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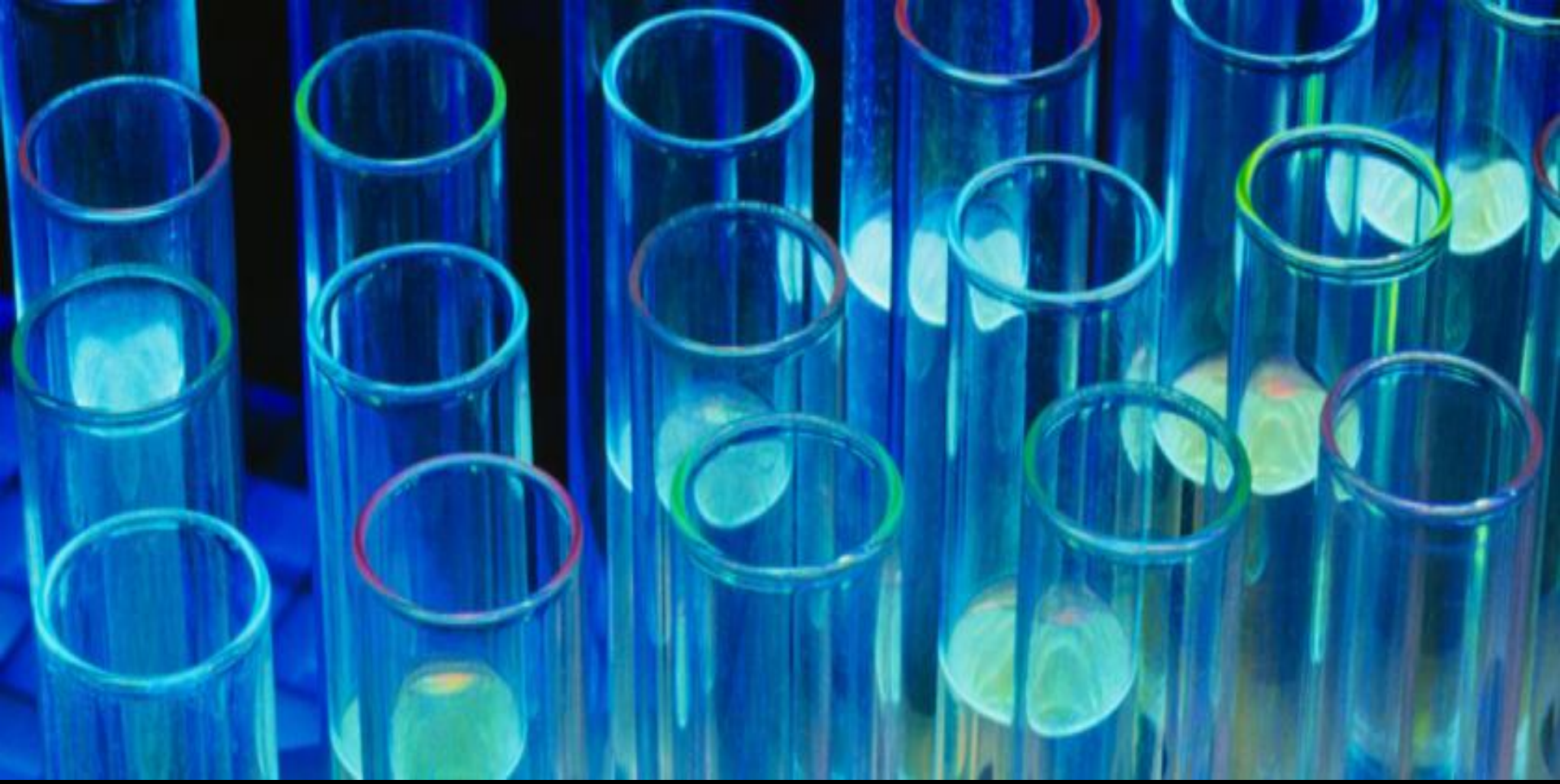
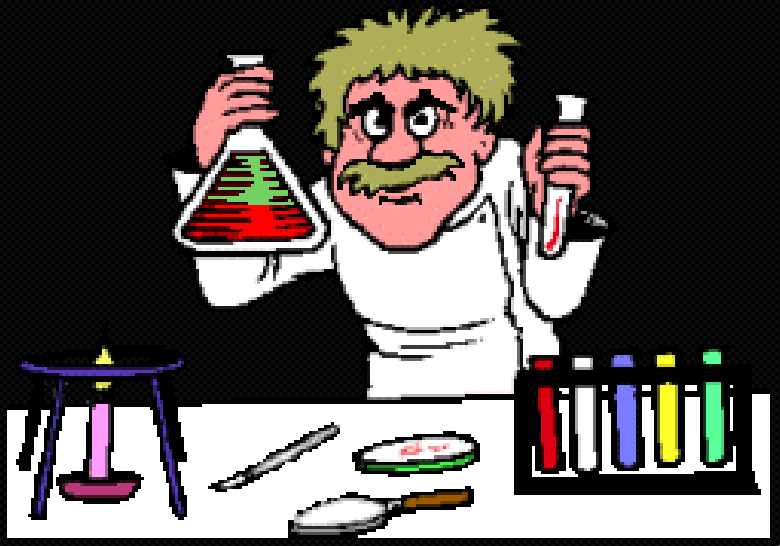


114-2
Supplementary Material 9 : Determination of Water Hardness

115.03.22 ~ 115.03.28 (time required: 1 hour)

1. Objective

- The primary goal of this study is to understand and determine water hardness by measuring the total concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in a water sample.



