Calcium and Water Hardness

INTRODUCTION

Calcium, Ca^{2+}

Calcium, in the form of the Ca^{2+} ion, is one of the major inorganic *cations*, or positive ions, in saltwater and freshwater. It can originate from the dissociation of salts, such as calcium chloride or calcium sulfate, in water.

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2\ Cl^-(aq)$$

$$CaSO_4(s) \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$$

Most calcium in surface water comes from streams flowing over limestone, $CaCO_3$, gypsum, $CaSO_4 \cdot 2H_2O$, and other calcium-containing rocks and minerals. Groundwater and underground aquifers leach even higher concentrations of calcium ions from rocks and soil. Calcium carbonate is relatively insoluble in water, but dissolves more readily in water containing significant levels of dissolved carbon dioxide.[1]

Sources of Calcium Ions	
• Limestone:	$CaCO_3$
• Dolomite:	$CaCO_3$–$MgCO_3$
• Gypsum:	$CaSO_4 \cdot 2H_2O$

The concentration of calcium ions (Ca^{2+}) in freshwater is found in a range of 0 to 100 mg/L, and usually has the highest concentration of any freshwater cation. A level of 50 mg/L is recommended as the upper limit for drinking water. High levels are not considered a health concern; however, levels above 50 mg/L can be problematic due to formation of excess calcium carbonate deposits in plumbing or in decreased cleansing action of soaps. If the calcium-ion concentration in freshwater drops below 5 mg/L, it can support only sparse plant and animal life, a condition known as *oligotrophic*. Typical seawater contains Ca^{2+} levels of about 400 mg/L.

Calcium Hardness as $CaCO_3$

When water passes through or over mineral deposits such as limestone, the levels of Ca^{2+}, Mg^{2+}, and HCO_3^- ions present in the water greatly increase and cause the water to be classified as *hard water*. This term results from the fact that calcium or magnesium ions in water combine with soap molecules, forming a sticky scum that interferes with soap action and makes it "hard" to get suds. One of the most obvious signs of water hardness is a layer of white film left on the surface of showers. Since most hard-water ions originate from calcium carbonate, levels of water hardness are often referred to in terms of *hardness as $CaCO_3$*. For example, if a water sample is found to have a Ca^{2+} concentration of 30 mg/L, then its *calcium hardness as $CaCO_3$* can be calculated using the formula[2]

Calcium Hardness as $CaCO_3$ (mg/L)	
• Soft:	0-20
• Moderately soft:	20-40
• Moderately hard:	40-80
• Hard:	80-120
• Very hard:	>120

$$(30\ mg/L\ Ca^{2+}) \times (100\ g\ CaCO_3 / 40\ g\ Ca^{2+}) = 75\ mg/L\ calcium\ hardness\ as\ CaCO_3$$

[1] The reaction occurring with limestone is: $CaCO_3(s) + CO_2(aq) + H_2O(l) \longleftrightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$.

[2] This formula takes into account that the molar mass of Ca is 40 g/mol, and of $CaCO_3$ is 100 g/mol.

Note that 30 mg/L Ca^{2+} and 75 mg/L calcium hardness as $CaCO_3$ are equivalent—they are simply two different ways of expressing calcium levels. The value of calcium hardness as $CaCO_3$ can always be obtained by multiplying the Ca^{2+} concentration by a factor of 100/40, or 2.5.

Another common measurement of water hardness is known as *total hardness as $CaCO_3$*. This measurement takes into account *both* Ca^{2+} and Mg^{2+} ions. On average, magnesium hardness represents about 1/3 of total hardness and calcium hardness about 2/3. If you are comparing your own test results of calcium hardness as $CaCO_3$ with results in publications that use units of total hardness as $CaCO_3$, you can estimate total hardness by multiplying the calcium hardness by 1.5. See Test 14, *Total Water Hardness,* for further information about this topic.

Expected Levels

The concentration of calcium ions (Ca^{2+}) in freshwater is found in a range of 4 to 100 mg/L (10–250 mg/L of calcium hardness as $CaCO_3$). Seawater contains calcium levels of 400 mg/L Ca^{2+} (1000 mg/L of calcium hardness as $CaCO_3$).

Table 1: Calcium, Calcium Hardness, and Total Hardness in Selected Sites

Site (fall season)	Calcium (mg/L Ca^{2+})	Ca hardness (mg/L as $CaCO_3$)	Total hardness (mg/L as $CaCO_3$)
Merrimack River, Lowell, NH	6.3	15.8	20.8
Mississippi River, Memphis, TN	48.0	120.0	178.3
Rio Grande River, El Paso, TX	84.0	210.0	297.5
Ohio River, Grand Chain, OH	24.0	60.0	86.3
Willamette River, Portland, OR	6.4	16.0	25.2
Missouri River, Garrison Dam, ND	53.0	132.5	215.8
Sacramento River, Keswick, CA	11.0	27.5	46.3
Hudson River, Poughkeepsie, NY	26.0	65.0	84.6
Platte River, Louisville, NE	72.0	180.0	250.8
Colorado River, Andrade, CA	76.0	190.0	294.2

Summary of Method

A Vernier Calcium Ion-Selective Electrode (ISE) is used to measure the calcium ion concentration in the water, in mg/L as Ca^{2+}, either on site or after returning to the lab. This value is then multiplied by a factor of 2.5 to obtain a value for calcium hardness as $CaCO_3$, in mg/L.

