Supplementary Material 9 - Determination Of Water Hardness

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I. Objective

By leveraging the strong chelating ability of EDTA to determine the concentrations of Ca^{2+} and Mg^{2+} in water, we can assess water hardness. The same method can also be applied to measure the calcium and magnesium content in hard water.

II. Technique

Water hardness can be determined using a titration method.

III. Introduction

Water hardness testing is one of the key factors in evaluating the quality of general water supply systems. Water hardness is defined by the amount of calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}) present in the water. However, in analysis, Ca^{2+} and Mg^{2+} are not distinguished separately.

Since most hardness results from precipitated carbonates in soil, hardness is typically expressed as parts per million (ppm) in terms of calcium carbonate ($CaCO_3$). A water supply with a hardness of 1 ppm means that one million grams of water contain 1 gram of $CaCO_3$, or equivalently, that 1 liter of water contains 1 milligram of $CaCO_3$.1L H_2O

$$1\ \text{ppm}\ CaCO_3 = \frac{1\text{mg}\ CaCO_3}{1\text{L}\ H_2O} \quad (\text{S9-1})$$

In the past, the effects of hard water were more noticeable when washing clothes with soap or bathing in a tub. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions react with soap to form insoluble salts, which adhere to clothing or the bathtub surface and create

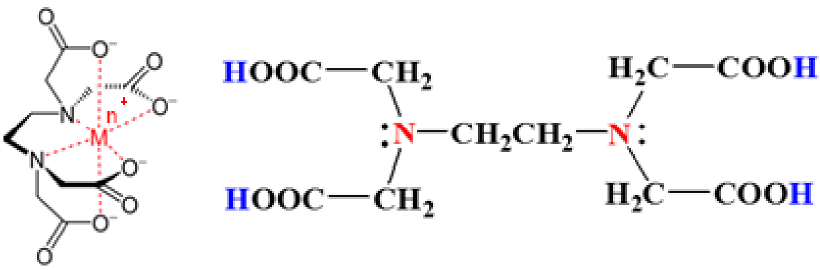

Figure 1. EDTA structure (Ethylenediaminetetraacetic acid) and its configuration under the hexacoordinate.

visible scum. One of the most significant advantages of detergents is that they are not affected by hard water, which is why detergents have largely replaced soap for laundry today.Water hardness can be determined by titration with EDTA (ethylenediaminetetraacetic acid, abbreviated as H_4Y). EDTA is a chelating agent and a weak acid that can release four hydrogen ions upon complete neutralization. Its structure is shown below:

Because the four acidic hydrogens can dissociate and both nitrogen atoms possess lone pairs of electrons, Y^{4-} can form complexes with central metal cations with coordination numbers of up to six. These complexes are highly stable, and the formation of metal EDTA complexes is typically controlled at a 1:1 molar ratio. Therefore, in the titration of a metal cation, the concentration of the metal ion can be determined from the amount of EDTA required to reach the endpoint of the reaction.

In this experiment, a standard Ca^{2+} solution is first prepared from calcium carbonate to standardize the EDTA solution. The standardized EDTA solution is then used to analyze unknown water samples. Since both EDTA and Ca^{2+} aqueous solutions are colorless, a wine-red calcium–magnesium indicator, Calmagite (denoted as H_3In), is used to detect the titration endpoint. This indicator forms a stable red complex with magnesium ions, $MgIn^-$.

If trace amounts of $MgIn^-$ are present in hard water, the initially added EDTA reacts first with free Ca^{2+} and Mg^{2+} ions. Once all Ca^{2+} and Mg^{2+} ions in the solution have formed chelates with EDTA, any additional EDTA will immediately dissociate $MgIn^-$ and chelate the Mg^{2+} ions. As a result, the indicator reverts to its blue color, indicating that the titration endpoint has been reached.

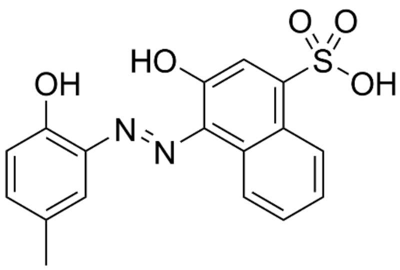

Figure 2. Molecular structure of the metal indicator Calmagite.

During the titration of hard water, an ammonia buffer solution (NH_3–NH_4^+) is used to maintain the solution at pH 10. Under these conditions, EDTA predominantly exists in the form of HY^{3-}. In this form, it forms stable complexes mainly with Group 2 metal ions and does not readily react with other ions commonly present in water, such as Fe^{3+}.

