

# Experiment 1: Determination of Water Hardness

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## What lab skills will you practice?

- Volumetric techniques
- Visual titrations

## What chemical concepts will you apply?

- Stoichiometry Silberberg: Chapter 3.4
- Dilutions Silberberg: Chapter 3.5
- Significant digits Silberberg: Chapter 1.6

## What report writing skills will you use?

- Recording data and observations
- Interpreting experimental data
- Answering Introduction and Discussion questions

## Reminders:

- Complete the pre-lab quiz and flowchart at least **one hour before lab**
- Bring **1 L of tap water** (unfiltered & unsoftened)
- Print & bring all Experiment 1 pages to lab

## Objective

Use a complexometric titration to determine the three hardness measures (temporary, permanent, and total hardness) of a sample of tap water, and compare the sample's water hardness to the values provided by the City of Calgary.

## Introduction

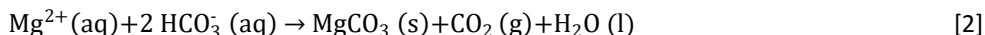
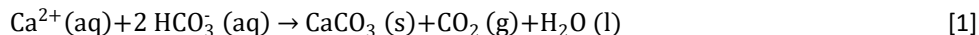
Water is a precious commodity for humans. Besides personal consumption, agriculture and industry use large amounts of potable and fresh water for their operations. Water from many sources can contain biological impurities like bacteria and viruses and inorganic impurities leached from minerals as salts.

For human consumption or industrial use, water has to meet very high standards for levels of allowed contaminants. After filtration to remove particulates, treatment with chlorine removes bacterial and viral organisms. Water softening methods lower the concentration of ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , etc. from dissolved minerals. Reverse osmosis (R.O.) processes can be used to further purify the water by removing these dissolved ions. Ion exchange resins are used domestically to "soften" water, replacing undesirable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in solution with  $\text{Na}^+$  ions. [1]

## Water Hardness

Water that is high in dissolved minerals, especially calcium and magnesium salts, is called **hard water**. In surface (river) water, like is used in Calgary, these dissolved minerals are eroded from mineral deposits, such as limestone, as the water passes over. Water hardness can be described in three ways:

**Temporary hardness** is caused by minerals that precipitate out when the water is boiled (mainly  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$ ). When water containing these ions is heated, the following reactions can take place:



The calcium and magnesium carbonates precipitate out of solution and can later be removed by filtration.

**Permanent hardness** is caused by minerals that cannot be removed by boiling. It is mainly caused by  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ , which remain in water even after boiling.

**Total hardness** is the sum of the temporary and permanent hardness values. Usually these are given in units of mg/L.

The effects of water hardness can be seen in many ways. Soft water produces an almost instantaneous lather with soap. Hard water produces lather with difficulty and forms an insoluble scum instead, resulting from the reaction of calcium and magnesium ions with the anionic soap molecules. Hard water can also form deposits ("limescale") on the inside of pipes and vessels used to contain hard water, such as teakettles and water heaters, and on surfaces on which hard water has been allowed to dry.

In this experiment, you will determine the temporary, permanent, and total hardness of a local tap water sample using **complexometric titration**. This technique uses a reaction between disodium ethylenediaminetetraacetate (disodium EDTA) and the dissolved  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions to determine the total concentration of these ions.

### What is a titration?

Titration is a method used to determine the concentration of one solution by reacting it with a second solution that we know the concentration of very precisely.

A typical set-up for a titration is shown in Figure 1. Usually, the buret is filled with **titrant** (the solution of known concentration – yellow in the diagram), while some of the **analyte** (the solution we are trying to analyze) is placed in a flask. The titrant is slowly added, until exactly enough titrant has been added to react with all of the analyte in the flask – this is the **equivalence point**.

Usually, we cannot see the equivalence point directly. To help make the endpoint visible, we can use a **color indicator** – a compound that will be one color before the equivalence point, and a different color after. One color indicator you may be familiar with is phenolphthalein, which is clear in acidic solution, changing to bright pink in basic solutions. Since the color change of the indicator may not happen exactly at the equivalence point, the point where the indicator changes color (and we usually stop titrating) is called the **endpoint**. The volume of titrant needed to reach this point is the **titre**.

In this experiment, we are performing a complexometric titration, where the reaction involved is a *complexation reaction*. In these reactions, a metal ion reacts with a complex-forming reactant (such as EDTA) to form a stable complex.

