

Tap Water Hardness:
A Tap Water Analysis Study

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Section: 07

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INTRODUCTION:

Eighty-five percent of Sacramento's tap water supply originates from surface water reservoirs, such as the American River. Because most of the water is supplied from rivers, tap water tends to contain dissolved minerals due to the dissolution of soluble cations and anions found in the soil at the bottom of the river. Common ions include: Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- as well as NO_3^- , which makes its way into rivers through fertilizers. Concentrations of these ions varies and given this, water is measured based on its "Water Hardness", which is defined as the amount of dissolved Calcium and Magnesium in water. Water Hardness tends to be measured based on the concentration of CaCO_3 of the water in ppm where 0 to 60 ppm is classified as soft, 61 to 120 ppm as moderately hard, 121 to 180 ppm as hard, and anything more than 180 ppm as very hard.

Water that's classified as hard or very hard tends to be associated with negative side effects that the EPA wants to avoid. A high level of Ca^{2+} and Mg^{2+} can result in a build up of CaCO_3 deposits in underground pipe line systems that are used to transport this water across the city of Sacramento, reducing the diameters of the water pipes and resulting in less water movement. A high level of NO_3^- on the other hand can have negative health related effects, primarily on the hemoglobin of infants. Additionally, hard water can also be found to be problematic in home uses as well, where using hard water to wash hands or dishes with soap can often times result in a reaction between the calcium in the water and the soap, effectively reducing the efficiency of the soap at removing dirt. For these reasons, the EPA has set legal limits to which the concentrations of these ions cannot exceed. NO_3^- for example has a legal limit of 10 ppm. In this study, I will analyze a tap water sample obtained locally to determine whether or not these legal limits are met.

EXPERIMENTAL METHOD:

I. ATOMIC ABSORPTION SPECTROSCOPY

A quantitative method of Atomic Absorption Spectroscopy was used for the determination of Mg^{2+} and Ca^{2+} concentration in local tap water. Tap water was collected at the location: 38°33'22'' N, 121°25'17'' in the Sacramento district, and used to create four samples. Samples included: three diluted tap water samples and one original tap water sample. Dilution factors that were used for the three diluted samples were: 1:50, 1:20 and 1:4. Five standard solutions were also prepared for each of the two ions listed above (a total of 10 standard solutions). The standards for Ca^{2+} consisted of five solutions, which were within the range of 1-10 ppm of Ca^{2+} , while the standards for Mg^{2+} consisted of five standard solution within a range of 0.1-1 ppm of Mg^{2+} . Standards were prepared using volumetric glassware that involved adding variable volumes of stock/semi-stock solutions with known concentrations using a volumetric pipet and adding that volume into a volumetric flask for dilution. Dilutions that were performed are included in the following table (Table 1):

Mg^{2+}			Ca^{2+}		
mL semi-Stock	Volumetric Flask	Ppm Mg^{2+}	mL Stock	Volumetric Flask	Ppm Ca^{2+}
1 mL	1,000 mL	0.108 ppm	1 mL	250 mL	2.45 ppm
2 mL	1,000 mL	0.216 ppm	2 mL	250 mL	4.89 ppm
3 mL	1,000 mL	0.324 ppm	1 mL	100 mL	6.11 ppm
5 mL	1,000 mL	0.540 ppm	3 mL	250 mL	7.33 ppm
8 mL	1,000 mL	0.864 ppm	4 mL	250 mL	9.78 ppm

Table 1. Dilutions performed in the makings of the five standards for each respective ion.

The standards, as well as the four tap water samples, were analyzed using an atomic absorption machine, which withdrew the sample into a spray chamber and sprayed the sample into a flame as a fine mist. Following this, a hollow cathode lamp shined light through the sample at a wavelength

specific in energy for the electronic transition of the element being analyzed, which in this case was magnesium or calcium. Light that wasn't absorbed by the sample passed through a monochromator, which eliminated any light that was not due to the cathode lamp, and eventually reached a photomultiplier or detector that compared the irradiance of the initial light with that of the transmitted light to get the transmittance as well as absorbance for the sample which was outputted on a digital display.

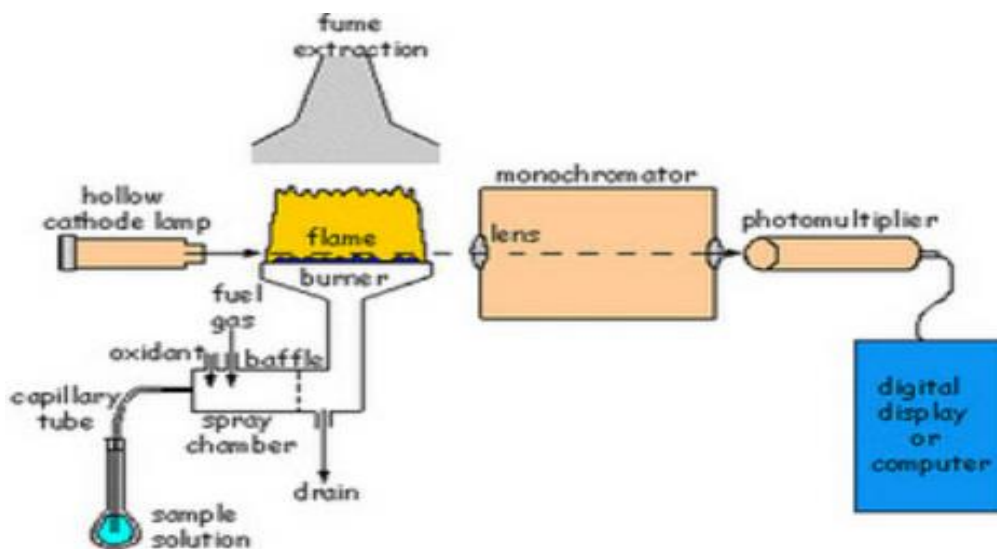


Figure 1. Flame atomic absorption spectrometer diagram⁵

All tap water samples and standards were run through this machine outputting an absorbance. Absorbances for each standard were matched with their respective concentrations and used to construct a Beer's Law Plot for each of the two elements, from which the equation for the best fit line of the plot was then used to calculate the concentration of Ca^{2+} and Mg^{2+} of the tap water samples by using their absorbance(s) to solve for "x" of the best fit line equation.

