used to determine the predominant form of alkalinity. V_p and V_{mo} were determined using Gran plots

rather than indicator color change. The Gran plots are located in Appendix A. The values for V_p and V_{mo} are shown in Table 5 below.

Table 5: V_p and V_{mo} Values

Trial Number	1	2	3
V_p (mL)			
Raw Water	0.0	0.0	0.0
Post Clarifier	1.3	1.6	1.7
Post Carbonation	0.4	0.5	0.3
Tap Water	0.0	0.0	0.0
Ground Water	0.2	0.5	0.3
V_{mo} (mL)			
Raw Water	7.9	7.9	7.6
Post Clarifier	1.0	1.0	0.9
Post Carbonation	1.8	1.7	2.7
Tap Water	3.3	2.6	2.5
Ground Water	13.4	13.4	13.8

When there were insufficient data to create a Gran plot, linear interpolation or indicator color change was used to determine V_p and V_{mo} . The total volumes in these calculations accounted for dilution during the titration. When one of the species was not present as a predominant form of alkalinity in Table 1, the equilibrium equations were used to determine the species concentration. For carbonate and bicarbonate, the following equation was used (Jensen, 2003):

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.3}$$

To determine the concentration of carbonic acid, the following equation was used:

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 10^{-6.3}$$

The total carbonate concentration was found by adding together the carbonate, bicarbonate, and carbonic acid concentrations for each sample. For alkalinity, $V_{4.3}$, $V_{8.3}$, and $V_{10.3}$ were found using the same Gran plots. Since the initial pH was below 10.3 for every sample except the post clarifier samples, only the post clarifier samples had caustic alkalinity values. Since the initial pH was below 8.3 for the raw water and tap water sample, there were no carbonate alkalinity values for those samples.

The reaction quotient, Q; free energy change, ΔG ; analytical pH, pH_a ; saturation pH, pH_s ; and Langelier Index values are shown in Table 6 below, along with the average and standard deviation values.

Table 6: Calcium Carbonate Equilibrium Data

Trial Number	1	2	3	Average	Standard Deviation
Q					
Raw Water	187	172	179	179	8
Post Clarifier	2690	2600	4720	3337	1199
Post Carbonation	625	569	1824	1006	709
Tap Water	226	171	138	179	44
Ground Water	154	111	80	115	37
ΔG (kcal)					
Raw Water	0.38	0.33	0.36	0.36	0.03
Post Clarifier	1.96	1.94	2.30	2.07	0.20
Post Carbonation	1.10	1.04	1.73	1.29	0.38
Tap Water	0.50	0.33	0.21	0.34	0.15
Ground Water	0.27	0.08	-0.12	0.08	0.19
pHa					
Raw Water	8.03	8.05	7.93	8.00	0.06
Post Clarifier	10.44	10.72	10.79	10.65	0.19
Post Carbonation	9.48	9.38	9.42	9.43	0.05
Tap Water	8.48	8.40	8.40	8.43	0.05
Ground Water	8.57	8.54	8.68	8.60	0.07
pHs					
Raw Water	7.75	7.81	7.67	7.74	0.07
Post Clarifier	9.00	9.30	9.12	9.13	0.15
Post Carbonation	8.67	8.61	8.15	8.48	0.29
Tap Water	8.12	8.16	8.25	8.17	0.07
Ground Water	8.37	10.74	8.76	9.29	1.27
Langelier Index Values					
Raw Water	0.28	0.24	0.26	0.26	0.02
Post Clarifier	1.44	1.42	1.68	1.52	0.15
Post Carbonation	0.81	0.77	1.27	0.95	0.28
Tap Water	0.36	0.24	0.15	0.25	0.11
Ground Water	0.20	-2.20	-0.08	-0.69	1.31

Discussion

From the total hardness, calcium, and magnesium averages, it can be assumed that these three values decrease from the raw water that enters the Norman Drinking Water Treatment Plant to the water after it goes through the primary clarifier. The total hardness decreased by about 100 mg CaCO₃/L; the calcium concentration decreased by about 20 mg CaCO₃/L; the magnesium concentration decreased by about 75 mg CaCO₃/L. The overall decrease is likely due to the lime addition, which is the process that intentionally softens water. Lime is added that causes CaCO_{3(s)} and Mg(OH)_{2(s)} to precipitate out of the solution and settle during the flocculation process. The data show that the decrease in magnesium concentration is greater than the decrease in calcium concentration. This means that the Mg(OH)_{2(s)} was precipitated at a greater rate than the CaCO_{3(s)}.

From the primary clarifier to post carbonation, the total hardness, calcium concentrations, and magnesium concentrations slightly increase. The total hardness and calcium concentrations both increased by about 10 mg CaCO₃/L, and the magnesium concentration remained about the same throughout this process. This indicates that the increase in total hardness is almost completely caused by the increase in calcium concentration. This is likely due to the recarbonation where CO₂ is added to the water which reduces the pH by increasing the amount of carbonic acid present in the water. Since calcium carbonate is more soluble at lower pH, more calcium is present in the dissolved form, and the hardness increases.

