TAP WATER ANALYSIS BY ATOMIC ABSORPTION SPECTROSCOPY AND ION CHROMATOGRAPHY

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INTRODUCTION

Tap water is supplied by a combination of surface water and underground reservoirs, and contains a variety of dissolved minerals. The "hardness" of the water depends on the type and concentration of salts present, and is usually reported as the concentration of $CaCO_3$; water in the range of 0-60 ppm $CaCO_3$ is said to be "soft," 61-120 is "moderate," 121-180 is "hard," and concentrations greater than 181 are considered "very hard."[1] Hard water can lead to mineral deposits on the insides of pipes, reducing their efficiency and eventually breaking down the material; in the home, hard water can reduce the effectiveness of soaps. In this study, a tap water sample was collected and analyzed for the presence of Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}. For the retrieval location of the tap water (38.548 degrees N, -121.424 degrees W), the water is reported to be 97% groundwater and 3% surface water.[4] Because groundwater makes up a majority of the water source, a higher concentration of Cl^- and SO_2^{2-} are to be expected, but these ions, along with Mg^{2+} and Ca^{2+}, are low priority pollutants with minimal effects.[1] NO_3^-, however, is a high priority pollutant that results from fertilizer; according to the EPA, levels above 10 mg/L are considered a health risk for young infants and pregnant women.[4] The concentrations of Ca^{2+} and Mg^{2+} were determined using atomic absorption spectroscopy, and Cl^-, NO_3^-, and SO_4^{2-} were determined using ion chromatography. The hardness of the tap water was also calculated.

EXPERIMENTAL METHODS

I. ATOMIC ABSORPTION SPECTROSCOPY

When an aqueous solution containing dissolved metals is taken up into an AAS (Figure 1), a nebulizer sprays the solution as a mist into a flame.[1] A hollow cathode lamp shines a beam of photons that possess the exact amount of energy required to cause atomic transitions in the metal atoms in the flame. The light from the lamp passes through the flame, through a monochromator,

and is picked up by a detector. The monochromator helps eliminate all other light except the desired spectral line emitted by the lamp (i.e. the light from the flame), while the detector measures the difference in light intensity due to the absorption of the sample atoms in the flame.

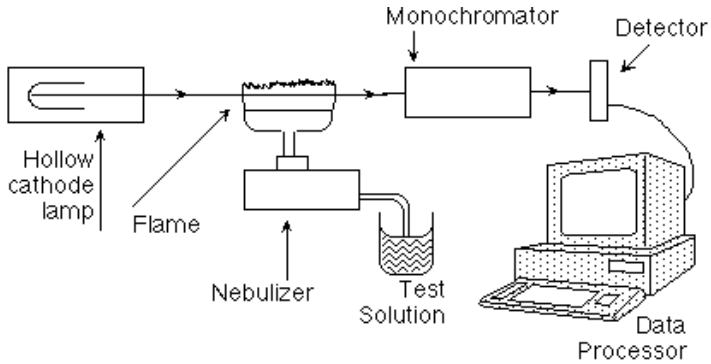

Figure 1. Atomic absorption spectroscopy schematic diagram.[3]

For absorption experiments, Beer's law plots are used to make calibration lines by plotting the absorbance and concentration of prepared standard solutions.[1] From the $CaCO_3$ standard solution used in the Water Hardness lab, a variety of dilutions were calculated and the ideal five were selected to be prepared in the range of 1 ppm and 10 ppm. The dilutions and resulting concentrations of Ca chosen are shown in Table 1. The concentration of the Mg stock solution was calculated, which was then diluted to create a daughter solution. The daughter solution was used to calculate and select five ideal standard solutions in the same manner as the Ca standards. The five Mg standards were created to range from 0.1 ppm to 1.0 ppm (Table 1).

Ca			Mg		
mL Stock	mL Diluted	ppm Ca	mL Semi-Stock	mL Diluted	ppm Mg
1.0	500.0	1.192	1.0	1000.0	0.1026
5.0	1000.0	2.982	3.0	1000.0	0.3078
4.0	500.0	4.771	5.0	1000.0	0.5130
3.0	250.0	7.157	4.0	500.0	0.8208
4.0	250.0	9.542	5.0	500.0	1.026

Table 1. Dilutions used in the creation of five Ca and five Mg standard solutions, and their resulting concentrations.