CALCIUM ION-SELECTIVE ELECTRODE

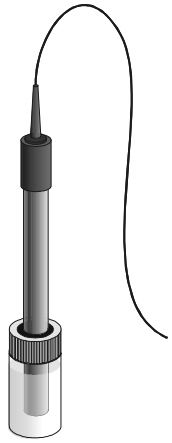
Materials Checklist

___ computer
___ Vernier computer interface
___ Logger *Pro*
___ Calcium Ion-Selective Electrode
___ tissues
___ Low Standard (10 mg/L Ca^{2+})
___ High Standard (1000 mg/L Ca^{2+})
___ wash bottle with distilled water
___ small paper or plastic cup (optional)

Advanced Preparation

The Vernier Calcium Ion-Selective Electrode (ISE) must be soaked in the Calcium High Standard solution (included with the ISE) for 15–30 minutes. **Important:** Make sure the ISE is not resting on the bottom, and that the small white reference contacts are immersed. Make sure no air bubbles are trapped below the ISE.

If the ISE needs to be transported to the field during the soaking process, use the Short-Term ISE Soaking Bottle. Remove the cap from the bottle and fill it 3/4 full with High Standard. Slide the bottle's cap onto the ISE, insert it into the bottle, and tighten. **Important:** Do not leave the ISE soaking for more than 24 hours. Long-term storage should be in the Long-Term ISE Storage Bottle.



ISE soaking for travel

Collection and Storage of Samples

1. This test can be conducted on site or in the lab. A 100 mL water sample is required.

2. It is important to obtain the water sample from below the surface of the water and as far away from shore as is safe. If suitable areas of the stream appear to be unreachable, samplers consisting of a rod and container can be constructed for collection. Refer to page Intro-4 of the Introduction of this book for more details.

Testing Procedure

1. Position the computer safely away from the water. Keep water away from the computer at all times.

3. Prepare the Calcium Ion-Selective Electrode (ISE) for data collection.
   a. The ISE should be soaking in the High Standard. Make sure that it is not resting on the bottom of the container, and that the small white reference contacts are immersed.
   b. Plug the ISE Sensor into Channel 1 of the Vernier interface.

2. Prepare the computer for data collection by opening the file "13 Calcium & Hardness" from the *Water Quality with Vernier* folder of Logger*Pro*.

4. You are now ready to calibrate the Calcium ISE.

   First Calibration Point

   a. Choose Calibrate ▸ CH1: Calcium ISE (mg/L) from the Experiment menu and then click Calibrate Now.
   b. Type **1000** (the concentration in mg/L Ca^{2+}) in the edit box.
   c. When the displayed voltage reading for Reading 1 stabilizes, click Keep.

   Second Calibration Point

   d. Rinse the ISE thoroughly with distilled water and gently blot it dry with a tissue. Be very gentle when blotting the membrane. **Important:** Failure to carefully rinse and dry the ISE will contaminate the standard.
   e. Place the tip of the ISE into the Low Standard (10 mg/L Ca^{2+}). Be sure that the ISE is not resting on the bottom of the bottle and that the small white reference contacts are immersed. Make sure no air bubbles are trapped below the ISE.
   f. After briefly swirling the solution, hold the ISE still and wait approximately 30 seconds for the voltage reading displayed on the computer screen to stabilize.
   g. Enter **10** (the concentration in mg/L Ca^{2+}) in the edit box.
   h. When the displayed voltage reading for Reading 2 stabilizes, click Keep, then click Done.

5. You are now ready to collect calcium concentration data.

   a. Rinse the ISE with distilled water and gently blot it dry.
   b. Place the tip of the probe into the stream at Site 1, or into a cup with sample water from the stream. Make sure the ISE is not resting on the bottom and that the small white reference contacts are immersed. Make sure that no air bubbles are trapped below the ISE.
   c. Click Collect to begin data collection.
   d. Click Keep to begin a 10 s sampling run. **Important:** Leave the probe tip submerged for the 10 seconds that data is being collected.
   e. When the sampling run is complete, stop data collection and record the mean calcium concentration value on the Data & Calculations sheet.

6. Return to Step 5 to obtain a second reading.

7. Convert the calcium concentration (mg/L Ca^{2+}) to units of calcium hardness (mg/L as $CaCO_3$). The calculation takes into account the difference in the molar masses of calcium (40 g/mol Ca^{2+}) and calcium carbonate (100 g/mol $CaCO_3$). To convert to units of calcium hardness, perform the following calculation:

$$\text{calcium hardness as } CaCO_3 = (\text{mg/L } Ca^{2+}) \times (100 \text{ g } CaCO_3 / 40 \text{ g } Ca^{2+})$$

$$= (\text{mg/L } Ca^{2+}) \times 2.5$$

   Record this value on the Data & Calculations sheet (round to the nearest 0.01 mg/L).

DATA & CALCULATIONS

Calcium and Calcium Hardness

Stream or lake: _____ Time of day: _____

Site name: _____ Student name: _____

Site number: _____ Student name: _____

Date: _____ Student name: _____

	A	B
Reading	Calcium ($mg/L\ Ca^{2+}$)	Calcium hardness ($mg/L\ CaCO_3$)
1		
2		
Average		

Column Procedure:

A. Record the calcium concentration ($mg/L\ Ca^{2+}$) from the computer.
B. Multiply calcium concentration ($mg/L\ Ca^{2+}$) by 2.5 to obtain calcium hardness (as $CaCO_3$).

Field Observations (e.g., weather, geography, vegetation along stream) _____

_____

_____

_____

Test Completed: _____ Date: _____

Vernier Lab Safety Instructions Disclaimer

THIS IS AN EVALUATION COPY OF THE VERNIER STUDENT LAB.

This copy does not include:

- **Safety information**
- **Essential instructor background information**
- **Directions for preparing solutions**
- **Important tips for successfully doing these labs**

The complete *Water Quality with Vernier* lab manual includes 16 water quality tests and essential teacher information. The full lab book is available for purchase at: http://www.vernier.com/cmat/wqv.html

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