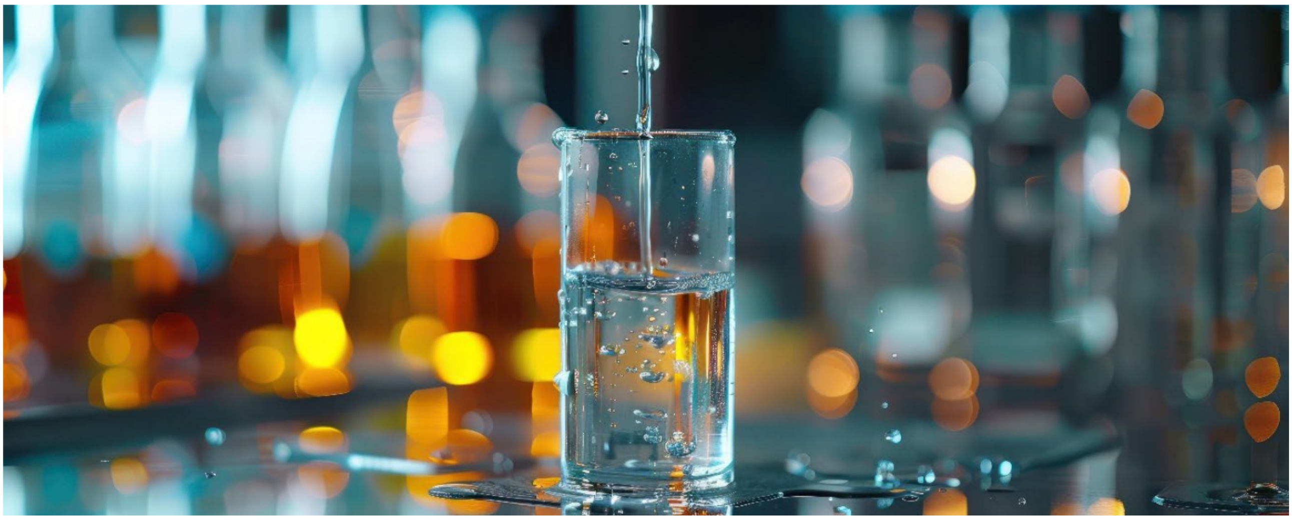
HSLU Hochschule Luzern

Practical 2:

Water Hardness: Chemistry, Measurement, and Effects



Environmental Chemistry and Biology HS2024

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Contents

1 Introduction

Water hardness is an essential parameter that reflects the concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in water. It significantly influences daily activities, such as washing and cooking, as well as industrial operations that rely on water as a key resource.

This experiment focuses on comparing the hardness of two water sources (tap water and bottled water). The titration method, using EDTA as a chelating agent, was employed to quantify water hardness. Additionally, pH measurements were used to assess the chemical behavior of both water types during the titration process.

By analyzing the collected data and interpreting the results through graphical and statistical methods, the study aims to highlight the differences between the two water sources, their practical implications, and their potential impact on household, industrial, and health-related applications.

1.1 Water hardness

Water hardness is a critical parameter that affects numerous daily activities, from washing clothes and dishes to industrial processes and agricultural practices. Understanding the hardness of water is essential for optimizing soap usage, preventing scale formation in pipes and boilers, and ensuring the efficient operation of various water-using appliances

Table 1: Classification of water hardness

°fH	mmol/L	Hardness
0 – 7	0 – 0.7	Very soft
7 – 15	0.7 – 1.5	Soft
15 – 25	1.5 – 2.5	Moderately hard
25 – 32	2.5 – 3.2	Fairly hard
32 – 42	3.2 – 4.2	Hard
$\leq$ 42	$\leq$ 4.2	Very hard

2 Materials and methods

2.1 List of materials

- Water sample (bottled water and tap water)
- 0.01[M] EDTA solution (standard solution)
- Indicator buffer tablets (Ammonia tablets)
- Pipette (10 mL)
- Burette (25 mL)
- Conical flask (100 mL)
- Distilled water
- White tile (to observe the color change)
- Magnetic stirrer
- Stick to mix
- 8 flasks of 100 ml
- pH meter

2.2 Procedure

At the beginning of the lab process, we measured 75 ml of tap water and filled 3 beakers with the same volume. Indicator buffer tablets (Ammonia [NH_3] tablets) were then added to the beakers with water and mixed until they dissolved. A volume of 50 ml of EDTA solution was then inserted into the burette, and the presence of air bubbles was checked to prevent errors in the titration process.