Because the hardness of the tap water sample was unknown, three dilutions were performed and analyzed along with the original tap water sample: 1:50, 1:20, and 1:4 dilutions.

II. ION CHROMATOGRAPHY

The ion chromatograph is used to separate anions in the sample (Cl^-, NO_3^-, and SO_4^{2-}) based on how they partition between a mobile phase and a stationary phase. An eluent is loaded onto the column and then the sample is injected; the constant addition of eluent forces the sample to flow through the column, and as it elutes, the anions will adhere to the surface of the column differently.[5] As shown in Figure 2, they enter a suppressor and are then detected by the conductivity detector. The electrical signal is plotted against time to produce a chromatogram.

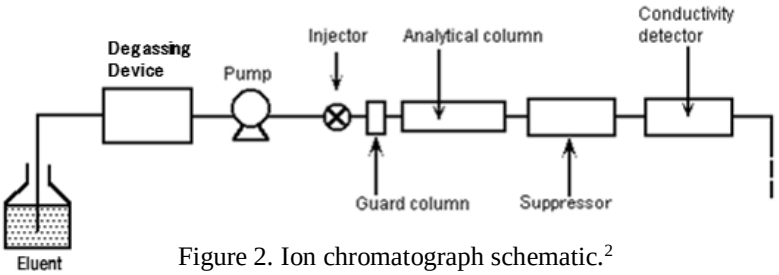

Figure 2. Ion chromatograph schematic.[2]

The instructor prepared and ran calibration standards for chloride, nitrate, and sulfate (Table 2).

Peak Name	Ret. Time (min)	Concentration (ppm)	Area (uS*min)
Chloride (Cl^-)	1.45	20	1.935
Nitrate (NO_3^-)	2.61	40	1.976
Sulfate (SO_4^{2-})	3.80	40	2.488

Table 2. Ion chromatography standards prepared by Dr. Toofan.

After the (undiluted) tap water sample was run through the ion chromatograph, peak areas for each ion were used to calculate the concentrations using the one-point calibration method (Equation 1).

$$\frac{Area\ (standard)}{Area\ (sample)} = \frac{Concentration\ (standard)}{Concentration\ (sample)} \qquad (1)$$

RESULTS

When the standard calcium concentrations were plotted versus absorbance, the calibration curve produced an R^2 value of 0.998 and exhibited a strong linear relationship (Figure 3). The concentration of Ca in the tap water sample was calculated to be 4.2 ppm with a 95% confidence interval of ± 0.6 ppm. Likewise, the magnesium calibration curve also displayed a strong linear

relationship, shown by its R^2 value of 0.994 (Figure 4). The concentration of Mg in the tap water sample was calculated to be 1.1 ppm with a 95% confidence interval of ± 0.5 ppm (Table 3).

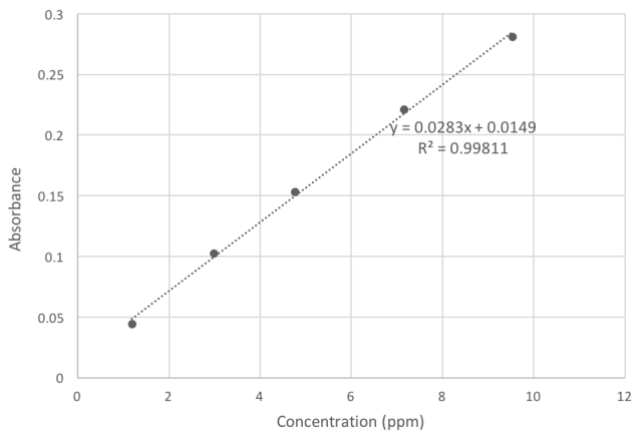

Figure 3. Calcium ion standard calibration curve.

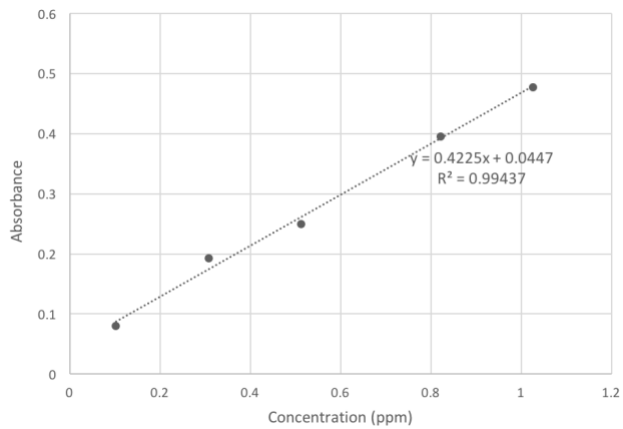

Figure 4. Magnesium ion standard calibration curve.

