Total Water Hardness

INTRODUCTION

When water passes through or over deposits such as limestone, the levels of Ca$^{2+}$, Mg$^{2+}$, and HCO$_3^-$ ions present in the water can greatly increase and cause the water to be classified as hard water. This term results from the fact that calcium and magnesium ions in water combine with soap molecules, making it “hard” to get suds. In Test 13, Calcium and Water Hardness, an Ion-Selective Electrode was used to determine calcium hardness, in mg/L as CaCO$_3$. In this test, total hardness will be determined. Total hardness is defined as the sum of calcium and magnesium hardness$^1$, in mg/L as CaCO$_3$. In addition to total hardness, the test described here will allow you to determine the concentration of Mg$^{2+}$, in mg/L.

High levels of hard-water ions such as Ca$^{2+}$ and Mg$^{2+}$ can cause scaly deposits in plumbing, appliances, and boilers. These two ions also combine chemically with soap molecules, resulting in decreased cleansing action. The American Water Works Association indicates that ideal quality water should not contain more than 80 mg/L of total hardness as CaCO$_3$. High levels of total hardness are not considered a health concern. On the contrary, calcium is an important component of cell walls of aquatic plants, and of the bones or shells of aquatic organisms. Magnesium is an essential nutrient for plants, and is a component of chlorophyll.

**Expected Levels**

Total hardness in freshwater is usually in the range of 15 to 375 mg/L as CaCO$_3$. Calcium hardness in freshwater is in the range of 10 to 250 mg/L, often double that of magnesium hardness (5 to 125 mg/L). Typical seawater has calcium hardness of 1000 mg/L, magnesium hardness of 5630 mg/L, and total hardness of 6630 mg/L as CaCO$_3$.

<table>
<thead>
<tr>
<th>Total Hardness (mg/L as CaCO$_3$)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft:</td>
<td>0-30</td>
</tr>
<tr>
<td>Moderately soft:</td>
<td>30-60</td>
</tr>
<tr>
<td>Moderately hard:</td>
<td>60-120</td>
</tr>
<tr>
<td>Hard:</td>
<td>120-180</td>
</tr>
<tr>
<td>Very hard:</td>
<td>&gt;180</td>
</tr>
</tbody>
</table>

*Evaluation copy*
Table 1: Ca Hardness, Mg Hardness, and Total Hardness in Selected Sites

<table>
<thead>
<tr>
<th>Site (fall season)</th>
<th>Ca hardness (mg/L as CaCO₃)</th>
<th>Mg hardness (mg/L as CaCO₃)</th>
<th>Total hardness (mg/L as CaCO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merrimack River, Lowell, NH</td>
<td>15.8</td>
<td>5.0</td>
<td>20.8</td>
</tr>
<tr>
<td>Mississippi River, Memphis, TN</td>
<td>120.0</td>
<td>58.3</td>
<td>178.3</td>
</tr>
<tr>
<td>Rio Grande River, El Paso, TX</td>
<td>210.0</td>
<td>87.5</td>
<td>297.5</td>
</tr>
<tr>
<td>Ohio River, Grand Chain, OH</td>
<td>60.0</td>
<td>26.3</td>
<td>86.3</td>
</tr>
<tr>
<td>Willamette River, Portland, OR</td>
<td>16.0</td>
<td>9.2</td>
<td>25.2</td>
</tr>
<tr>
<td>Missouri River, Garrison Dam, ND</td>
<td>132.5</td>
<td>83.3</td>
<td>215.8</td>
</tr>
<tr>
<td>Sacramento River, Keswick, CA</td>
<td>27.5</td>
<td>18.8</td>
<td>46.3</td>
</tr>
<tr>
<td>Hudson River, Poughkeepsie, NY</td>
<td>65.0</td>
<td>19.6</td>
<td>84.6</td>
</tr>
<tr>
<td>Platte River, Louisville, NE</td>
<td>180.0</td>
<td>70.8</td>
<td>250.8</td>
</tr>
<tr>
<td>Colorado River, Andrade, CA</td>
<td>190.0</td>
<td>104.2</td>
<td>294.2</td>
</tr>
</tbody>
</table>