To begin the titration, we ensured that everything was set up correctly. We prepared tables to note down our readings, a white tile to observe the color change, a magnetic stirrer to mix during titration, and a pH reader to measure the pH level at regular intervals (normally after each 1 ml).

With everything set up, we began letting the EDTA solution into the ammonia and water mixture in drops to achieve precise readings. We observed the color changes as well as recorded the pH level at regular intervals to determine when the endpoint of the titration was reached.

The experiment was also repeated with a bottled water and ammonia solution following the same process. The initial pH level was measured, and the color change during the titration was monitored as EDTA solution was gradually added. The goal was to record the changes in color and pH at different stages.

The data collected during the experiments would later be used to determine the water hardness for each test and to evaluate it through statistical analysis. Care was taken to avoid parallax error to ensure accurate measurements.

2.3 Pictures of proceedings

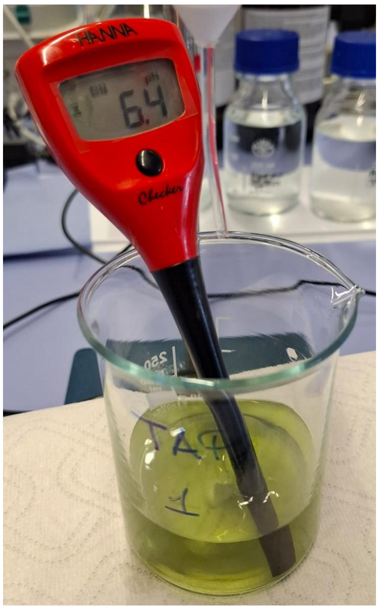

Figure 1: pH measurement

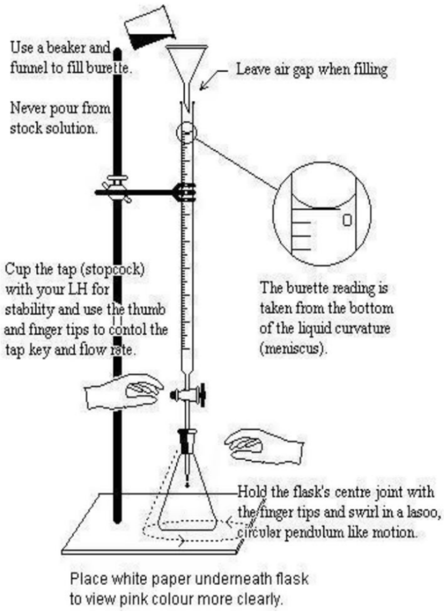

Figure 2: Titration procedure

Figure 3: Moment of titration

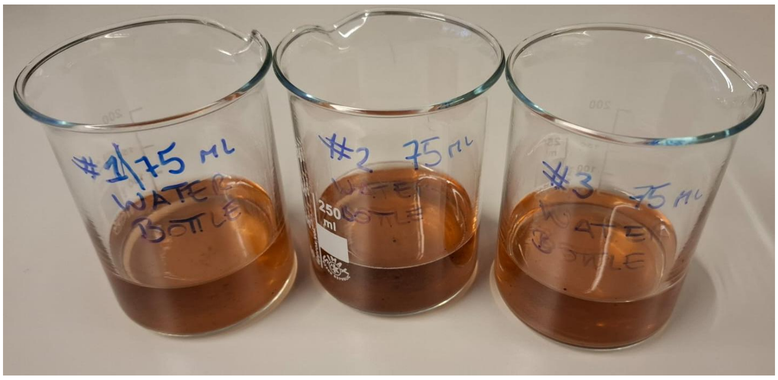

Figure 4: Solution of tap water and ammonia

3 Results

3.1 Experiment parameters

The parameters of the experiment provide an overview of what data were useful so that water hardness could be calculated.