From the post carbonated water to a Norman water tap, the total hardness, calcium concentration, and magnesium concentration values remain about the same. The total hardness increased by 3 mg CaCO₃/L; the calcium concentration increased by 7 mg CaCO₃/L; the magnesium concentration decreased by 4 mg CaCO₃/L. These slight increase in calcium concentration could have been caused by excess calcite that lines pipes dissolving in the water (Radziul et al., 1965). The slight decrease in magnesium concentration could have been caused by Mg(OH)_{2(s)} being filtered out in the final filtration process at the Norman Drinking Water Treatment Plant.

From the average total alkalinity values, it can be assumed that the alkalinity decreases from the raw water that enters the Norman Drinking Water Treatment Plant to the water after it goes through the primary clarifier. The total alkalinity decreased by about 100 mg CaCO₃/L, which is almost exactly the same as the decrease in water hardness. While the pH is higher at this point in the water treatment process, which would increase alkalinity, the alkalinity likely decreases because the dissolved carbonate species in the water decrease. For example, the bicarbonate concentration from the raw water to the post clarifier water decreases by about 2.5 mM. This decrease is likely related to the water hardness—it takes one mole of carbonate per mole of calcium precipitated from the water.

From the post clarifier to the post carbonation stages, the total alkalinity remained about the same. The carbonate alkalinity, however, decreased by about 20 mg CaCO₃/L. Since the carbonate alkalinity depends on and is inversely related to the amount of carbonic acid in the water, this decrease was caused by the increase in carbonic acid from the recarbonation process.

From the post carbonation to the tap water, the total alkalinity increased by about 6 mg CaCO₃/L. This could be caused by the slight increase in water hardness, or, more specifically, the increase in calcium concentration in the water. If calcium is not being precipitated out, the carbonate species remain in the water.

Table 7 below shows reference values for total hardness and calcium hardness from Norman tap water and ground water from the Garber-Wellington Aquifer provided by Geri Wellborn at the Norman Drinking Water Treatment Plant.

Table 7: Reference Hardness Values

Parameter	Tap Water	Groundwater
Total hardness (mg CaCO ₃ /L)	79-85	99
Calcium hardness (mg CaCO ₃ /L)	30-35	50
Magnesium hardness (mg CaCO ₃ /L)	Not reported	Not reported

For the tap water sample, the calculated value for total hardness was slightly higher than the reference value—the calculated value was 90 mg CaCO₃/L, which is 5 units of mg CaCO₃/L higher than the upper range of the reference value. While this difference is relatively small, the difference could have been caused by different methods for measuring hardness, such as a soap test kit, or taking water samples from different taps that have differing amounts of CaCO_{3(s)} lining the pipes that could have dissolved in the water (USGS, n.d.).

On the other hand, the calculated value for the calcium concentration of the tap water was about double the reference value at an average of 62 mg CaCO₃/L. This indicates that the total hardness in the reference tap water has a greater rate of dissolved magnesium to dissolved calcium. Again, this difference could be caused by using different samples of tap water that are irregularly mixed or travel through pipes with different amounts of calcite build up. Additionally, the reference water could have potentially been filtered before measuring the calcium concentration. Carbon filters can cause calcium to adsorb to the carbon in the filter, lowering the concentration in the water (Morr et al., 2006).

For the groundwater sample, the calculated value of total hardness is much smaller than the total hardness from the reference value—19 mg CaCO₃/L vs 99 mg CaCO₃/L. The value of calcium concentration is also much smaller than the reference value for calcium concentration—7 mg CaCO₃/L vs 50 mg CaCO₃/L. This large difference is caused by collecting ground water from two different wells. The University of Oklahoma maintains their own wells that are separate from the Norman wells. These wells potential use different treatment processes to treat the groundwater. While the total hardness values and calcium concentrations are much smaller than a typical sample from the Garber Wellington aquifer, which has an average water hardness of 278 mg/L, the well water at the University of Oklahoma may go through processes that soften the water (OWRB, 2013). Moreover, the well location could play a role in the water hardness. Since the Garber-Wellington Aquifer is so large, different samples of water from the same well can have very different total hardness concentrations.

The reaction quotient, Q; free energy change, ΔG; and Langelier Index values were used to determine if each water sample is in equilibrium with CaCO_{3(s)}. Since the Q values for each sample (except the trial 3 ground water sample) are larger than K = 10^{1.99}, these samples are not at equilibrium and will proceed towards the reactants. The Q value for trial 3 of the ground water sample is 80, which is less than 10^{1.99}. This sample is close to equilibrium but would proceed toward the products. Since all of the ΔG values (except the trial 3 ground water sample) are larger than 0, the reaction will proceed to the left, and precipitation of CaCO_{3(s)} will tend to occur. The ΔG value for trial 3 of the ground water sample is -0.12 kcal, which is less than zero. This sample would proceed to the right to reach equilibrium. The Langelier Index values also determine saturation level. In this case, since all of the Langelier Index values are greater than 0 (except for the trial 2 and 3 ground water samples), the solutions are all supersaturated with respect to

$\text{CaCO}_{3(s)}$, and precipitation will tend to occur. The Langelier Index values for trials 2 and 3 of the ground water sample are -2.20 and -0.08, respectively. Since these values are less than 0, the solution is undersaturated with respect to CaCO_3 , and dissolution would tend to occur (Jenkins et al., 1973).

