Determination of Ca\(^{2+}\) and Mg\(^{2+}\) in a Sample of Sea Water

I. Required Reading

In addition to reading this project description and answering questions in the prelab section, you should read the following chapters of the course textbook (Fundamentals of Analytical Chemistry (8th edition) by D.A. Skoog, D.M. West, F.J. Holler, S.R. Crouch): Chapter 17. References to specific book sections and chapters are provided in the project description below.

II. Introduction

The most common multivalent ions in natural waters are Ca\(^{2+}\) and Mg\(^{2+}\). These ions react similarly with chelating agents such as ethylenediaminetetraacetic acid (EDTA), so the total concentration of Ca\(^{2+}\) and Mg\(^{2+}\) can be found by titrating with standard EDTA solutions. The individual concentration of Ca\(^{2+}\) can also be found by first removing Mg\(^{2+}\) from the solution, and then titrating the remaining Ca\(^{2+}\) with EDTA.

As in all EDTA titrations the solution must be buffered to get precise results. This topic is covered thoroughly in Chapter 17, and you should review that material carefully before beginning this experiment. To obtain the separate concentrations of Ca\(^{2+}\) and Mg\(^{2+}\) we can take advantage of solubility differences between the hydroxides of the two cations. Mg(OH)\(_2\) is much less soluble than Ca(OH)\(_2\), so by increasing the pH of the unknown sample the Mg\(^{2+}\) can be precipitated out as the insoluble Mg(OH)\(_2\) hydroxide leaving only the Ca\(^{2+}\) to be titrated with EDTA. Subtraction then provides the concentrations of each component. This experiment assumes that other cations that might also react are absent or negligible. The most common indicator for EDTA titrations is Eriochrome Black T, and we will use it to titrate the cation mixture. This indicator does not work so well at the high pH used for the second (Ca\(^{2+}\)) titration, so solid Hydroxynaphthol Blue is used in that case. The endpoint with both indicators occurs when a persistent change from red to purple-blue is observed.

III. Preparation of Standard Na\(_2\)H\(_2\)EDTA Solution

Na\(_2\)H\(_2\)EDTA·2H\(_2\)O (MW 372.25) was dried for you by the stockroom personnel for at least 1 hr at 80 °C and cooled down in a desiccator. When prepared in this way Na\(_2\)H\(_2\)EDTA·2H\(_2\)O is reproducibly contaminated by 0.3 wt% of water that is not included in the chemical formula of the dihydrate. This impurity should be taken into account in determining the concentration of the standard solution. (See Section 37E-2 for additional details). Make sure the EDTA used in your experiment has two sodium atoms, not four.

Start heating 250-300 mL nanopure water in an Erlenmeyer flask in preparation to the next step. While the water is heating, weigh accurately about 0.3 g of the dried chelating agent; proper weighing techniques are briefly described in Section 2E-4. Dissolve the chelating agent in 250-300 mL of nanopure water in a beaker under heating. (Note: do not add all water to the beaker at once. Dissolve in less water at first, 100 mL or so, and then add the rest of water, avoid splashes.) After the chelating agent is fully dissolved, cool the solution and transfer it quantitatively into a 500 mL volumetric flask. Be sure to rinse out the beaker with small quantities of nanopure water several times to get good quantitative transfer into the volumetric flask. Fill the volumetric flask up to the mark with nanopure water and mix well. Label the
standard solution carefully. You will not be "standardizing" this solution. Its concentration will be known to you on the basis of the weighing and dilution operations, so make this solution carefully.

IV. Determination of Total Ca(II) and Mg(II) in a Water Sample

You will be provided with about 20 mL of an unknown sample containing Ca$^{2+}$ and Mg$^{2+}$ in the approximate amounts contained in sea water. Use this sample carefully, so that you can carry out all the required determinations. Swirl carefully to be sure the unknown solution is well mixed before you start.

Before you titrate your unknown you should titrate a blank that contains some Ca$^{2+}$ and Mg$^{2+}$. The blank is prepared by adding exactly 1.00 mL of "Ca/Mg Spike" to 50 mL of nanopure water in a 250 mL Erlenmeyer flask (100 mL flask will work as well). To this add 3 mL of pH 10 buffer with a disposable pipette and several drops of Eriochrome Black T indicator solution. Use 4 drops if the indicator solution looks thick; use 10 drops if it looks diluted; consult your TA if you are not sure. Once you decide on the number of drops to use you should stick with it for the rest of your titrations; otherwise your results may be inconsistent. This solution should be reddish in color. If it is bluish, then the “Spike” solution is not strong enough. Add the “Spike” solution in 1.00 mL increments until the solution is reddish. Record the exact total volume of spike added and use the same volume throughout the remainder of this experiment.