3.1.1 Initial values

The initial values of water and ammonia samples, at 0 mL EDTA, are as follows:

Table 2: Initial values

Type	mL	pH Sample 1	pH Sample 2	pH Sample 3	pH Average
Tap	0	7.0	7.1	7.0	7.03
Bottled	0	7.4	7.5	N.D.	7.45

3.1.2 Titration parameters

Measurements were made on two different types of water (tap and bottle) three times each, and then the initial and final parameters of each sample were marked so that the water hardness for each milliliter of EDTA could be easily calculated.

3.1.3 pH parameters

Just as the parameters were computed for the titration calculation, pH measurements were also made under the same circumstances. Having known the amount of EDTA poured into the solution of water and ammonia, it was possible to correctly identify the amount of solvent needed to allow the fluid to change color, consequently facilitating the calculation of water hardness.

3.2 Formulas

3.2.1 Water hardness

The formula for calculating water hardness, expressed in °fH, takes into account the volume of water inside the beaker, the molarity of the EDTA solution and its volume used, and finally the total volume of the sample:

$$\text{Hardness (mg/L CaCO}_3) = \frac{M_{\text{EDTA}} \times V_{\text{EDTA}} \times 1000 \times 100}{V_{\text{sample}}}$$

Equation 1: Water hardness

3.2.2 Mean

Tables to be completed require calculating an average value of repeated experiments on the same type of water. For this, the following formula is used:

$$\overline{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

Equation 2: Arithmetic mean formula

3.2.3 pH drop

To enhance the graphical visualization of pH variations, the average pH values were transformed using the following formula:

$$T(\text{pH}) = \exp(\text{pH} - 7)$$

Equation 3: pH drop formula

3.3 Visible results

The results image shows the final colorations of the samples after titration. The yellow exhausted color is clearly visible.

Figure 5: Beakers with final solutions

3.4 pH results

3.4.1 Tap water

The experiment with tap water was conducted up to 15mL EDTA until the desired final color (dirty yellow) was achieved, which generally indicates the end of the test. The final results were then recorded:

Table 3: Tap water pH measurements

mL	pH Sample 1	pH Sample 2	pH Sample 3	pH Average	T(pH)
0	7.0	7.1	7.0	7.03	1.03
1	7.0	7.0	7.0	7.00	1.00
2	6.8	6.8	6.8	6.80	0.819
3	6.7	6.6	6.6	6.63	0.691
4	6.5	6.6	6.5	6.55	0.638
5	6.5	6.4	6.3	6.40	0.549
6	6.3	6.1	6.1	6.17	0.436
7	6.1	5.8	5.9	5.93	0.343
8	6.0	5.6	5.7	5.77	0.292
9	5.8	5.5	5.5	5.60	0.247
10	5.6	5.4	5.5	5.50	0.223
11	5.4	5.4	5.4	5.40	0.202
12	5.4	5.3	5.3	5.33	0.188
13	5.3	5.3	5.3	5.30	0.183
14	5.3	5.3	5.3	5.30	0.183
15	5.3	5.3	5.2	5.27	0.177

