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Lab Partner: Alex Rudolph  
Lab Section: C127, Wednesday, 6:45pm-9:45pm  
AI: Zhongchao(Kevin) Zhao  
Date: Oct. 11th, 2017

**Water Hardness**

**Objective:**
- Learn and understand the technique of titration and perform it correctly.  
- Use the concepts of molarity and solution stoichiometry to perform a quantitative analysis of metal ions found in natural water samples.

**Introduction:**

The method titration \[^1\] is used to determine the concentration of an unknown. It’s using a known concentration solution called titrate as the standard solution add to an unknown concentration solution called analyte. Mostly, the titrate is put into the burette and the analyte is put into the conical flask with several drops of indicators. The indicators should be sensitive to pH changes. Also, titration reactions can only happen when the formula of the reaction is certain. In this laboratory, we used the equation $MIn^- + HEDTA^{3-} \rightarrow MEDTA^{2-} + MIn^{2-}$ where “In” stands for the indicator and “M” stands for the metal ions that is being transferred; and the molar ration for the reactions is 1:1.

The indicator used in the lab was Eriochrome Black-T \[^2\], the structure of this molecule is shown in Figure 1, when it’s added to the analyte Ca$^{2+}$ solutions, it will form a rose color; when EDTA added and reach the end point, the color will turn to a blue color. The color change is due to the pH of the solution has become more basic. When the indicator dissolved in water, the Na was removed by water molecules, giving the solution a negative charge.

The hydrogen protons removed from the hydroxides with the increasing of pH. The first hydrogen was removed when the pH approaches 7.0, with a color change from red to blue shown by the equation $H_2O + H_2In^- \leftrightarrow HIn^{2-} + H_3O^+$. This represent the amount of
EDTA and Ca$^{2+}$ in the water sample is at equilibrium. The second hydrogen was removed when the pH approaches 12 with a color change from blue to orange shown by the equation $HIn^{2-} + H_2O \leftrightarrow In^{3-} + H_3O^+$. This show the amount of EDTA is taking more space in the water sample.

Another essential molecule in this lab is the EDTA [3], also called Ethylenediaminetetraacetic acid. The structure of this is known as a hexadentate ligand which shows in Figure 2, which can isolate the metal ions. And therefore, it’s using in this lab. When EDTA is exposed to very high pH level, the hydrogens within the 4 hydroxide groups on the end of the molecule fall to allow Ca$^{2+}$ attach to the main part. When the metal ions attached to the remaining part, it’s shown as a structure like Figure 3 [4]. For this experiment, a small amount of Mg$^{2+}$ was sued to speed up the reaction so that the equilibrium point will be more accurate.

When analyzing the data of the titration, the data points differences in concentration are always very small numbers, which is hard to make a conclusion. The equation $p = -\log x$ is used which x is the concentration of the sample to enlarger the data points and make it easy to analyze.

Determine the water hardness is essential to check the quality of the water by the positive ions present in water sample. The more positive ions present in the water sample, the harder the water is [5].

For this experiment, the data collected from the experimental procedure will be used to calculate the concentration for different solutions. By using the equation $M_0 = \frac{n_0}{v_0}$ where M stands for molarity, n stands for moles and v stands for volume. Molarity can be calculated.

**Procedure:**

**Materials & Equipment:**

Stand; Clamp

50mL Burette; 25mL Pipette; Pipette filler

10mL Measuring Cylinder; 2×250mL Volumetric Flask; Waste Beaker
0.01M EDTA Solution; Eriochrome Black T indicator; NH₃ Buffer; 0.01M CaCO₃; MgEDTA; Distilled Water; Water Sample

**Procedure:**

The first step taken is preparing the analyte. The 25mL volumetric flask was rinsed 3 times by CaCO₃ solution. The rinsed CaCO₃ was drained into a waste beaker. Once the pipette has been rinsed out three times, 25mL CaCO₃ was pipetted into a clean 250mL volumetric flask. Then, 10mL of NH₃ buffer was added to the solution by the 10mL measuring cylinder. Next, 1mL of MgEDTA was added to the solution by the 10mL measuring cylinder to speed up the color change. Distilled water was then added to the volumetric flask and make the total be 75mL to dilute the solution. Finally, 4 drops of Eriochrome Black T were added to the solution. The solution was stirred to make it evenly distributed.