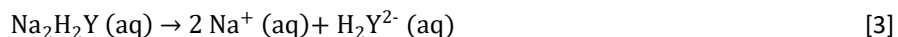
Complexation is a good type of reaction to use in a titration because it is *fast* and it has a *large equilibrium constant (K)*, so that the reaction will proceed nearly “to completion” – at each step during the titration, we can assume that all of the available reactants are consumed.

For any titration, knowing the relationship between the moles of analyte in your titration sample and the moles of titrant used to reach the equivalence point will allow you to determine the concentration of your analyte. With care, manual titrations can be extremely accurate – although many modern laboratories carry out analyses instrumentally (as you will in Experiments 2 and 3), manual titrations are still commonly performed.

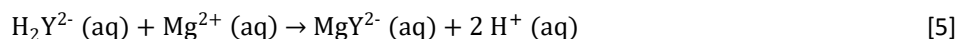
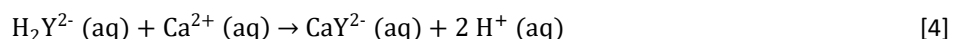
### EDTA Chemistry

The complexing reagent used in this experiment is ethylenediaminetetraacetic acid (EDTA), a weak tetraprotic<sup>1</sup> acid. In order to simplify the writing of chemical reactions, EDTA is often abbreviated as **H<sub>4</sub>Y**. The tetrabasic anion of this acid,  $\text{Y}^{4-}$ , forms stable complexes with virtually all divalent ( $\text{M}^{2+}$ ) and trivalent ( $\text{M}^{3+}$ ) metal cations. Regardless of the charge on the metal ion, they react in a 1:1 ratio to  $\text{Y}^{4-}$  to form the complex ( $\text{MY}^n$ ).

In the laboratory, it is often more convenient to use the disodium salt of EDTA ( $\text{Na}_2\text{H}_2\text{Y}$ ) than the fully protonated  $\text{H}_4\text{Y}$  form. The disodium salt dissociates completely in solution:



The  $\text{H}_2\text{Y}^{2-}$  anion can then react with metal cations in solution, such as calcium and magnesium to form a stable complex:



Titrating with EDTA will react with both the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the analyte, so the results of your titrations will yield the **combined concentration of both ions**.

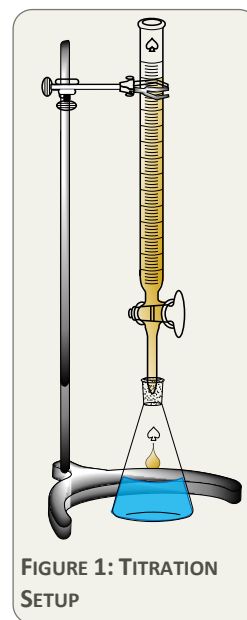


FIGURE 1: TITRATION SETUP

<sup>1</sup> Remember from the Greek naming prefixes that *tetra* means “four” – so EDTA is a weak acid with four protons ( $\text{H}^+$ ). See Chapter 2.8.

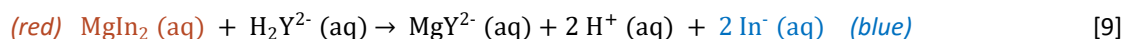
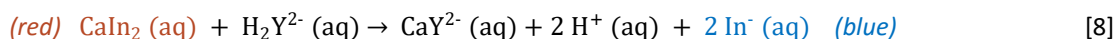
## Equivalence Point and Endpoint of EDTA Titrations

In visual titrations, we must assume that the endpoint occurs as near as possible to the equivalence point. The validity of this assumption depends on the choice of an appropriate indicator as well as the level of care taken in performing the titration.

In this experiment, you will use a color indicator to visualize the endpoint of your titration. For complexometric titrations, the indicator used is also a complexing reagent. For this laboratory, you will use **calmagite** (abbreviated as  $\text{In}^-$ ), which forms complexes with calcium and magnesium in a similar manner to EDTA:



During the titration, you will add the indicator to your tap water before any EDTA has been added, and allow the EDTA to react with the calmagite-metal complexes. The reaction you will actually be observing is therefore:



During the titration, you will start with the red metal-calmagite complex in solution. As EDTA is added, the solution color will fade to purple. **The endpoint is the moment when the first drop of titrant changes the purple color to blue**, and the volume of titrant added to reach this point is your titre. Very little calmagite is needed to create a strongly colored solution with a distinct color change at the endpoint, making calmagite a good choice for a titration indicator.