Graphical rappresentation

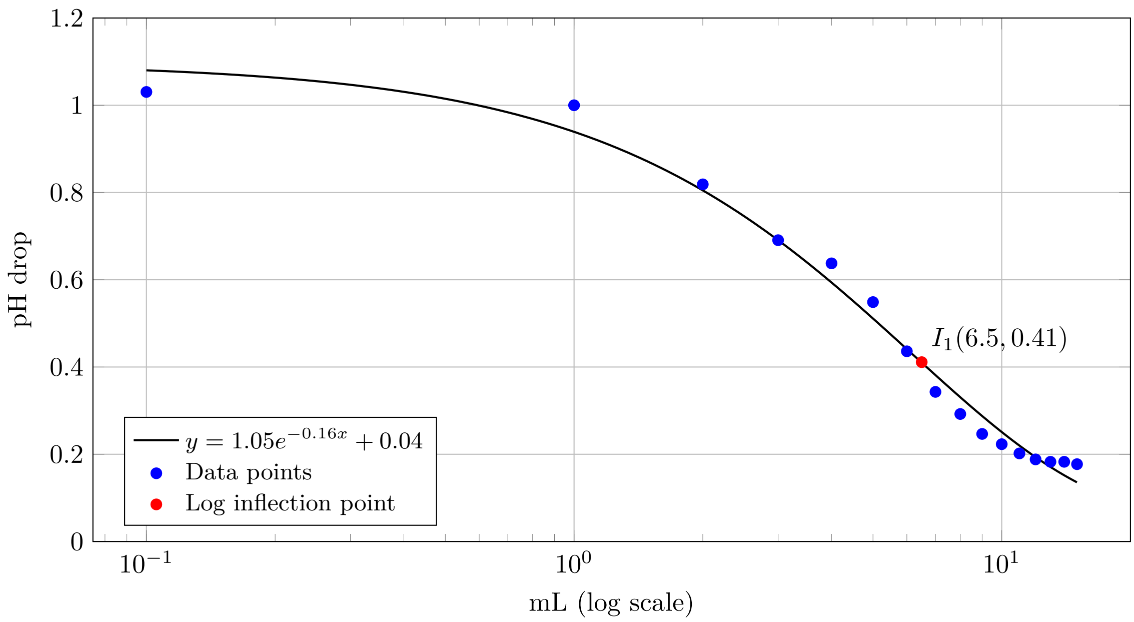

Figure 6: Graph of pH drop for tap water

The graph, given by the function $y = 1.05e^{-0.16x} + 0.04$, shows an exponential decrease T(pH) as EDTA is added.

The logarithmic scale for volume highlights the gradual decrease at low levels of EDTA and the inflection point (I_1), where the solvent's color changes noticeably. Initially, the pH decreases slightly (from 7.0 to 6.8), as the amount of EDTA is insufficient to fully bind the hardness ions. With more EDTA, the pH drops more significantly.

3.4.2 Bottled water

The experiment with bottled water was conducted up to 25mL EDTA. The pH values were measured for two samples, and their average was calculated as shown below:

Table 4: Bottled water pH measurements

(0 – 13 mL)					(14 – 25 mL)			
mL	**pH Sample 1**	**pH Sample 2**	**pH Average**	**T(pH)**	**pH Sample 1**	**pH Sample 2**	**pH Average**	**T(pH)**
0	7.4	7.5	7.45	1.568	6.6	6.5	6.55	0.638
1	7.3	7.4	7.35	1.419	6.5	6.4	6.45	0.577
2	7.2	7.3	7.25	1.284	6.5	6.3	6.40	0.549
3	7.2	7.3	7.25	1.284	6.4	6.2	6.30	0.497
4	7.1	7.2	7.15	1.162	6.3	6.2	6.25	0.472
5	7.0	7.1	7.05	1.051	6.2	6.1	6.15	0.427
6	7.0	7.0	7.00	1.000	6.1	5.9	6.00	0.368
7	7.0	6.9	6.95	0.951	6.1	5.9	6.00	0.368
8	6.9	6.8	6.85	0.861	6.0	5.8	5.90	0.333
9	6.9	6.7	6.80	0.819	5.9	5.7	5.80	0.301
10	6.8	6.65	6.73	0.763	5.8	5.7	5.75	0.287
11	6.7	6.6	6.65	0.705	5.8	5.6	5.70	0.273
12	6.7	6.55	6.63	0.691	5.7	5.6	5.65	0.259