As the buffer smells, you may want to do this procedure in the hood. To accelerate the process, prepare 3-4 blank solutions in parallel. The buffer and the indicator solutions have been prepared for you in advance by the teaching staff following standard recipes (Section 37E- 1). The Ca/Mg Spike will also be prepared for you by the stockroom staff; it contains arbitrary amounts of Ca$^{2+}$ and Mg$^{2+}$ designed to consume a few mL of the standard EDTA in the blank titration. Figure out how much spike solution you will need for all of your titrations in this project. Take this amount in a vial to your bench, and use the same spike solution throughout the lab section. If you dilute it during the lab, your results will not be accurate.

The main purpose of the titration of the blank is to establish a consistent endpoint color for your titrations. Carry out at least three blank titrations to the same endpoint color. Then, in all titrations of your unknown throughout today’s section you will also add a fixed volume of the Ca/Mg Spike solution before you titrate to the same endpoint used for the blank titrations. The volume of standard EDTA solution required to titrate the blank will, of course, need to be subtracted from the volume of EDTA required to titrate the solutions containing unknown + Ca/Mg Spike in order to compute the amounts of Ca$^{2+}$ and Mg$^{2+}$ in the unknown.

The endpoint is signaled by a change of the solution from red to blue. An intermediate bluish-purple color, obtained approximately a milliliter before the solution turns blue, is a good target color to use to mark the endpoint.

This change of color from red to blue is not as abrupt as other indicators you used in previous weeks. Furthermore, it is a relatively slow reaction – the full color change may take several seconds to complete. For your first few titrations, you should approach the end point slowly and record frequently the color-volume observations in your notebook. Titration of unknown and blank to the same color improves the accuracy of the endpoint determination. Keep a sample of the bluish-purple blank titration at hand as you titrate the unknown so that you can make an easy visual comparison of the endpoint colors.
You may want to practice several times at first with this endpoint. This can be done by adding a few drops of tap water to the sample near the endpoint and re-surveying the color change. It is always a good idea to put a paper towel below the flask to help make the color transition more visible. The solution will turn from red (or pink) to blue with a purple intermediate as EDTA is added. There is some uncertainty associated with determination of the purple endpoint. Record (1) the volume at which the color begins to change, (2) the volume of the endpoint, and (3) the final volume for the color transition. This allows you to assess the uncertainty of your measurement.

In order to determine the total amount of Ca\(^{2+}\) and Mg\(^{2+}\) in your unknown you should dilute a fraction of the unknown by a factor of 5. Be sure to dilute the unknown with nanopure water in a thoroughly cleaned volumetric flask, or you may introduce more Ca\(^{2+}\) and Mg\(^{2+}\) ions. You can do your dilution in one of the following ways:

<table>
<thead>
<tr>
<th>Take mL of the unknown (measured exactly, e.g., with a pipette):</th>
<th>Dilute to mL in a volumetric flask:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00</td>
<td>50.00</td>
</tr>
<tr>
<td>5.00</td>
<td>25.00</td>
</tr>
<tr>
<td>2.00</td>
<td>10.00</td>
</tr>
<tr>
<td>1.00</td>
<td>5.00</td>
</tr>
</tbody>
</table>

As you only have about 14 mL of the unknown we prefer that you use one of the methods that requires less sample. If you do not have the necessary volumetric flask, you can get them from the stockroom.

Pipette 1.00 mL of the dilute unknown and the same volume of Ca/Mg Spike as used above into an Erlenmeyer flask. Add about 50 mL of nanopure water to your unknown. Then add 3 mL of pH 10 buffer solution using a disposable pipette and several drops of Eriochrome Black T indicator solution (you should use the same number of drops in all of your titrations for consistency). As the buffer has a smell of ammonia; you may want to add it in the hood. To accelerate the process, you may want to prepare 3-4 samples in parallel rather than sequentially. Titrate 2-3 unknown samples to the endpoint color established in the blank titration (refer to the table in part VI for the minimal number of the required titrations). Determine the total concentration of Ca\(^{2+}\) and Mg\(^{2+}\) ions in the sea water from the mean of all acceptable titrations of the unknown.

V. Determination of Ca(II) Content in the Mixture

In this part of the lab, you will determine just the Ca\(^{2+}\) content of your solution. You will start with titrating several blanks before you titrate the unknown in order to practice locating this tricky endpoint. After getting enough confidence and titrating the blank, you will carry out accurate titrations of Ca\(^{2+}\) on several unknown samples (refer to the table in section VI for the minimal number of the required titrations). Determine the total concentration of Ca\(^{2+}\) and Mg\(^{2+}\) ions in the sea water from the mean of all acceptable titrations of the unknown.

