

Experiment 6: EDTA Determination of Total Water Hardness

Purpose:

Determine the hardness in an unknown laboratory and tap water samples.

THEORY:

Harris, D. C. (2003); “Quantitative Chemical Analysis 6th ed.”; pp. 259-267, 272-277.

Water hardness is an expression for the sum of the calcium and magnesium cation concentration in a water sample. These cations form insoluble salts with soap, decreasing soap's cleaning effectiveness. They also form hard water deposits in hot water heaters. The standard way to express water hardness is in ppm CaCO_3 which has the formula weight of 100.1 g/mole.

An excellent way to determine water hardness is to perform a complexometric titration using a standard ethylenediaminetetraacetic acid (EDTA) solution. Due to steric hindrances, EDTA will complex with calcium and magnesium in a **one-to-one** molar ratio. The endpoint in this experiment will be determined using a calmagite indicator. The indicator imparts a red color to the solution while there are calcium and magnesium ions that have not complexed with EDTA. Once the endpoint has been reached and there is no more uncomplexed Ca or Mg, the indicator will give a blue color. **No hint of red color will be left.**

This lab will be graded primarily on the accuracy of your individual results. Due to the fact that you will be using the EDTA as a primary standard, it is important that you be extremely careful in your weighing procedure. Any mistakes will carry through the entire experiment and greatly affect the accuracy of your results. Careful titrations will give you high precision and accuracy.

PRELAB EXERCISE (2 pts/each):

1. Why it is important to estimate the hardness of the potable water?
2. What is the primary standard used?
3. What kind of reaction takes place between the magnesium and the EDTA?
4. At what pH condition is the titration performed? Why?
5. What indicator is used in the analysis? What is its color change?

PROCEDURE

1. The EDTA Solution.

You will be using the disodium salt of EDTA (M.W. = 372.24 g/mole). It has been dried for 1 week at 80°C to drive off any superficial moisture. It is in the TA desiccator. Be sure to return it to the desiccator when you are through with it. Weigh carefully about **0.9 g of EDTA** (record to the nearest 0.1 mg). Quantitatively transfer this into a 250 mL volumetric flask then add **2-3 mL of pH 10 ammonia buffer**. Fill the flask about halfway to the mark with **deionized water** and swirl to dissolve. This process can take up to 15 minutes. Once dissolved, dilute to the mark and then cap and invert the flask at least 6 times to get a uniform solution. Keep the solution capped.

2. The Unknown.

Your TA will prepare your unknown solution in a 100 mL volumetric flask. **You must turn in this flask to the TA 1 week prior to performing this laboratory.** Obtain your flask and dilute it to mark with **deionized water**.

3. The Blank and Titration Procedure.

In order to correct for any error attributable to the deionized water and the indicator color transition, you will be analyzing a blank solution. The volume of EDTA used to titrate the blank will be subtracted from all other titration volumes.

Pipette a 10.00 mL sample of deionized water into a clean 250 mL Erlenmeyer flask. Add about 1mL of ammonia buffer, using a 10mL graduated cylinder. At this point heat the flask on the hot plate until condensation forms on the inside rim of the flask. Immediately add a few drops of indicator. If the solution turns blue, there is no measurable calcium or magnesium in solution and you will not have a blank correction. If the solution stays red or violet, immediately start titrating with the EDTA solution. Titrate until there is no trace of red or violet in your solution. Be sure to go dropwise as you approach the endpoint. The kinetics of the indicator reaction are slow; heating aids in speeding up the transition from red to blue. However, it is necessary to titrate slowly as you approach the endpoint so that it is not overshoot.

The color change upon reaching the endpoint for this titration is subtle. Two pieces of advice will help improve your results. First, ask a TA or the instructor to inspect your solution near the endpoint of your first titration to be sure you really are at the endpoint. Second, try to reach the same color for each titration of your unknowns and standards. This consistency in technique will improve the precision of your measurements.

4. Titrating the Unknown.

Repeat the above procedure, substituting 10.00 mL portions of your unknown sample, in place of the 10.00 mL deionized water sample. Repeat the unknown titration between 3 and 6 times depending upon time constraints. Typically, the more titrations you perform, the better the results.