Graphical representation

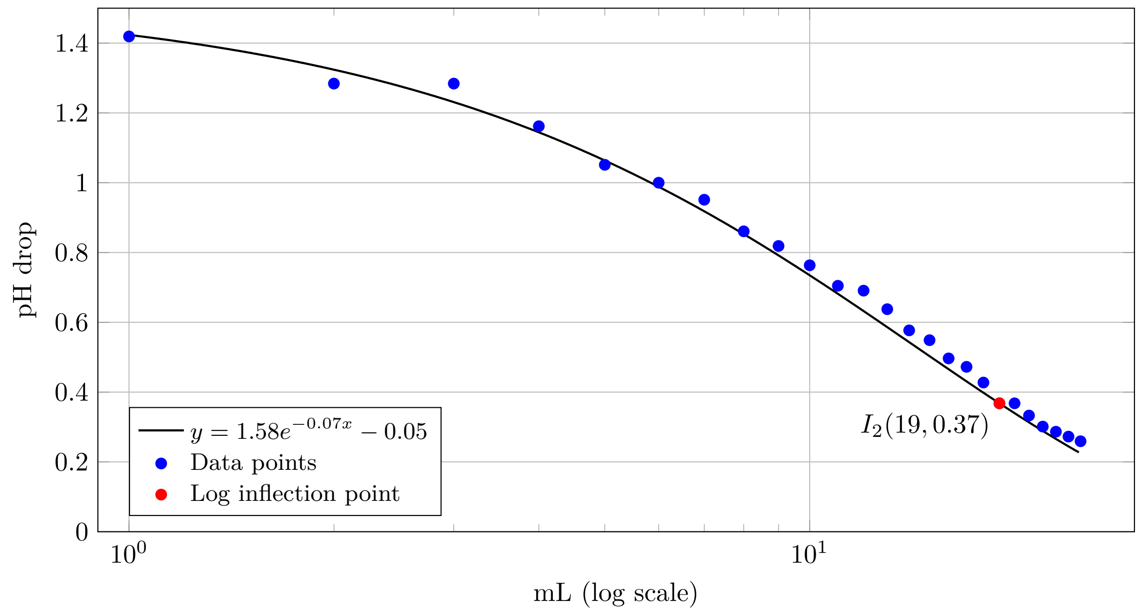

Figure 7: Graph of pH drop for bottled water

The graph, given by the function $y = 1.58e^{-0.07x} - 0.05$, as per the intuition given by the experiment done previously, also shows an exponential decrease in $T(\text{pH})$ with the addition of EDTA.

The logarithmic scale for volume was used again to show the gradual decrease at EDTA levels and the inflection point (I_2), where the color of the solvent changes noticeably. In this experiment, the pH has a more abrupt change around an amount of 19mL EDTA poured into the solution of bottled water and ammonia.

4 Water hardness results

4.1 Legend and formulas

4.1.1 Legend

- **ID**: Sample number of the water solution
- $\mathbf{V_{s,i}}$: Initial volume of the water sample (mL)
- $\mathbf{V_{b,i}}$: Initial volume of EDTA inside the burette (mL)
- $\mathbf{V_{b,f}}$: Final volume of EDTA inside the burette (mL)
- $\mathbf{\Delta V}$: Volume of EDTA used (mL)
- $\mathbf{V_{s,f}}$: Final volume of the water and EDTA sample (mL)

4.1.2 Formulas

The following formulas were used to complete the tables and to calculate water hardness:

- **Volume of EDTA used**

$$\Delta V = V_{b,f} - V_{b,i}$$

Equation 4: Volume of EDTA used

- **Final volume of water + EDTA sample**

$$V_{s,f} = V_{s,i} + \Delta V$$

Equation 5: Total sample volume

- **Hardness conversion**
  The conversion of water hardness from mg/L $CaCO_3$ to °fH was done on the basis of [Equation 1]:

$$\text{Hardness}\,(°\text{fH}) = \text{Hardness (mg/L CaCO}_3) \cdot 10^{-1}\ °\text{fH} \cdot \text{L/mg}$$

Equation 6: Water hardness in °fH

- **Standard deviation**

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \overline{x})^2}$$

Equation 7: Standard deviation formula

4.2 Tap water

As emphasized in the chapter 2.2, the following table shows the initial and final values of the experiment, highlighting at what ΔV the solution of water and ammonia changed color. The ΔV values represent on the graph the logarithmic inflection points (I_1, I_2), previously identified and commented on in the chapter 3.4.