Summary of Method

The sample is first adjusted to a pH of 10 using a buffer solution. The sample is titrated to its equivalence point using a standard EDTA solution. EDTA draws the calcium and magnesium ions into a complex, so neither one has free ions in solution. The Calmagite indicator initially turns red in the presence of magnesium, then turns blue when enough EDTA solution has been added to combine with all calcium and magnesium ions. The total hardness of the sample is calculated using the precise volume of EDTA solution added when the indicator changes color, as well as the EDTA concentration, in mol/L. If calcium concentration was determined in Test 13, magnesium concentration can also be calculated (in mg/L Mg²⁺).

Here is a summary of the measurements and calculations in Test 14. Sample values are included.

a. Total hardness as CaCO₃, obtained using the EDTA titration = 120 mg/L (sample value)

b. Mg hardness as CaCO₃ = total hardness – calcium hardness (Test 13) = 120 – 70 = 50 mg/L

c. Mg²⁺ = (50 mg/L as CaCO₃) × (24 g Mg²⁺ / 100 g CaCO₃) = 12 mg/L as Mg²⁺

EDTA is an abbreviation for ethylenediaminetetraacetic acid.
TOTAL WATER HARDNESS

Materials Checklist

___ sampling bottles
___ 100 mL graduated cylinder
___ 250 mL Erlenmeyer flask
___ 25 or 50 mL buret
___ Hardness 1 Buffer Solution
___ two Calmagite³ indicator powder pillows
___ 0.01 M EDTA⁴ titrant (TitraVer Standard Solution)
___ water bottle with distilled water

Collection and Storage of Samples

1. This test must be conducted in the lab. Collect at least 300 mL of sample water.

2. It is important to obtain the water sample from below the surface of the water and as far away from the 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 for more details.

Testing Procedure

1. Obtain a clean buret and rinse it with a few mL of the 0.0100 M EDTA titrant (TitraVer Standard Solution). Fill the buret a little above the 0 mL level with the EDTA solution. Drain a small amount of the solution so it fills the buret tip and leaves the EDTA solution at the 0 mL mark (or just below it). Record the buret level on the Data & Calculations sheet, to the nearest 0.01 mL.

2. Prepare the water sample for titration.
   a. Use a graduated cylinder to measure 50 mL of your water sample into a 250 mL Erlenmeyer flask.
   b. Add 1 mL of Hardness 1 Buffer Solution to the Erlenmeyer flask using the 1 mL calibrated dropper. Gently swirl the contents of the flask to mix.
   c. Add the contents of one Calmagite³ powder pillow to the Erlenmeyer flask. Gently swirl the contents of the flask to mix. The solution should now be red in color.

3. Titrate the sample you prepared in Step 2.
   a. Slowly add 0.01 M EDTA titrant to the sample in the Erlenmeyer flask—start with 1 mL additions. Swirl the sample after each addition of titrant.
   b. Near the equivalence point, the red color will start to fade, and become more violet (mixture of red and blue). You should reduce the addition volume to 1 drop at a time. Note: The reaction at the equivalence point is very slow (~1 second), so take your time.
   c. When the last tinge of red starts to disappear and turn to a pure blue color, you have reached the equivalence point. Record the final buret volume (to the nearest 0.01 mL) on your Data & Calculations sheet.

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³ Calmagite is contained in ManVer 2 Hardness Indicator Powder Pillows.
⁴ Hach TitraVer Hardness Titrant is labeled as 0.01 M EDTA, and also as an equivalent concentration of 0.02 N.
d. If you are unsure whether you have reached the equivalence point, simply record the buret volume, then add another drop of EDTA titrant. If the color becomes a truer blue color, use the new buret reading; if not, use the previous buret reading.