The second step is to set up the titration. The 50mL burette was attached to the stand by a clamp. The waste beaker was placed under the burette. Then wash the burette by EDTA solution several times, the waste was poured into the waste beaker. Then, EDTA solution was poured into the burette, and ensure there was no bubbles in the lower level by opening the stopcock and let some EDTA drain into the waste beaker. Once there were no bubbles, the stopcock was closed, the volume showed on burette was recorded and the waste beaker was removed.

Then, put the volumetric flask to at the center under the burette, the stopcock was opened for the EDTA solution drop into the flask. One person monitored the color change of the solution with stirring the solution, the other one monitored the volume and the flow of EDTA. Once the color started to turn purple, the flow of EDTA was slowed down to drops. One drop was added at a time until the color stopped changing. The solution will reach a medium blue color. The new volume shown on the burette was recorded. If too much EDTA was added to the solution, the color will become more orange. This process was repeated several times until the molarity of EDTA was calculated and the percentage error was within 0.5%.

After the molarity of EDTA was determined, the second part of titrations were set up to be performed. The apparatus remained the same. The analyte in the volumetric flask was changed to the water sample “Bedford”. Before the sample was poured into the flask, the pipette and the flask was washed and rinsed efficiently for at least 3 times. After them was cleaned, the water sample was transferred by pipette to the flask; then, the buffer and
MgEDTA was added by the 10mL measuring cylinder and the distilled water was added to make the water line approaches 75mL.

The process was the same as before and this was done more times to ensure the difference of EDTA volume added was less than 0.1mL.

After the process was finished, apparatus was cleaned up and return to the original location.

**Equations:**

\[ M_{EDTA}V_{EDTA} = n_{EDTA} = n_{sample} = M_{sample}V_{sample} \]

where M is the molarity, V is the volume used, n is the number of moles.

\[ M = \frac{\text{moles of solute}}{\text{titre of solution}} \]

\[ \text{ppm} = \frac{\text{mg of solute}}{\text{liters of solution}} \]

**Result:**

Table 1 shows the results of the first 3 titrations, which the concentration of EDTA solution was standardized by the given concentration of Ca\(^{2+}\) solution. The mole of EDTA is the same as mole of Ca\(^{2+}\). The average concentration was 0.00843M, and the standard deviation was \(2\times10^{-4}\).

<table>
<thead>
<tr>
<th>(M_{CaCO_3}/M)</th>
<th>(V_{CaCO_3}/mL)</th>
<th>(n_{CaCO_3}/mol)</th>
<th>(V_{iEDTA}/mL)</th>
<th>(V_{fEDTA}/mL)</th>
<th>(V_{EDTA}/mL)</th>
<th>(M_{EDTA}/M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>25.0</td>
<td>0.00025</td>
<td>20.0</td>
<td>49.2</td>
<td>29.2</td>
<td>0.0086</td>
</tr>
<tr>
<td>0.01</td>
<td>25.0</td>
<td>0.00025</td>
<td>20.0</td>
<td>50.0</td>
<td>30.8</td>
<td>0.0081</td>
</tr>
<tr>
<td>0.01</td>
<td>25.0</td>
<td>0.00025</td>
<td>15.0</td>
<td>44.2</td>
<td>29.2</td>
<td>0.0086</td>
</tr>
</tbody>
</table>

Table 1: Standardized Concentration of EDTA.
Table 2 shows the result of the following sets of titrations, which the concentration of Ca\(^{2+}\) in water sample was determined by the standardized EDTA solution. The volume of water sample used was 25mL. The moles of CaCO\(_3\) was determined based on the moles of EDTA. The average concentration of the CaCO\(_3\) was 0.0034M, and standard deviation was 5\times10^{-5}.

<table>
<thead>
<tr>
<th>Initial Volume of EDTA /mL</th>
<th>Final Volume of EDTA /mL</th>
<th>Volume of EDTA used /mL</th>
<th>Moles of EDTA /mol</th>
<th>Volume of water sample/mL</th>
<th>Concentration of CaCO(_3)/M</th>
<th>CaCO(_3) in ppm/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.0</td>
<td>37.3</td>
<td>10.3</td>
<td>0.0000869</td>
<td>25</td>
<td>0.0035</td>
<td>350.2</td>
</tr>
<tr>
<td>35.0</td>
<td>45.0</td>
<td>10.0</td>
<td>0.0000843</td>
<td>25</td>
<td>0.0034</td>
<td>340.0</td>
</tr>
<tr>
<td>31.0</td>
<td>41.1</td>
<td>10.1</td>
<td>0.0000852</td>
<td>25</td>
<td>0.0034</td>
<td>343.4</td>
</tr>
</tbody>
</table>

**Table 2: Determination of Concentration of Ca\(^{2+}\) Ion in Bedford Water Sample**
**Discussion:**

The results from titration were very precise, giving very similar results in various trials conducted. However, the results from the first set of titrations were a little bit smaller than the given 0.01M. But the difference was within 0.002 and the trials were precise, so, it can be assumed this difference was due to the experimental errors, such as the measurement of volume. The same error may also occur in the second set, since the same technique and equipment was used.