4.2.1 Data set

Table 5: Tap water hardness

ID	$\mathbf{V_{s,i}}$	$\mathbf{V_{b,i}}$	$\mathbf{V_{b,f}}$	$\mathbf{\Delta V}$	$\mathbf{V_{s,f}}$
Tap 1	75	50	40	10	85
Tap 2	75	50	42	8	83
Tap 3	75	50	43	7	82

4.2.2 Hardness calculation

Using the formula [Equation 1] and [Equation 6]:

$$\text{Tap 1}\,(^\circ\text{fH}) = \frac{0.01[M] \cdot 10\text{mL} \cdot 1000 \cdot 100}{10 \cdot 85\text{mL}} \approx 11.76^\circ\text{fH}$$

Equation 8: Hardness of Tap 1

$$\text{Tap 2}\,(^\circ\text{fH}) = \frac{0.01[M] \cdot 8\text{mL} \cdot 1000 \cdot 100}{10 \cdot 83\text{mL}} \approx 9.64^\circ\text{fH}$$

Equation 9: Hardness of Tap 2

$$\text{Tap 3}\,(^\circ\text{fH}) = \frac{0.01[M] \cdot 7\text{mL} \cdot 1000 \cdot 100}{10 \cdot 83\text{mL}} \approx 8.54^\circ\text{fH}$$

Equation 10: Hardness of Tap 3

4.2.3 Statistical analysis

Using the measured water hardness values, statistical analyses were performed. The following calculations were carried out:

Median calculation
The median is the middle value of the ordered dataset:

$$\text{Ordered set: } \{8.54^\circ\text{fH},\ 9.64^\circ\text{fH},\ 11.76^\circ\text{fH}\}$$

$$\text{Median} = 9.64^\circ\text{fH}$$

Standard deviation calculation
According to the formula [Equation 7]:

$$\sigma_{tap} = \sqrt{\frac{(8.54-9.98)^2 + (9.64-9.98)^2 + (11.76-9.98)^2}{3-1}} \approx \sqrt{2.68} \approx 1.64^\circ\text{fH}$$

Equation 11: Tap water standard deviation

Water hardness table

Table 6: Tap water hardness measurements with deviations

Sample	Hardness (°fH)	$\mathbf{x_i - \overline{x}}$ (°fH)
Tap 1	11.76	+1.78
Tap 2	9.64	-0.34
Tap 3	8.54	-1.44

4.3 Bottled water

Just as just computed for tap water samples, data will be processed for bottled water samples.

4.3.1 Data set

Table 7: Bottled water hardness

ID	$\mathbf{V_{s,i}}$	$\mathbf{V_{b,i}}$	$\mathbf{V_{b,f}}$	$\mathbf{\Delta V}$	$\mathbf{V_{s,f}}$
Bottled 1	75	50	30	20	95
Bottled 2	75	50	32	18	93

4.3.2 Hardness calculation

Using the formula [Equation 1] and [Equation 6]:

$$\text{Bottled 1 (°fH)} = \frac{0.01[M] \cdot 20\text{mL} \cdot 1000 \cdot 100}{10 \cdot 95\text{mL}} \approx 21.05\text{°fH}$$

Equation 12: Hardness of Bottled 1

$$\text{Bottled 2 (°fH)} = \frac{0.01[M] \cdot 18\text{mL} \cdot 1000 \cdot 100}{10 \cdot 93\text{mL}} \approx 19.35\text{°fH}$$

Equation 13: Hardness of Bottled 2

4.3.3 Statistical analysis

Using the measured water hardness values, statistical analyses were performed. The following calculations were carried out:

Median calculation
The median is the middle value of the ordered dataset:

$$\text{Ordered set: } \{19.35\text{°fH}, 21.05\text{°fH}\}$$

$$\text{Median} = \frac{19.35 + 21.05}{2} \approx 20.20\text{°fH}$$

Standard deviation calculation
According to the formula [Equation 7]:

$$\sigma_{\text{bottled}} = \sqrt{\frac{(19.35 - 20.20)^2 + (21.05 - 20.20)^2}{2 - 1}} \approx \sqrt{1.45} \approx 1.20\text{°fH}$$

Equation 14: Bottled water standard deviation

Water hardness table

Table 8: Bottled water hardness measurements with deviations

Sample	**Hardness (°fH)**	$\mathbf{x_i - \overline{x}}$ **(°fH)**
Bottled 1	21.05	+0.85
Bottled 2	19.35	-0.85

5 Discussion

The comparison between the tap water and bottled water results highlights significant differences in their chemical composition, specifically in terms of water hardness. These differences are attributable to the source and treatment processes for each type of water.