5. Common Tap Water

Pipette 50.00 mL of common tap water into a 250 mL Erlenmeyer flask. Titrate as above. It is only necessary to perform one trial.

NOTE: This sample can exhibit less prominent change in color.

Calculations:

If you are not sure how to do any of the individual steps in these calculations, see one of your instructors for help. Errors in calculation can lead to significantly inaccurate final answers, and poor grades on accuracy.

1. Calculate molar concentration of EDTA.
2. For each titration, start by calculating the net volume of titrant used. Then subtract the volume of titrant used in the blank titration. Call this the corrected net volume.

3. Use the corrected net volume of titrant to determine the number of moles of EDTA used in the titration (volume x conc.).
4. Use the stoichiometry of the titration reaction to calculate moles of Ca in this titration.
5. Next, calculate the molar concentration of the unknown by dividing the molar mass of Ca by the volume of the test solution that you started with (the volume of unknown used in the titration).
6. Finally, convert the mole Ca / L concentration to ppm CaCO₃.
 - a. Express (mole Ca / L) as (mole CaCO₃ / L) using the 1:1 ratio (1 Ca per CaCO₃)
 - b. Convert (mole CaCO₃ / L) to (g CaCO₃ / L) using the molar mass of CaCO₃.
 - c. Convert (g CaCO₃ / L) to (mg CaCO₃ / L) using a metric system conversion.
 - d. (mg CaCO₃ / L) is the same as ppm CaCO₃ for dilute aqueous solutions.

Comparative KUB data

The Knoxville Utilities Board tests our water supply for both Magnesium and Calcium. The paragraph below includes their data from 2003 (obtained by e-mail communication). KUB calculates water hardness two ways (which give equivalent results):

1. By separate measurements of the individual ions (probably using atomic spectroscopy), then adding the results together to get total water hardness.
2. By an EDTA titration (Method 2340C, Standard Methods for the Analysis of Water and Wastewater, 20th Ed.)

For a six month period in 2003, the average hardness for KUB tap water was 95 mg/L, expressed as CaCO₃, with a range from 78 to 108 mg/L. Note that measurements at individual water outlets may vary significantly from KUB results measured at the water plant, due to hard water deposits in pipes, and different degrees of "water standing in the pipes."

LAB REPORT (on regular paper, portions may be submitted as spreadsheet printouts).

1. Name, date, and unknown #
2. Complete sample calculation, with correct units and significant figures.
 - Show calculation of [EDTA]
 - Show calculation of [Ca] in unknown sample in mole/L
 - Show calculation of [Ca] in unknown sample in ppm CaCO₃
 - Show calculation of 95% confidence interval.
3. Result for common tap water (ppm CaCO₃)
4. Result for unknown sample (ppm CaCO₃)
 - report each individual value and average value
5. Standard deviation and %RSD for replicate analyses of unknown
6. 95% confidence interval for unknown concentration
7. Chemical reaction for the titration
8. Submit a one page discussion of your results. It should include among other, comments an analysis of the standard deviations, mean results, possible sources of error and how they can be corrected.
9. Answers to Discussion Questions

Discussion Questions

1. If a student has a non-zero blank correction, but forgets to include that correction in his/her calculations:
 - a. Would his/her calculated [EDTA] be correct, too high, or too low?
 - b. Would his/her calculated [Ca] in the unknown be correct, too high, or too low?
 - c. Explain your answers briefly.
2. Locate some background information on the sources and effects of hard water. A web search with the phrase "hard water" or "water softening" will give you a start. One useful site is: <http://ianrpubs.unl.edu/water/g1274.htm>
 - a. Where does hard water come from?
 - b. What health problems does hard water cause?
 - c. What other problems does hard water cause?
 - d. What is the most common way to soften hard water (i.e. how does a commercial water softener work?)
 - e. Is Knoxville water (see KUB data above) hard or soft?
3. How does your data for tap water compare to KUB's values? Be careful with units! Can you think of any reasons why your data might not agree with KUB's?
4. Consider the possibility that the EDTA used in this experiment was not as dry as it should have been.
 - a. What would the effect be on the [EDTA] in the EDTA solution?
 - b. What would the effect be on the determined [Ca] in the unknown?