The titration reaction equation is as follows:

Main reaction formula

$$HY^{3-}(aq) + Ca^{2+}(aq) \rightleftharpoons CaY^{2-}(aq) + H^{+}(aq) \quad (S9\text{-}2)$$
$$HY^{3-}(aq) + Mg^{2+}(aq) \rightleftharpoons MgY^{2-}(aq) + H^{+}(aq) \quad (S9\text{-}3)$$

Titration endpoint

$$HY^{3-}(aq) + MgIn^{-}(aq) \rightleftharpoons MgY^{2-}(aq) + HIn^{2-}(aq) \quad (S9\text{-}4)$$

Burgundy Sky blue

IV. Equipment

- 50 mL burette, 100 mL volumetric flask, 100 mL beaker, stirrer
- magnetic stir bar, 250 mL Erlenmeyer flask, 125 mL Erlenmeyer flask
- funnel, butterfly clamp, watch glass, ring stand, ring stand

V. Chemicals

- Calcium carbonate ($CaCO_3$)
- ethylenediaminetetraacetic acid (EDTA)
- NH_3/NH_4^+ buffer solution (pH 10.0)
- 6.0 M hydrochloric acid solution
- 0.1% Calmagite
- tap water

VI. Procedure

1. Standardization of EDTA solution

1. Weigh 0.040 g $CaCO_3$ into a 100 mL beaker, add 25.0 mL DI water, then slowly add ~10 drops of 6.0 M HCl. Cover with a watch glass and allow the solid to fully dissolve.

2. Rinse the beaker walls with DI water using a dropper, then heat until just before boiling, noting CO_2 evolution.

Caution: *CO_2 evolution*

3. After adding another 50.0 mL of deionized water, carefully pour the solution into a 100 mL volumetric flask.

4. Then add a small amount of deionized water multiple times to the graduation mark of the volumetric flask.

5. Stopper the volumetric flask and invert to mix for at least five minutes.

6. Rinse the burette with EDTA and fill with 15.0 mL EDTA.

7. Pipette 5.0 mL Ca^{2+} solution, add 6.0 mL pH 10 buffer and 2 drops Calmagite which will turn the solution wine-red/lilac.

8. Titrate with EDTA until the solution turns clearly blue; record EDTA volume.

9. Repeat steps 7 and 8 twice.

10. The data from the three titrations are averaged to determine the concentration of EDTA.

2. **Use calibrated EDTA to titrate general tap water**

1. Take 5.0 mL of tap water, add 6.0 mL of pH = 10.0 buffer solution, 2 drops of Calmagite indicator, and appear red.

2. The solution from step 1 is titrated with EDTA, and the volume of EDTA consumed is recorded.

3. Repeat steps 1 and 2 twice to determine the hardness of tap water.

VII. Precautions

1. Because the EDTA endpoint blue is hard to judge, all titrations should reach similar color to minimize error, and a photo of results must be included in the report.

2. Over-titration causes the blue color to revert to lilac, so observe color changes carefully.

3. Always wear a lab coat, goggles, and gloves during the lab session.

4. Handle all chemicals with care, as they may be toxic or hazardous. Follow all laboratory safety regulations and the instructions of the TAs at all times.

5. Removal of any chemicals or laboratory equipment from the lab is strictly prohibited.

Supplementary Material 9 - Determination of Water Hardness

Name: ____________ **Student ID: __________________________**

Department: _______ **Group: __________** **Date: ___________**

I. Experimental Data and Results

(1) Weight of the beaker ____________________________

(2) Weight of the beaker plus calcium carbonate __________

(3) Weight of calcium carbonate________________________

(4) Number of moles of calcium carbonate _______________

(5) Volume of the calcium ion solution _________________

(6) Concentration of calcium ions ______________________

(7) Number of moles of calcium ions in each titration __________

Standardization of EDTA Solution

Trial	1	2	3
(1) Initial burette reading			
(2) Final burette reading			
(3) Volume of EDTA used			
(4) Average volume of EDTA required to titrate calcium ions			
(5) Concentration of EDTA			

Determination of Hard Water

(1) Volume of water sample__________________________

(2) Initial burette reading ___________________________

(3) Final burette reading ____________________________

(4) Volume Average volume of EDTA required to titrate 1 L of water

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(5) Number of moles of EDTA in 1 L of water ___________

= Number of moles of calcium carbonate in 1 L of water

(6) Mass of calcium carbonate in 1 L of water _______________

(7) Water hardness (1 ppm = 1 mg/L), expressed as ppm $CaCO_3$

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(8) of EDTA used

II. Question and Discussion

1. Dissolve 0.5566 g of magnesium carbonate in 6 M HCl and dilute to 500 mL with water.

   a. How many moles of magnesium carbonate are present in the sample?

   b. What is the concentration of magnesium ions?

   c. How many moles of magnesium ions are present?

2. Take 45 mL of the solution from Question 1 and titrate it with EDTA. The endpoint is reached after using 55.6 mL of EDTA.

   a. How many moles of EDTA were used in the titration?

   b. What is the concentration of the EDTA solution?

3. A 250 mL sample of hard water is titrated with the EDTA solution from Question 2. The endpoint is reached after using 32.1 mL of EDTA.

   a. How many moles of EDTA were used in the titration?

   b. How many moles of magnesium ions are present in the water sample?

   c. If the magnesium ions originate from magnesium carbonate, how many moles of magnesium carbonate are present in 1 L of hard water?

   d. If 1 ppm magnesium carbonate = 1 mg/L, what is the hardness of the water in ppm as magnesium carbonate?

4. According to the standards published by the World Health Organization (WHO), what are the criteria for classifying water as hard or soft? Based on the experimental results, how would the tested tap water be classif