5.1 Tap water analysis

The tap water samples exhibited a lower overall hardness, with values ranging between 8.54°fH and 11.76°fH. The statistical analysis revealed a median value of 9.64°fH and a standard deviation of 1.64°fH, indicating a moderate variability among the samples. The lower hardness can be linked to municipal water treatment processes, which often include softening steps to reduce scale formation in pipelines and appliances.

The graph of pH drop for tap water (Figure 6) showed a clear exponential decrease as EDTA was added, with a notable inflection point ($I_1(6.5, 0.41)$). This point represents the volume of EDTA required to chelate a significant proportion of hardness ions (Ca^{2+} and Mg^{2+}). The gradual pH decline suggests a relatively low concentration of these ions, consistent with the observed hardness levels.

5.2 Bottled water analysis

In contrast, the bottled water samples showed a higher hardness, with values of 19.35°fH and 21.05°fH. The median hardness was calculated as 20.20°fH, and the standard deviation was 1.20°fH, indicating slightly less variability compared to tap water. The elevated hardness levels suggest that the bottled water source was less treated or derived from a mineral-rich spring, where higher concentrations of Ca^{2+} and Mg^{2+} are naturally present.

The corresponding pH drop graph (Figure 7) also demonstrated an exponential decline, but with a more abrupt change at the inflection point ($I_2(19, 0.37)$). This sharper decrease implies a higher buffering capacity due to the greater presence of hardness ions. The results align with the classification of water hardness, where bottled water falls into the "moderately hard" to "fairly hard" range.

5.3 Implications of findings

The differences in water hardness between tap and bottled water have practical implications. Tap water's lower hardness is advantageous for household and industrial use, minimizing scale formation and reducing soap consumption. However, bottled water's higher mineral content may offer health benefits, as it provides essential minerals like calcium and magnesium. These findings highlight the importance of choosing the appropriate water source based on its intended use.

From a methodological perspective, the use of EDTA titration proved to be a reliable technique for determining water hardness. The precision of measurements, as evidenced by the low standard deviations, underscores the effectiveness of the experimental setup. Additionally, the use of statistical analysis provided a comprehensive understanding of the data distribution and variability.

5.4 Limitations and future recommendations

While the experiments yielded accurate results, some limitations should be acknowledged. The small sample size (three tap water samples and two bottled water samples) may not fully represent the variability of each water source. Future studies could include a larger number of samples from diverse locations to enhance the generalizability of the findings.

Moreover, the analysis focused solely on calcium and magnesium ions as contributors to hardness. Investigating the presence of other ions, such as iron or manganese, could provide a more complete picture of water quality. Expanding the scope of the analysis to include other parameters, such as alkalinity and conductivity, would further enrich the understanding of water chemistry.

5.5 Questions

1. Compare the results of Bottled water vs tap water used for different samples. How are the results compared to the water quality from the municipality in Horw?

   R:
   Bottled water likely shows greater variability in both pH and hardness due to treatment. Tap water, have close pH as the Horw municipality.

   Notable deviations in tap or bottled water from Horws baseline may indicate differences in sourcing, treatment, or branding focus.

2. Based on the Table 1, compare your results and discuss.

   R:
   Tap water:
   Aligned closely with Horws municipal water but slightly softer, indicating potential treatment or a different water source within the same municipality.

   Bottled wated:
   Its higher hardness (19.5 fH) reflects a significant difference from both tap (9.5) and Horw municipal water (11.4). The elevated mineral content might cater to consumers seeking health benefits but could lead to more scaling in appliances.

   Overall:
   The results demonstrate that bottled water can vary significantly in mineral composition and hardness, while municipal and tap water are usually consistent and designed for practicality and balance.