Ion	Line Equation	Dilution Factor	Absorbance	Conc. by Equation (ppm)	Conc. in Original Solution (ppm)
Ca	y = 0.0283x + 0.0149	none	0.133	4.169	4.169
Mg	y = 0.4225x + 0.0447	1 : 4	0.165	0.285	1.139

Table 3. Calculated concentrations of Ca and Mg ions in original tap water sample.

The concentrations of chloride, nitrate, and sulfate were calculated using a combination of the ion chromatography calibration curve (Figure 5) and the one-point calibration method, the results of which are shown in Table 4.

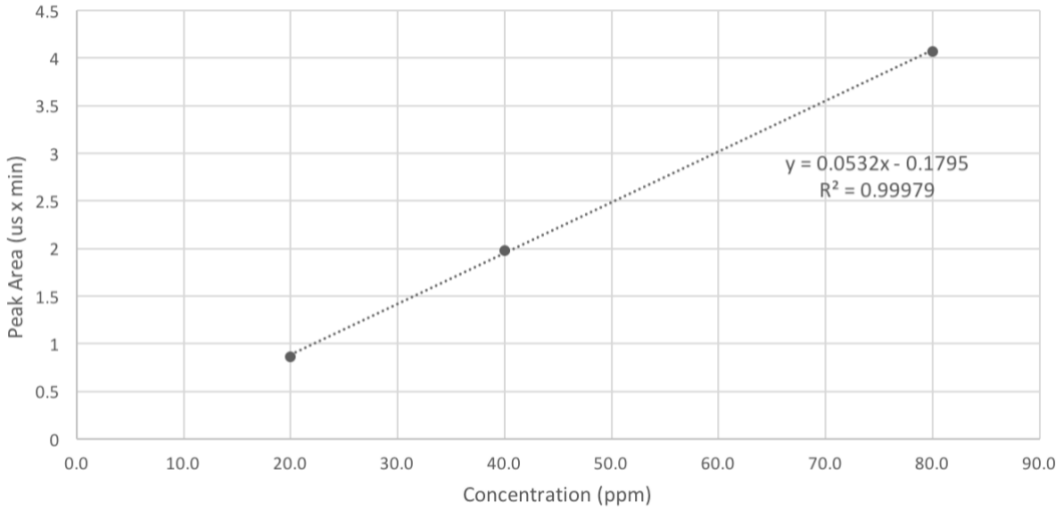

Figure 5. Ion chromatography calibration curve created using two student standards and one instructor standard.

Compound	Retention Time (min)	Peak Area (us x min)	Estimated Conc. (ppm)
Cl^-	1.46	0.527	5.45
NO_3^-	2.67	0.459	9.29
SO_4^{2-}	3.86	0.465	7.48

Table 4. Concentration of ions calculated using ion chromatography.

The hardness of the tap water sample was calculated by converting the concentrations of Ca and Mg to $CaCO_3$ and adding the two together, the result of which was 15.1 ppm.

DISCUSSION

For the Mg^{2+} and Ca^{2+} levels in the tap water, both absorbance measurements were within the limits of their standards, so the measurements were reliable, and were below the expected range for these constituents. For Cl^-, NO_3^-, and SO_4^{2-}, the measured peak areas were all below the range of the standards, so their reliability is reduced and their concentrations can only be estimated. The nitrate concentration was within the legal limit (Maximum Contaminant Level = 10 ppm), as was chloride (MCL = 500 ppm) and sulfate (MCL = 500 ppm).[4] Out of the five ions analyzed, only the test for magnesium required the tap water to be diluted; this result may have more error than the other four that used the original tap water sample because each dilution introduces more possible error. The calculated water hardness for the tap water was approximately 15 ppm, which falls within the "soft" range.

REFERENCES

1. Dixon, Roy. *Chemistry 31 Laboratory Manual*. CSU Sacramento. Fall 2017.

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5. Wenzel, Thomas. "Basic Principles of Ion Chromatography." *Chemistry LibreTexts*, Sonoma State University. 3 January 2017.