Follow this procedure for the blank and unknown titrations. For the blank: start with 50 mL of nanopure water. For the unknown: start with 50 mL of nanopure water to which 1.00 mL of undiluted unknown is added with a pipette. In either case, add Ca/Mg Spike as you did before (the same volume of Ca/Mg Spike as used in part IV). Also add 30 drops of 50 wt% NaOH solution to each unknown/blank and swirl carefully for several minutes to complete precipitation of Mg\(^{2+}\) as Mg(OH)\(_2\). Note that you may not see any visible precipitate as the particles are very...
small. The 50% NaOH will be provided to you by the teaching staff. Add about 0.1 g of the indicator solid Hydroxynaphthol Blue to the unknown/blank solution. Wait for the indicator to dissolve. The initial solution should be pink or reddish in color.

**Note for TAs: Hydroxynaphthol Blue is a solid power, and it will need to be weighed multiple times. Furthermore, it require care in handling as it easily disperses in the air. To avoid overcrowding in the balance room, start sending students to weigh 6 portion of the indicator approximately one hour before they are going to need it. Students will need at least 6 portions for one slow + two fast titrations of the blank and one slow + two fast titrations of the unknown.**

Titrates the first sample rapidly to find the approximate endpoint. However, keep in mind that color change in this reaction is even slower than the previous one because of the competing precipitation equilibria going on in the system. After reaching the first appearance of blue at the endpoint, allow each sample to stand for at least 5 minutes, with occasional swirling so that any Ca(OH)₂ precipitate has time to re-dissolve. As Ca(OH)₂ precipitate re-dissolves, the solution might turn back to pink color. Titrates to the endpoint with additional standard EDTA, if necessary. Repeat this again, if the color again changes back to pink on standing. The volume of EDTA used to titrate this blank will be slightly smaller than that obtained in part IV because the NaOH effectively precipitated all the Mg²⁺ in the blank, leaving only Ca²⁺ in the solution.

**VI. Summary of Titrations Performed in This Lab**

<table>
<thead>
<tr>
<th>Titration</th>
<th>What is titrated</th>
<th># of times</th>
<th>Indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank for Ca²⁺ &amp; Mg²⁺</td>
<td>x mL spike* + water + pH 10 buffer + indicator</td>
<td>2-3 practice titrations that will let you get used to the colors and determine the endpoint approximately; 2 slow titrations</td>
<td>Eriochrome Black T</td>
</tr>
<tr>
<td>Unknown Ca²⁺ &amp; Mg²⁺</td>
<td>x mL spike + water + 1 mL diluted unknown + pH 10 buffer + indicator</td>
<td>1 fast titration to determine the end point approximately; 2 slow titrations</td>
<td>Eriochrome Black T</td>
</tr>
<tr>
<td>Blank for Ca²⁺</td>
<td>x mL spike* + water + NaOH + indicator</td>
<td>2-3 practice titrations that will let you get used to the colors and determine the endpoint approximately; 2 slow titrations</td>
<td>Hydroxynaphthol Blue</td>
</tr>
<tr>
<td>Unknown Ca²⁺</td>
<td>x mL spike + water + 1 mL undiluted unknown + NaOH + indicator</td>
<td>1 fast titration to determine the end point approximately; 2 slow titrations</td>
<td>Hydroxynaphthol Blue</td>
</tr>
</tbody>
</table>

**VII. What to Submit in Your Report**

As usual, turn in your prelab at the beginning, and your duplicate copies of all the notebook pages at the end of the laboratory session. Remember: your lab will count for nothing if your lab notebook pages are not submitted or contain meaningless information. Be sure to
include your name and student number, the project title, and the code of the unknown on the title page.

Use your data to calculate and report the concentrations of Ca\(^{2+}\) and Mg\(^{2+}\) in your “sea water” sample in your write up. Report your results in units of mol/L in your original (not diluted!) unknown solution. Do not forget to take into account the fact that the unknown was diluted to different extents in determining total Ca\(^{2+}\) and Mg\(^{2+}\) and in determining Ca\(^{2+}\) alone. Refer to the discussion notes for the calculation approach.

Calculate and report the standard deviation for both concentrations using techniques for propagating the errors. For simplicity, assume that the only sources of uncertainties are:

- EDTA solution volume needed to the titration of both ions in the unknown
- EDTA solution volume needed to the titration of both ions in the blank
- EDTA solution volume needed for titration of Ca\(^{2+}\) in the unknown
- EDTA solution volume needed for titration of Ca\(^{2+}\) in the blank

You will have 2-3 measurements for each of these volumes; enough to estimate your standard deviations. You may neglect uncertainties associated with preparation of the standard EDTA solution, dilution of the unknown, and pipetting the diluted unknown. At this stage of your undergraduate career, you should be able to do these procedures without mistakes.