3. Why hard water is formed and how can be avoided?

   R:
   Hard water forms when water flows through mineral-rich rocks, such as limestone dissolving calcium and magnesium ions. It can be avoided by using water softening systems, such as ion exchange resins or reverse osmosis, to remove or reduce these minerals before use.

4. Discussion about titration involving EDTA.

   R:
   Before equivalence point:

   - The solution contains a significant amount of free calcium and magnesium ions. These ions form complexes with EDTA as it is added;
   - A buffer (commonly ammonium chloride and ammonia) maintains the pH at around 10, ensuring that EDTA can effectively bind to the metal ions. The pH remains relatively stable.

   At equivalence point:

   - All the calcium and magnesium ions have reacted with EDTA. The pH might exhibit a slight inflection point but remains near 10 because of the buffering action.

   After equivalence point:

   - Excess EDTA is added. Since EDTA itself doesnt significantly affect the pH, the solution remains buffered at approximately pH 10. A minor pH increase may occur if the buffer capacity is exceeded.

5. What is the significance of measuring water hardness?

   R:
   Measuring water hardness is essential to assess its suitability for domestic, industrial, and agricultural use. Hard water in drinking supplies can cause scaling in pipes and appliances, reducing efficiency, but it also provides essential minerals like calcium and magnesium, beneficial for health. Extremely hard water may impact taste and lead to excessive scaling, while very soft water can be corrosive. Environmentally, hard water can affect aquatic ecosystems by altering pH and mineral balance, impacting plant and animal life.

6. Discussion about statistical analyses:

   R:
   The difference in hardness between bottled and tap water is $19.5 - 9.5 = 10.0$°fH, indicating bottled water has higher mineral content.

   - **Tap water**:
     The average hardness of 9.5 řfH classifies it as “soft” water. This is beneficial for reducing scaling in appliances and improving cleaning efficiency but may lack the mineral content present in harder water.
   - **Bottled water**:
     With an average hardness of 19.5 řfH, falls into the “moderately hard” category. This is typical for mineral waters marketed for added health benefits due to higher levels of calcium and magnesium.
   - **Implications**:
     - For health: Bottled water may provide more essential minerals, though excessive hardness can affect taste;
     - For use: Tap water’s lower hardness makes it more practical for household and industrial use, avoiding issues like scaling.

5.6 Conclusion

The experimental analysis of water hardness has provided significant insights into the chemical properties of tap and bottled water. Tap water was observed to have a lower hardness, with a median value of 9.64°fH and a standard deviation of 1.64°fH, which is indicative of consistent softening practices in municipal water treatment. This lower hardness reduces scale formation, optimizes the use of cleaning agents, and ensures compatibility with industrial processes, making tap water ideal for household and utility purposes.

On the other hand, bottled water displayed a higher hardness, with values centered around 20.20°fH and a standard deviation of 1.20°fH. The higher mineral content, particularly calcium and magnesium ions, suggests that bottled water often originates from natural springs or sources with minimal treatment. While this makes bottled water less ideal for some industrial applications, it may enhance its appeal for drinking purposes due to the potential health benefits of its mineral composition.

These results emphasize the importance of understanding water hardness when selecting a water source for specific applications. For instance, tap water's lower hardness is advantageous for reducing energy consumption in heating systems and prolonging the lifespan of appliances by minimizing scale formation. Conversely, bottled water's higher mineral content can be beneficial for dietary supplementation, especially in regions where calcium and magnesium deficiencies are prevalent.

In summary, the distinction between tap and bottled water is evident not only in their hardness levels but also in their behavior during titration and pH analysis. These findings serve as a foundation for further exploration into water quality and its implications for both domestic and industrial uses. By extending the scope of such investigations, it is possible to develop more tailored approaches to water treatment and usage, ultimately contributing to improved efficiency, sustainability, and public health outcomes.

List of Tables

List of Figures

List of Equations

Declarations about AI tools

- "*ChatGPT-4 with canvas*" was used as a tool to enhance vocabulary.
  All original sentences come from our individual thoughts and were refined with the support of this tool.
  https://chatgpt.com/
- "DeepL" was used as a translator.
  https://www.deepl.com