In order for this reaction to proceed to completion, the solution pH needs to be between 9 and 11. To maintain an appropriate solution pH, you will add an ammonia/ammonium chloride pH buffer to the analyte solution.

## Drinking Water and Water Hardness

Total water hardness is commonly reported in terms of  $\text{CaCO}_3$  concentration, in mg/L. This measure treats all dissolved minerals as if they were calcium carbonate in order to report a single value. Drinking water may be classified according to varying levels of hardness:

TABLE 1: GENERAL HARDNESS RATINGS OF DRINKING WATER [2]

Hardness Rating	$\text{CaCO}_3$ concentration (mg/L)
Soft	0 to 75
Medium hard	75 to 150
Hard	150 to 300
Very hard	300 and greater

Water hardness is also frequently reported in **parts per million (ppm)**. In aqueous solution, this measure is equivalent to mg/L.

## References

[1] Silberberg, M.S.; Amateis, P.; Lavieri, S.; Venkateswaran, R.; *Chemistry: The Molecular Nature of Matter and Change*, 2<sup>nd</sup> Canadian Edition; McGraw-Hill Ryerson Limited; Mississauga, ON, 2016; p. 491-2.

[2] The City of Calgary. "Water Hardness": <http://www.calgary.ca/UEP/Water/Pages/Drinking-water/Water-quality/Water-Hardness-FAQ.aspx> (accessed June 1, 2016).

The tap water in EEEL, or any filtered or softened water (including bottled water), cannot be used for this lab.

R.O. or reverse osmosis water is mineral-free, clean water. It is dispensed from the **white** faucets in the lab.

Your TA will demonstrate how to fold filter paper to fit into the funnel.

You don't need to fill your burette exactly to 0.00 mL! Between 0-5 mL is fine.

## Preparing for lab

Before coming to lab, make sure you have:

- Read the lab manual introduction to familiarize yourself with course policies.
- Read Experiment 1 and Appendix G.
- Completed the online pre-lab quiz – *at least one hour before lab*
- Completed the procedure flow chart on Page 8.
- Brought 1 L of tap water
- Prepared yourself by wearing clothing that will completely cover you below the knee, a lab coat and safety goggles. (See the lab manual Introduction and guidelines on D2L)

## Experimental Procedure

For this experiment you will work in pairs.

Each partner must submit an individually written lab worksheet.

### Notes

1.  $\text{Na}_2\text{EDTA}$  is an irritant – avoid contact with bare skin.
2. All glassware must be cleaned with low-pH soap (provided in the laboratory) to remove any mineral deposits, then rinsed thoroughly with R.O. water.
3. Read the procedure carefully to find places where you can save time. For example, you can start Part 2 while you are boiling the water for Part 1.

## Part 1: Preparation for Permanent Water Hardness Titration

### 1. Boil the water:

- ↪ Using a clean 100 mL graduated cylinder, measure 250 mL of your tap water into a clean 400 mL beaker.
- ↪ Cover the beaker with a watch glass and place it on a hot plate set to 500°C. Heat the water for 20 minutes, turning the hot plate down to 300°C once the water begins to boil. Allow the water to boil for 20 minutes.

### 2. Cool and filter the water:

- ↪ Carefully remove the beaker from the hotplate and let it cool for a minute on the bench, then place it in a cold water bath for a further 5 minutes.
- ↪ Filter the cooled water sample into a clean 250 mL volumetric flask using a clean long stem funnel supported on a ring stand. After, place the volumetric flask in an ice-water bath for 5 minutes, until the flask is room-temperature.
- ↪ Once cooled, remove the flask from the ice bath and add R.O. water to bring the level of water in the flask to the 250 mL mark. Stopper the flask, and mix the solution thoroughly by inverting the flask several times. You will use this water for the titration in Part 3.

## Part 2: Determination of Total Water Hardness

### 1. Prepare a burette:

- ↪ If you have not already done so, obtain a 50 mL burette from the lab instructor and rinse it twice with small amount of 0.002 M  $\text{Na}_2\text{EDTA}$  solution. Fill the burette and record the initial volume **to  $\pm 0.01$  mL** in Table 3 on your worksheet.