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<http://wcponline.com/2008/07/21/ozone-treatment-iron-manganese-sulfide-ion-part/>

Appendix A: Gran Plots

Raw Water:

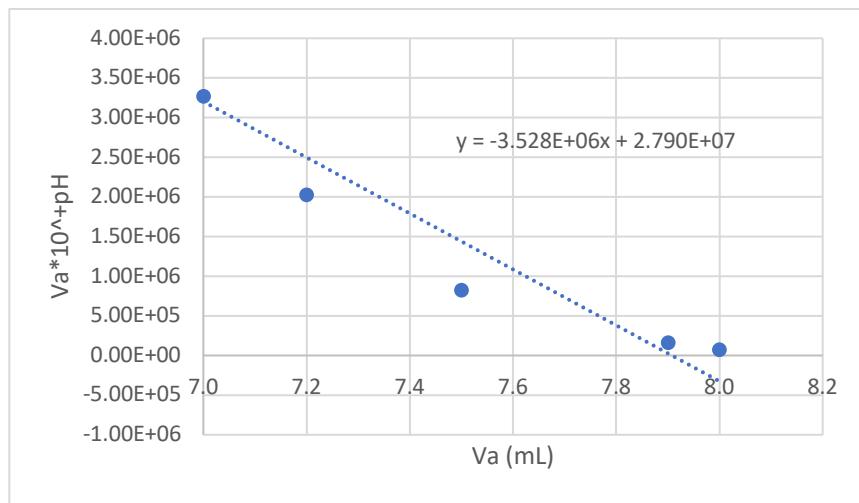


Figure 1: Raw Water Trial 1 Gran Plot for $V_{4.3}$ Determination

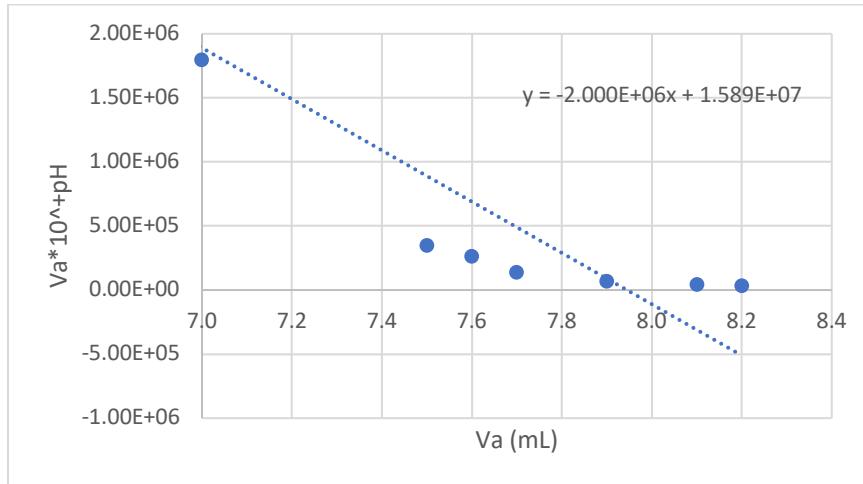


Figure 2: Raw Water Trial 2 Gran Plot for $V_{4.3}$ Determination

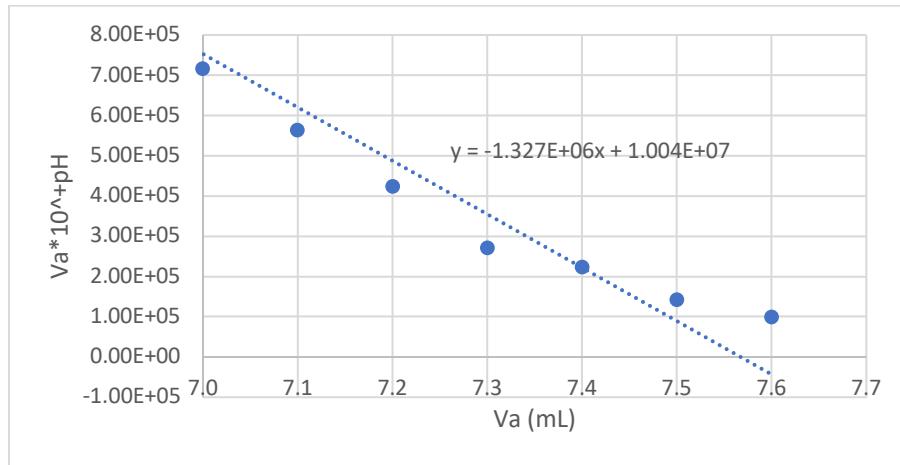


Figure 3: Raw Water Trial 3 Gran Plot for $V_{4.3}$ Determination

Post Clarifier:

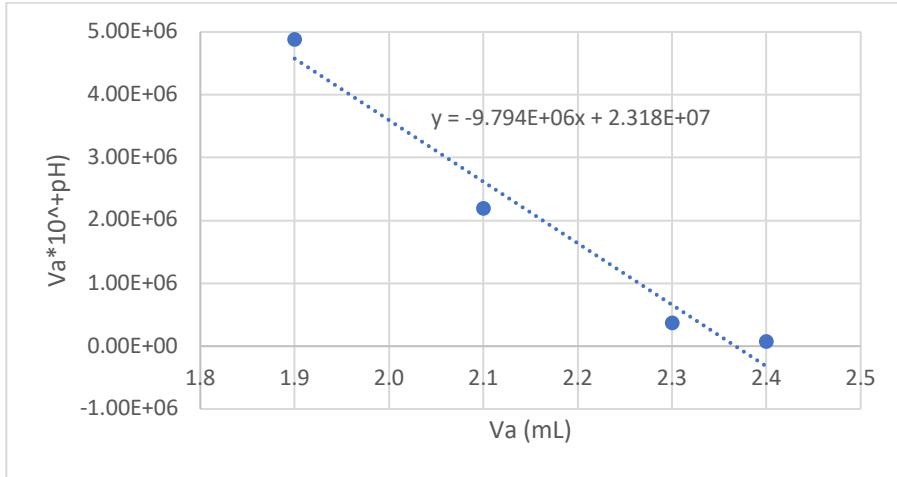


Figure 4: Post Clarifier Trial 1 Gran Plot for $V_{4.3}$ Determination

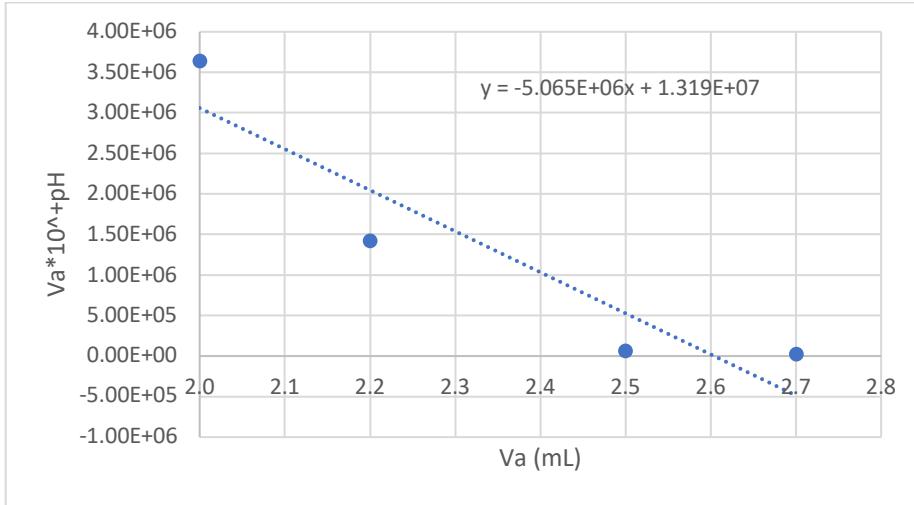


Figure 5: Post Clarifier Trial 2 Gran Plot for $V_{4.3}$ Determination

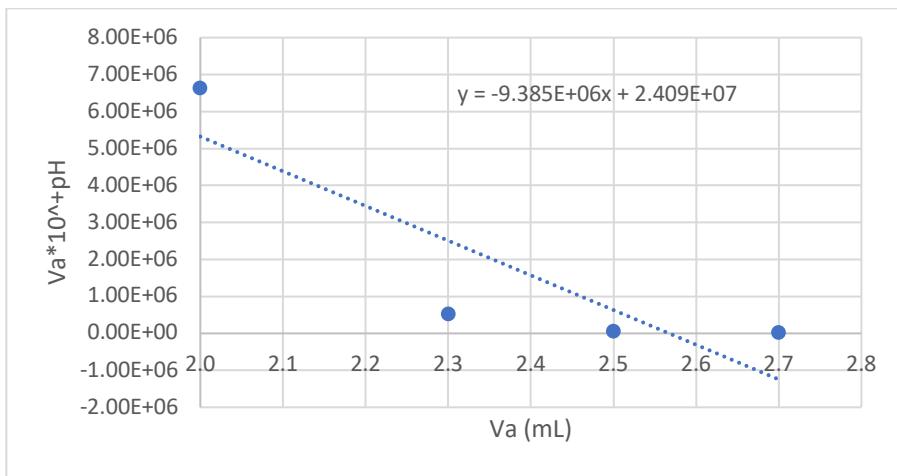


Figure 6: Post Clarifier Trial 3 Gran Plot for $V_{4.3}$ Determination