II. ION CHROMATOGRAPHY

A quantitative method of ion chromatography was used to determine the concentrations of anions in the tap water, where the anions of interest include: Cl^- , NO_3^- , and SO_4^{2-} . Determination of the concentration of these ions included running a reference standard mixture through an Ion Chromatography machine through which a chromatogram was produced. The reference mixture

containing all three of the anions at known concentrations was injected into the Ion Chromatogram through which elution was performed by consistently adding a mobile phase of water mixed with Na₂CO₃ and NaHCO₃ through a column coated with a stationary phase of positively charged polymers through which the three anions partitioned between the two phases resulting in a separation of the components. Components were then individually eluted out of the column from which a detector is then used to capture the conductivity of the eluent. Resolved peaks for the three components were produced on a chromatogram from which a correlation between peak area and concentration was established for each of the three anions. This correlation was then used in a one-point calibration method to estimate the concentrations of the anions using the equation:

$$\frac{\text{Area (Standard)}}{\text{Area (Sample)}} = \frac{\text{Concentration (Standard)}}{\text{Concentration (Sample)}}$$

RESULTS AND DISCUSSION

Results of the Atomic Absorption analysis can be seen in the following table:

Ion	Dilution Factor	Absorbance	Calibration Curve Equation	Concentration of Diluted Sample	Concentration of Undiluted Sample	95% Confidence Interval
Ca ²⁺	N/A	0.123	y = 0.0293x + 0.0115	N/A	3.8 ppm	± 0.3 ppm
Mg ²⁺	1:20	0.118	y = 0.4532x + 0.0079	0.243	5.0 ppm	± 2 ppm

Table 2. Ca²⁺ and Mg²⁺ concentrations

Concentrations were calculated using calibrations curves for each of the two ions. The quality of the data was determined to be reasonably precise, given that the two curves displayed an R² value of 0.9929 for the Magnesium (Figure 2), and 0.9994 for the Calcium (Figure 3), both of which are

very close one, indicating a strong linear relationship between Concentration and Absorbance, as expected from a Beer's Law plot.

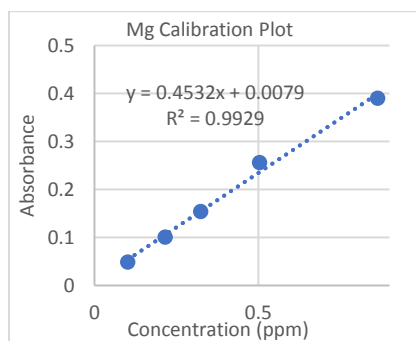


Figure 2. Magnesium ion calibration curve

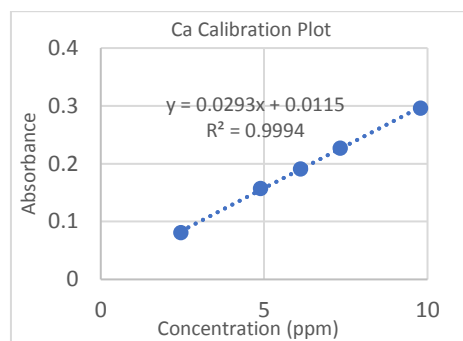


Figure 3. Magnesium ion standard calibration curve.

Likewise, the percent standard deviation was calculated to be 0.68% indicating that there was very little variability in relation to the mean.

Anion concentrations in the tap water were estimated using a one-point calibration method, resulting in the following estimated concentrations:

Compound	Retention Time (min.)	Peak Area	Estimated Concentration
Cl ⁻	1.40	2.570	25.2 ppm
NO ₃ ⁻	2.55	0.338	6.49 ppm
SO ₄ ²⁻	3.88	1.108	18.4 ppm

Table 3: Cl⁻, NO₃⁻ and SO₄²⁻ concentrations

The EPA has set legal limits for each of these anions. These limits include: 10 ppm for NO₃⁻, 250 ppm for Cl⁻, and 250 ppm for SO₄²⁻. Based on the results obtained, it seems that the Tap Water provided in the Sacramento County meets the standards set by the EPA. Although these results do meet the EPA limits, they do not match the reported values for the City of Sacramento Water Quality Analysis of 2016, which reported that their average concentrations for surface water as: ND or Not Detectable for Cl⁻, 7.2 ppm for SO₄²⁻, ND-3.4 ppm for NO₃⁻, 9.9-13 ppm for Ca²⁺ and 1.5 to 3.5 ppm for Mg²⁺. Results for the anions obtained over the course of this experiment have shown to be significantly higher than that of those reported by the City of Sacramento water

agencies. Possible factors that could have contributed for these differences include: these concentrations being outdated seeing that they were measured in 2016, recent weather changes, such as more rain, and seasonal changes. But the most likely reason for these differences is the possibility for error. As mentioned earlier, the anions in the solution were estimated using a one-point calibration which involved using the concentrations of a reference solution and their response in an ion chromatogram, and a 0,0 point to create a calibration plot. Using such a method often results in a significant degree of error, which is why the values obtained were labeled as “estimates”. Given this, it is highly probable that the differences seen in my results and those reported by the City of Sacramento Department of Utilities could be due to this error.

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