The water sample used in this lab is from Bedford, Indiana. According to the diagram on the right, the water hardness should be expected as relatively large number of ions in, the sample should be hard water.

The hardness of water may lead to serious problem when it’s found in drinking water, and when it interacts with negative ions, it may damage bodies of people. When EDTA is exposed too much, the hydrogens fall off, allowing it to attract cations.

**Conclusion:**

The following chart provide the water hardness per ppm.

<table>
<thead>
<tr>
<th>Degree of Hardness</th>
<th>Grains per Gallon (gpg)</th>
<th>ppm (or mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td>&lt;1.0</td>
<td>&lt;17.0</td>
</tr>
<tr>
<td>Slightly Hard</td>
<td>1.0-3.5</td>
<td>17.1-60</td>
</tr>
<tr>
<td>Moderately Hard</td>
<td>3.5-7.0</td>
<td>60-120</td>
</tr>
<tr>
<td>Hard</td>
<td>7.0-10.5</td>
<td>120-180</td>
</tr>
<tr>
<td>Very Hard</td>
<td>&gt;10.5</td>
<td>&gt;180</td>
</tr>
</tbody>
</table>

Based on the chart, the water sample we used in the lab can be determined as very hard.
Reference:

(2) 钴黒 T_百度百科 https://baike.baidu.com/item/%E9%93%AC%E9%BB%91T (accessed Oct 17, 2017).


### Part 1: STANDARDISE MEDIA

<table>
<thead>
<tr>
<th>C2CO₃ mol/L</th>
<th>Vmedia/mL</th>
<th>nC2CO₃/mol</th>
<th>Vf/mL</th>
<th>VEDTA/mL</th>
<th>CEDTA/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>25</td>
<td>0.00075</td>
<td>20</td>
<td>0.492</td>
<td>0.0086</td>
</tr>
<tr>
<td>0.01</td>
<td>25</td>
<td>0.00075</td>
<td>20</td>
<td>0.50</td>
<td>0.0081</td>
</tr>
<tr>
<td>0.01</td>
<td>25</td>
<td>0.00075</td>
<td>45.5</td>
<td>0.463</td>
<td>0.0086</td>
</tr>
</tbody>
</table>

Trial 1 & Trial 3 has the same result.
So, that's the correct Molarity of EDTA.

**Average Concentration of EDTA**

\[
\frac{(0.0086 + 0.0081 + 0.0086)}{3} = 0.00843 \text{ M.}
\]

**STANDARD DEVIATION**

\[
\sigma_1 = \frac{0.0002}{2} = 10^{-4}
\]

### Part 2: Water Hardness

<table>
<thead>
<tr>
<th>VEDTA/mL</th>
<th>Vf/mL</th>
<th>VF/mL</th>
<th>nEDTA/mol</th>
<th>Vf₂⁻⁺</th>
<th>Vf⁺⁺⁺⁺⁺⁺</th>
<th>CEDTA/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.1</td>
<td>20.0</td>
<td>31.1</td>
<td>0.000736</td>
<td>25</td>
<td>0.0037</td>
<td>37.4</td>
</tr>
<tr>
<td>8.90</td>
<td>8.0</td>
<td>2.9</td>
<td>0.000751</td>
<td>25</td>
<td>0.0030</td>
<td>30.2</td>
</tr>
<tr>
<td>10.3</td>
<td>37.0</td>
<td>37.3</td>
<td>0.000869</td>
<td>25</td>
<td>0.0035</td>
<td>350.2</td>
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<tr>
<td>10.0</td>
<td>35.0</td>
<td>45.0</td>
<td>0.000743</td>
<td>25</td>
<td>0.0034</td>
<td>340.0</td>
</tr>
<tr>
<td>10.1</td>
<td>31.0</td>
<td>41.1</td>
<td>0.000852</td>
<td>25</td>
<td>0.0034</td>
<td>343.4</td>
</tr>
</tbody>
</table>