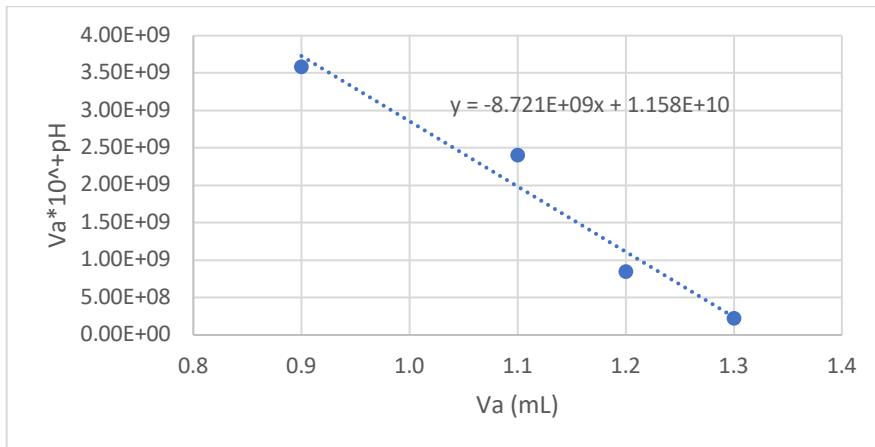


Figure 7: Post Clarifier Trial 1 Gran Plot for $V_{8.3}$ Determination

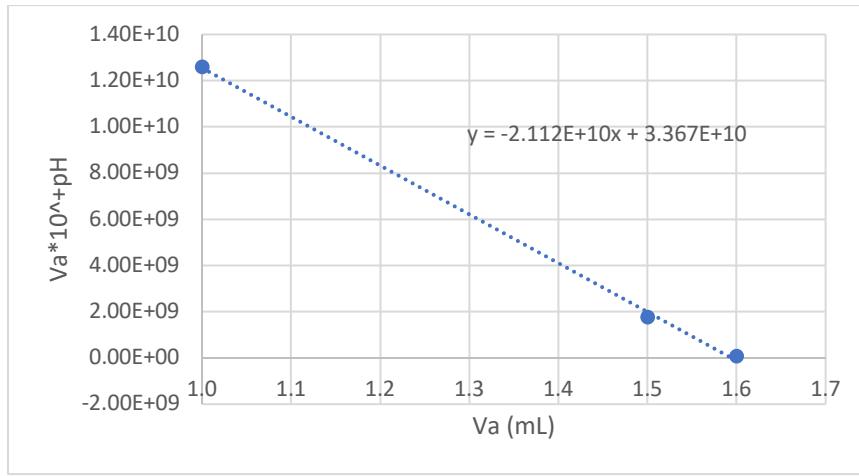


Figure 8: Post Clarifier Trial 2 Gran Plot for $V_{8.3}$ Determination

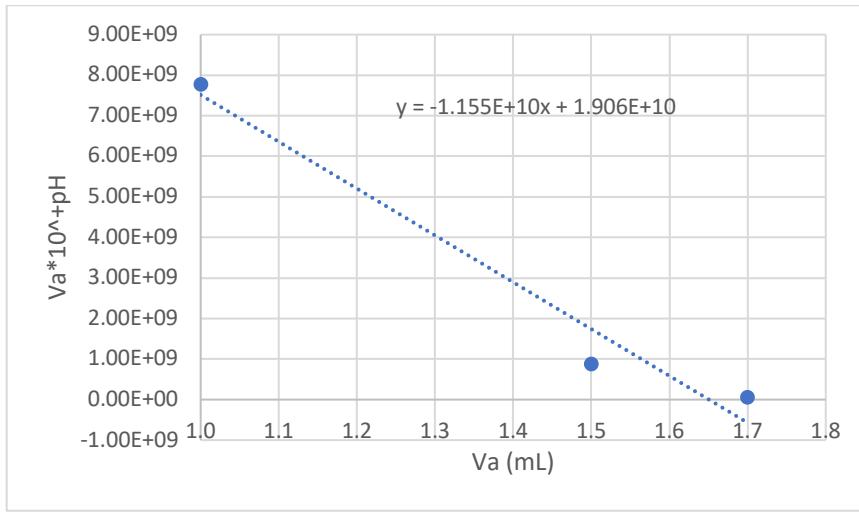


Figure 9: Post Clarifier Trial 3 Gran Plot for $V_{8.3}$ Determination

Post Carbonation:

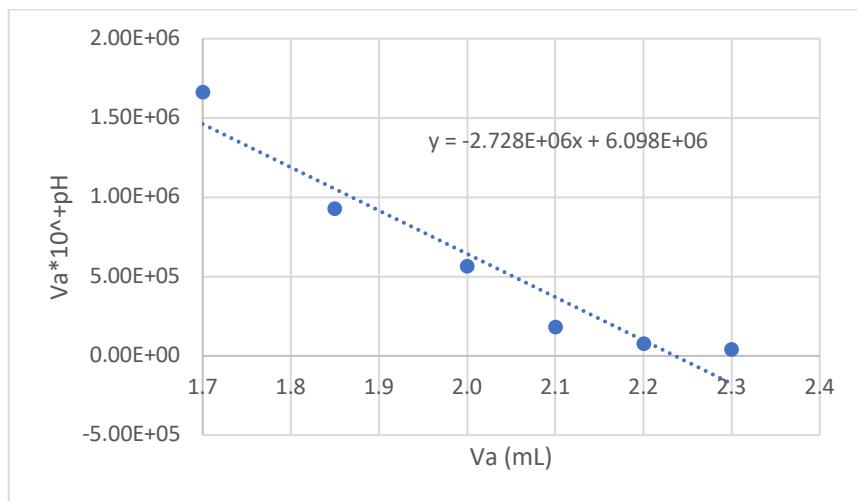


Figure 10: Post Carbonation Trial 1 Gran Plot for $V_{4.3}$ Determination

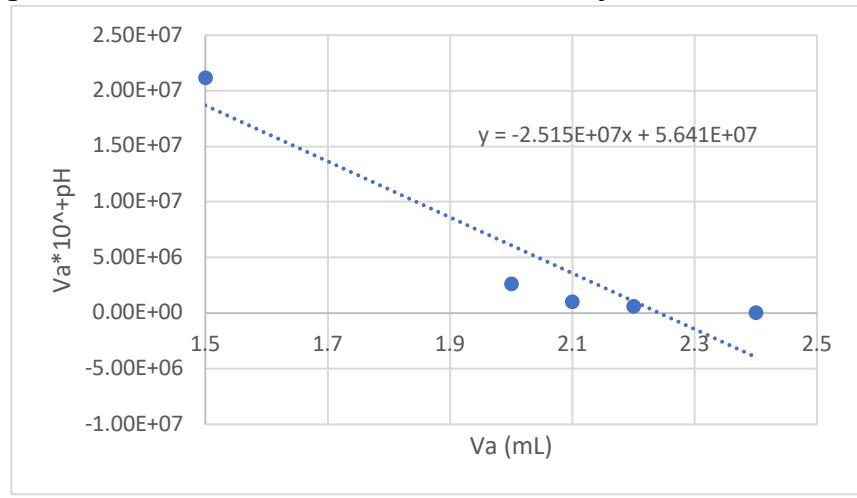


Figure 11: Post Carbonation Trial 2 Gran Plot for $V_{4.3}$ Determination

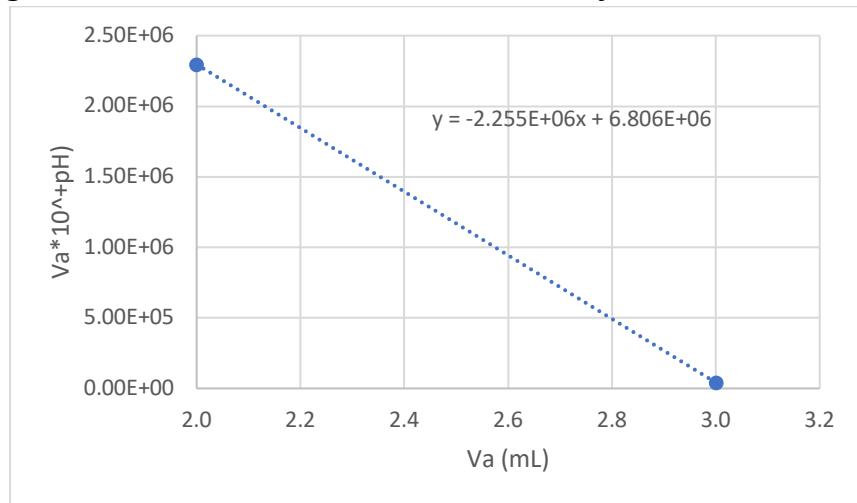


Figure 12: Post Carbonation Trial 3 Gran Plot for $V_{4.3}$ Determination

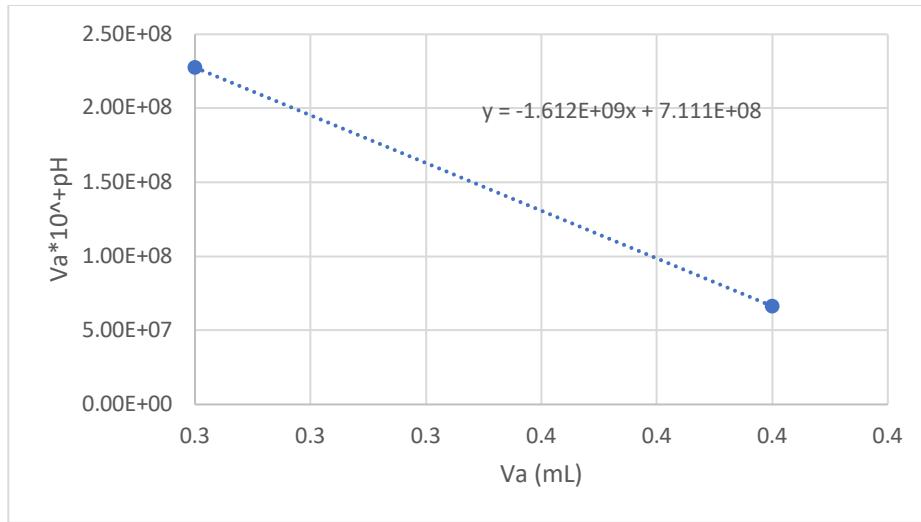


Figure 13: Post Carbonation Trial 1 Gran Plot for $V_{8.3}$ Determination

Tap Water:

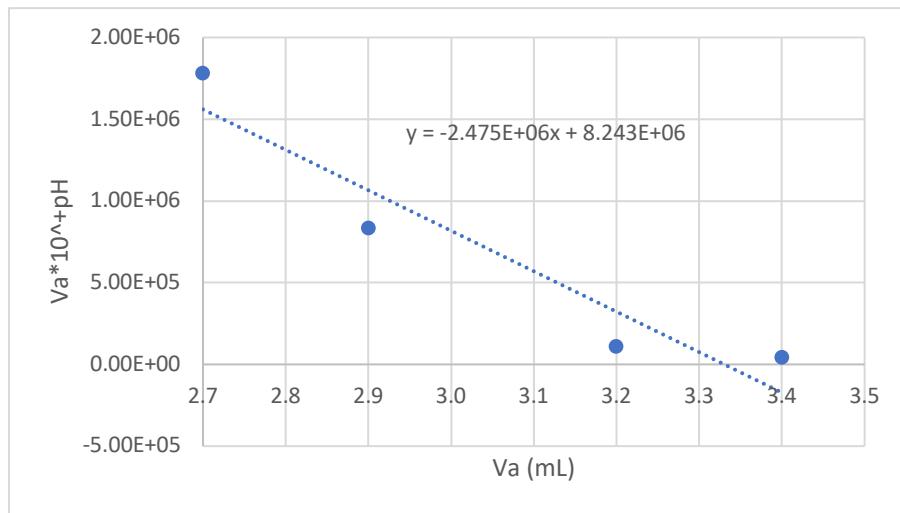


Figure 14: Tap Water Trial 1 Gran Plot for $V_{4.3}$ Determination

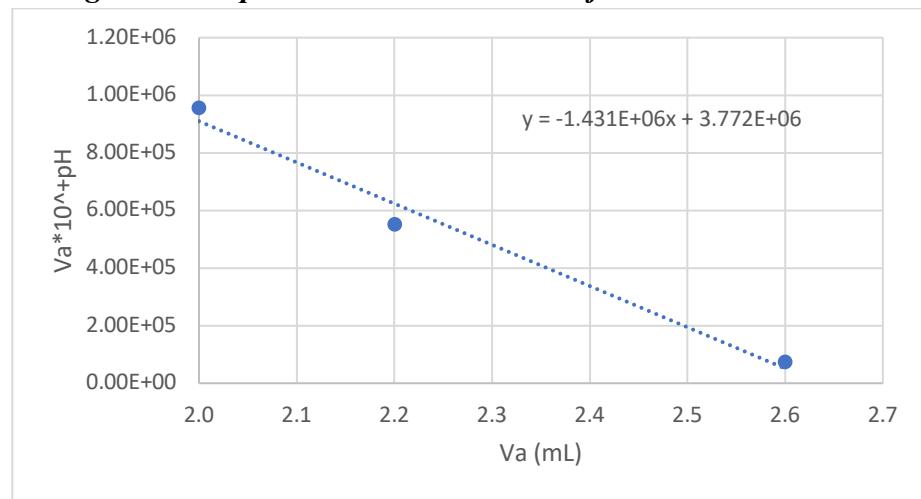


Figure 15: Tap Water Trial 2 Gran Plot for $V_{4.3}$ Determination

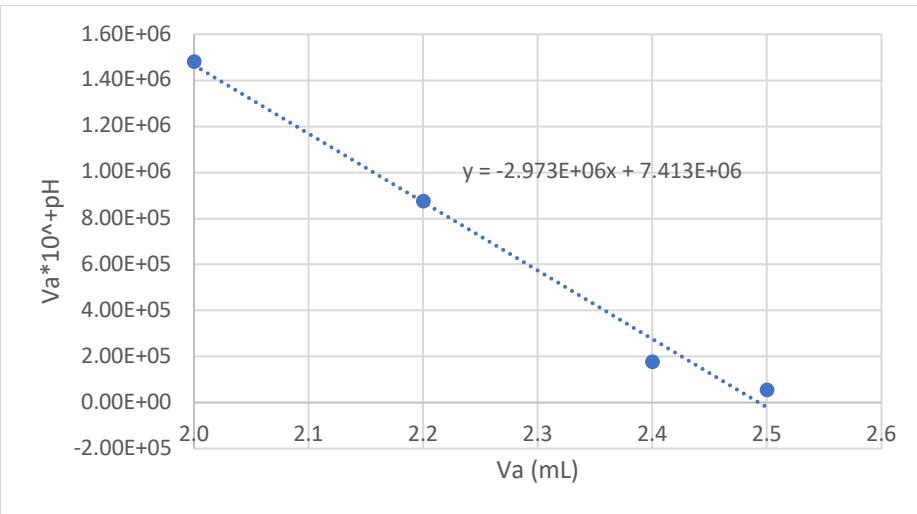


Figure 16: Tap Water Trial 3 Gran Plot for $V_{4.3}$ Determination

Groundwater:

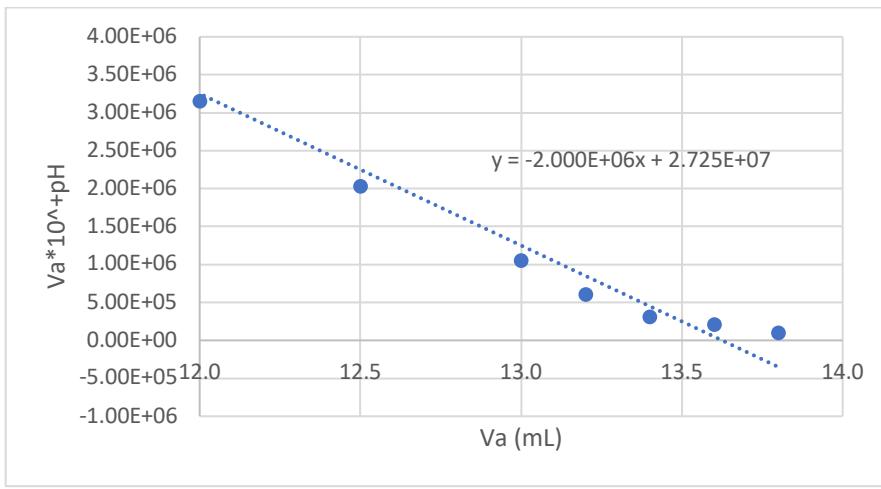


Figure 17: Groundwater Trial 1 Gran Plot for $V_{4.3}$ Determination

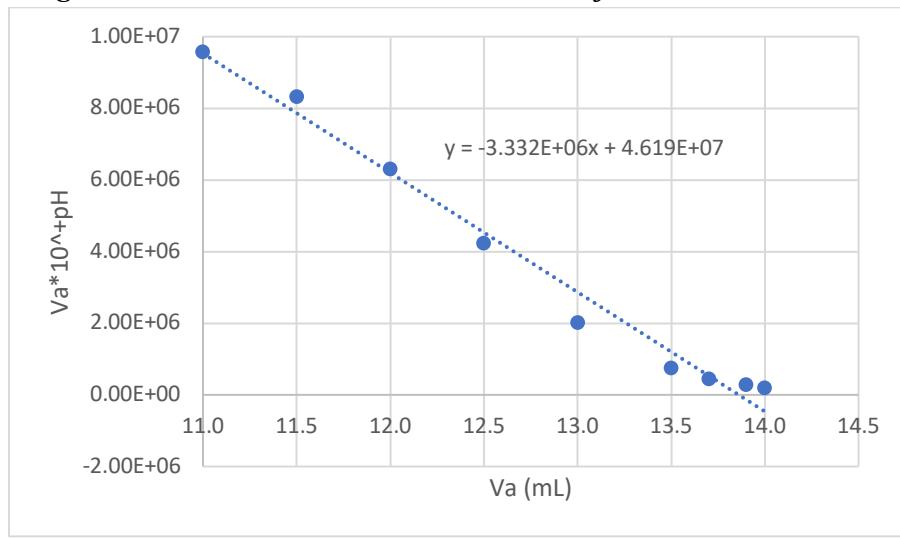


Figure 18: Groundwater Trial 2 Gran Plot for $V_{4.3}$ Determination

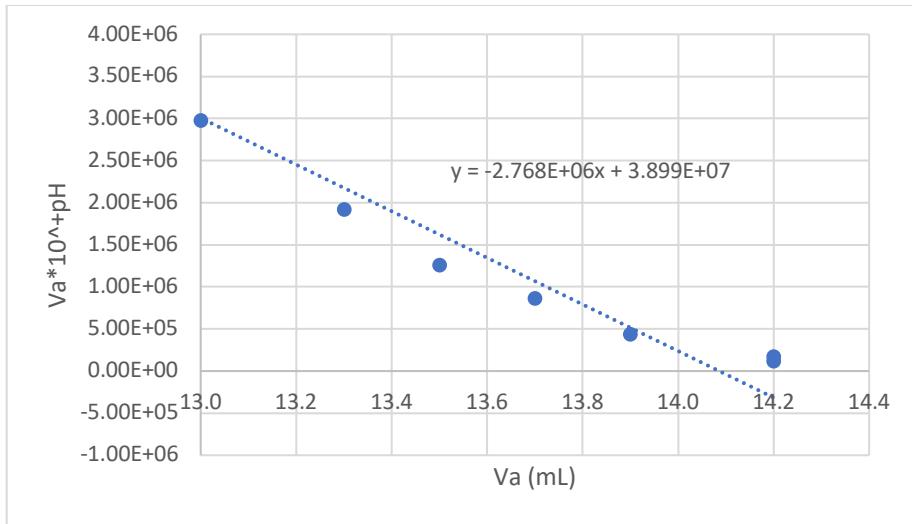


Figure 19: Groundwater Trial 3 Gran Plot for $V_{4.3}$ Determination