4. Perform a second titration trial. To do this, discard the first titration mixture, as directed by your instructor. If you have enough titrant left for a second titration, simply record the current buret level; if not, refill the buret and record the buret level. Rinse the 250 L Erlenmeyer flask twice with distilled water, then repeat Steps 2–3.

Calculations
1. To determine the titrant volumes used, subtract the initial volume from the final volume for each trial. Record the titrant volumes for the two trials on the Data & Calculations sheet. **Important:** If the titrant volumes for the two trials are not in close agreement, you should repeat Steps 1–3 of the Testing Procedure until you have two trials that are close.

2. Calculate the value for total water hardness.
   a. For each trial, determine total water hardness using the equation
      \[
      \text{total water hardness as } \text{CaCO}_3 \text{ (mg/L)} = (\text{titrant volume}) \times 20.0
      \]
   b. Record the total water hardness value on the Data & Calculations sheet.

Optional Calculations
3. Calculate magnesium hardness (mg/L as CaCO\(_3\)) and magnesium concentration (mg/L Mg\(^{2+}\)).
   a. On the second table of the Data & Calculations sheet, record the calcium hardness value you obtained in Test 13, and the total water hardness value from the first part of this test.
   b. Calculate magnesium hardness (mg/L as CaCO\(_3\)). Use the equation
      \[
      \text{magnesium hardness (mg/L as CaCO}_3\text{) } = \text{total hardness } - \text{calcium hardness}
      \]
   c. Calculate Mg\(^{2+}\) concentration, using the formula
      \[
      \text{Mg}^{2+} = (\text{magnesium hardness as CaCO}_3\text{) } \times (24 \text{ g Mg}^{2+}/100 \text{ g CaCO}_3)\]
   d. Record the values for magnesium hardness and Mg\(^{2+}\) concentration on the Data & Calculations sheet.
DATA & CALCULATIONS

Total Water Hardness

Stream or lake: ____________________________  Time of day: ____________________________

Site name: ________________________________  Student name: __________________________

Site number: ______________________________  Student name: __________________________

Date: ____________________________________  Student name: __________________________

<table>
<thead>
<tr>
<th>Column</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total water hardness</td>
<td>Initial</td>
<td>Final</td>
<td>Titrant</td>
<td>Total water hardness</td>
</tr>
<tr>
<td></td>
<td>buret reading (mL)</td>
<td>buret reading (mL)</td>
<td>volume (mL)</td>
<td>(mg/L as CaCO₃)</td>
</tr>
<tr>
<td>Example</td>
<td>0.10 mL</td>
<td>9.22 mL</td>
<td>9.12 mL</td>
<td>182 mg/L</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Column Procedure, total water hardness:
A. Initial buret reading (mL)
B. Final buret reading (mL)
C. Titrant volume (mL) = B – A
D. Total water hardness (mg) = C \times 20.0

<table>
<thead>
<tr>
<th>Column</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium calculations (optional)</td>
<td>Calcium hardness (from Test 13) (mg/L as CaCO₃)</td>
<td>Total hardness (from 14) (mg/L as CaCO₃)</td>
<td>Magnesium hardness (mg/L as CaCO₃)</td>
<td>Magnesium concentration (mg/L as Mg²⁺)</td>
</tr>
<tr>
<td>Example</td>
<td>132 mg/L</td>
<td>182 mg/L</td>
<td>50 mg/L</td>
<td>12 mg/L</td>
</tr>
</tbody>
</table>

Column Procedure, magnesium concentration:
A. Record value from Test 13
B. Record value from Test 14 (above)
C. Magnesium hardness (mg/L as CaCO₃) = B – A
D. Magnesium concentration (mg/L as Mg²⁺) = C \times 0.24

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

Test Completed: __________________ Date: _______
Vernier Lab Safety Instructions Disclaimer

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