**2. Titrate:**

- ↪ Using a clean 100 mL graduated cylinder, measure 250 mL of your tap water into a clean 400 mL beaker.
- ↪ Rinse a 25 mL volumetric pipet 2-3 times with small amount of the water you are analyzing. Pipet 25.00 mL of this water into a clean 200 mL Erlenmeyer flask.
- ↪ Cover the flask with a watch glass and bring it and a 10 mL graduated cylinder to the fume hood. At the fume hood, add 10 mL of  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer to the flask and re-cover it.
- ↪ At your bench, add 1 mL of calmagite indicator to the flask. Titrate with  $\text{Na}_2\text{EDTA}$  solution until you reach the endpoint (refer to the Experiment Introduction section). Record the final burette reading, again **to  $\pm 0.01$  mL**.
- ↪ Repeat the titration 3 more times, so that you have 4 titres total. Three of your titres should be within 0.1 mL of each other. If not, consult your TA before continuing.

**Part 3: Permanent Water Hardness Titration****1. Prepare a burette:**

- ↪ If you did not already do so for Part 2, obtain a 50 mL burette from the lab instructor. Rinse it twice with a small amount of 0.002 M  $\text{Na}_2\text{EDTA}$  solution, then fill it to the zero mark. Record the initial reading on the burette **to  $\pm 0.01$  mL** in Table 2 on your worksheet.

**Titrate:**

- ↪ Rinse a 25 mL volumetric pipet 2-3 times with a small amount of the boiled tap water. Pipet 50.00 mL of this water into a clean 200 mL Erlenmeyer flask.
- ↪ Cover the flask with a watch glass and bring it, and a 10 mL graduated cylinder, to the fume hood. Add 10 mL of  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer to the flask.
- ↪ Add approximately 1 mL of calmagite indicator to the flask. Titrate with  $\text{Na}_2\text{EDTA}$  solution until the endpoint. Refer to the Introduction of the experiment for the color change. Record the final burette reading **to  $\pm 0.01$  mL**.
- ↪ Repeat the titration 3 more times so that you have 4 titres total. Three of your titres should be within 0.1 mL of each other. If not, consult your TA before continuing.

The ammonia buffer solution has a strong, disagreeable odor. Keep it capped and in the fume hood at all times!

Never pipet directly from a volumetric flask. Pour some solution into a small beaker, and pipet from that.

See the lab manual Introduction chapter for details on laboratory policies and due dates.

## Lab Report

Record all observations and work **in non-erasable pen** on the worksheet pages provided as part of this Experiment. Staple together the report pages and the cover page, and submit your completed report to your lab section's dropbox outside SA 116. You have **one week** to complete and submit your report.

If your report is late, hand it in to the *Late Report Box* outside SA 116, and notify your TA and the Lab Coordinator by email when you have submitted it. Marks will be deducted for late reports: ½ mark per half-day and 1 mark per weekend day (i.e. reports dropped off after 4 PM on Friday will receive a -2 deduction).

## Marks Breakdown

The general marking scheme for the lab worksheet is as follows:

Criteria	Marks
Introduction & Procedure	3
Data Tables	1
Calculations	6.5
Discussion Questions	4
Conclusion & References	1.5
Deductions	
Up to two marks each could be deducted for:	
• Incomplete pre-lab flowchart	
• Writing in pencil or erasable ink	
• Inappropriate significant figures	
• Missing or inappropriate units in calculations	
	<i>Total:</i> <i>/16</i>

# CHEMISTRY 209

## FALL 2016

<b>WORKSHEET LABORATORY REPORT</b> Experiment 1: Determination of Water Hardness	
Student Name:	
Date Experiment Performed:	
Lab Section:	Lab Room:
Lab TA Name:	
Lab Partner Name:	

Student Signature:
Date:

Please staple this cover sheet to the front of your worksheet report (3 pages, including this one).

**Submit your completed worksheet to the blue lab report boxes within one week of your lab.**

## Procedure Flow Chart: Pre-lab Assignment

Fill in the blanks in the flowchart below:

Before beginning, clean all glassware with: \_\_\_\_\_ and \_\_\_\_\_

### Part 1: Temporary Hardness

#### 1. Boil water: 20 min

Tap water needed:  
\_\_\_\_\_ mL

Glassware/Equipment:

- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_

While waiting:

### Part 2: Total Hardness

#### 1. Prepare burette

Rinse with: \_\_\_\_\_

Fill with: \_\_\_\_\_

#### 2. Cool & filter water

Time in cool bath:  
\_\_\_\_\_ min

Glassware/Equipment:

- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_

#### 2. Titrate

In each Erlenmeyer flask:

- \_\_\_\_\_
- \_\_\_\_\_
- \_\_\_\_\_

Glassware/Equipment:

- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_

Rinse pipet with: \_\_\_\_\_

### Part 3: Temporary Hardness

#### 3. Prepare burette

Rinse with: \_\_\_\_\_

Fill with: \_\_\_\_\_

#### 4. Titrate

In each Erlenmeyer flask:

- \_\_\_\_\_
- \_\_\_\_\_
- \_\_\_\_\_

Glassware/Equipment:

- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_
- ✓ \_\_\_\_\_

Rinse pipet with: \_\_\_\_\_

### Cleanup:

Leftover tap water disposed in:

Titration waste disposed in:

Filter paper disposed in:



## Introduction

1. *State the objective:* In your own words, briefly state the objective of this laboratory experiment.
2. *Reaction studied:* Give the overall balanced equation for the reaction you observed in this experiment.
3. *Highlights of the technique:* What was the purpose of boiling and filtering the water in Part 1?
4. *Highlights of the technique:* Why was it important to cool the water before filtering it in Part 1?

## Procedure

State the source of the experimental procedure and whether any modifications were made:

## Data and Results

TABLE 1: STANDARDS AND REFERENCE VALUES

(TO BE FILLED OUT BEFORE LAB)

Concentration of stock Na <sub>2</sub> EDTA (M):
Collection location of tap water sample:
North or South reservoir:
City of Calgary water hardness value:

TABLE 2: DETERMINATION OF PERMANENT WATER HARDNESS (PART 1)

	Initial buret reading (mL)	Final buret reading (mL)	Titre: Volume of Na <sub>2</sub> EDTA used (mL)
Titration 1			
Titration 2			
Titration 3			
Titration 4			

TABLE 3: DETERMINATION OF TOTAL WATER HARDNESS (PART 2)

	Initial buret reading (mL)	Final buret reading (mL)	Titre: Volume of Na <sub>2</sub> EDTA used (mL)
Titration 1			
Titration 2			
Titration 3			
Titration 4			

TABLE 4: SUMMARY OF CALCULATED RESULTS

	Part 1: Permanent Hardness	Part 2: Total Hardness	Temporary Hardness
Average titre (mL)			
Titre standard deviation			
Grubbs test G value			
Recalculated average titre (or "unchanged")			
Hardness (M CaCO <sub>3</sub> )			
Hardness (mg/L CaCO <sub>3</sub> )			
% error			

## Calculations

Show all work (including units) for all calculation steps.

- For Part 1, determine the volume of Na<sub>2</sub>EDTA used in each titration **and** the average titre value. Record your final values in Table 2 and Table 4, respectively. *You need only show one example of the 'volume used' calculation.*

- If the data point was identified as an outlier, recalculate your average titre value (excluding the outlier), and record your final value in Table 4.

4. Calculate the permanent hardness, in M (mol/L) and mg/L  $\text{CaCO}_3$  of your water sample, and record your final values in Table 4.

**Repeat the above calculations for the titrations of Part 2 (total hardness) and record the calculated values in Tables 3 & 4.**

5. Calculate the temporary hardness of the water sample, in M (mol/L) and mg/L  $\text{CaCO}_3$ , and record the final value in Table 4.
6. Determine the % error of your total hardness value (compared to the relevant City of Calgary reference value) and record the value in Table 4.

## Discussion

1. *State your major findings:* What is the “hardness rating” of your water sample?
2. *Significance of your results:* Based on the hardness rating of your water sample, what are the implications (adverse effects or precautions) of using this water domestically or in industrial processes?
3. *Accuracy of your results:* Comment on the accuracy of your water hardness value, using the values you have calculated to support your claims.
4. *Precision and reproducibility:* Comment on the precision of your results. Use statistical or numerical values to support your claims.

5. *Sources of error/uncertainty*: List two assumptions that you made during the determination of your water hardness value. For each assumption, explain how your final result would be affected if the assumption was incorrect.

## Conclusion

Briefly summarize the findings of your experiment:

## References

Provide sources for all outside information used in writing your report.

This may include: Literature source for hardness values, source for stock solution concentrations, lab partner for any data/observations you did not gather personally, your textbook, or any other sources. Each reference listed here should support in-text citations at the relevant place in your report worksheet. See Appendix K for formatting guidelines.