2. Principle

- Water hardness is defined as the amount of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in the water.
- It is typically expressed as parts per million (ppm) of calcium carbonate ($CaCO_3$), where 100 ppm represents 100 mg of $CaCO_3$ per liter of water (0.1 g/L).
- **100 ppm = 100 mg / L = 0.1 g / L**

EDTA

- Water hardness is determined via EDTA titration.
- EDTA (H_4Y) is slightly acidic and acts as a hexadentate ligand, using four carboxyl groups and two nitrogen lone pairs to form stable 1:1 complexes with metal cations.

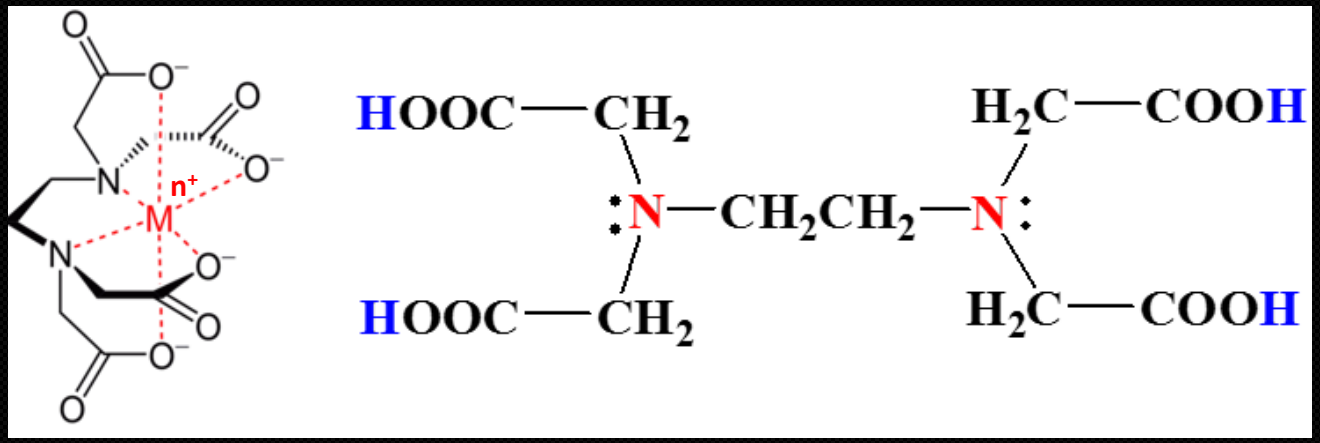


Figure 1. Chemical structure of **E**thylene**d**iamine**t**etra**a**cetic acid (EDTA) and its hexadentate coordination geometry with a metal cation (M^{n+}).

Indicator Mechanism of Titration

- Calmagite (H_3In) is used as the indicator. At pH 10, it forms a burgundy complex with Mg^{2+}.
- As EDTA is added, it displaces the indicator from the metal. At the endpoint, the free indicator turns the solution sky blue.

$$EDTA\ (H_4Y) \longrightarrow HY^{3-} + 3H^{+} \quad (at\ pH = 10)$$

$$HY^{3-} + Ca^{2+} \longrightarrow CaY^{2-} + H^{+}$$

- Titration endpoint (at pH = 10):

$$\underset{\text{Burgundy}}{HY^{3-} + MgIn^{-}} \longrightarrow \underset{\text{Sky blue}}{MgY^{2-} + HIn^{2-}}$$

3. Equipment and Chemicals

Equipment

In cabinet	Provided by TA
Beaker (100 mL) x 2	Plastic Dropper x 1
Hot plate stirrer x 1	Burette Clamp
Iron stand	Burette (50 mL) x 1
Watch glass	
Stir bar x 1	
Volumetric flask (100 mL) x 1	
Erlenmeyer flask (125 mL) x 4	
Erlenmeyer flask (250 mL) x 2	

Chemicals

6.0 M Hydrochloric acid (HCl) ✱✱✱	Ethylenediaminetetraacetic acid (EDTA) ✱✱
0.1 % Calmagite ✱✱	Calcium Carbonate ($CaCO_3$) ✱
pH = 10.0 NH_3/NH_4^+ Buffer solution ✱✱✱	

✱ : Corrosive ✱ : Toxic ✱ : Irritant

References：https://pubchem.ncbi.nlm.nih.gov/_Extract day:2026.02.05

4. Experimental Procedures

Step 1 : Preparation and Standardization of the Primary Standard ($CaCO_3$)

1. Initial Dissolution
   - **Weighing:** Accurately weigh 0.040 g of $CaCO_3$ into a 100 mL beaker.
   - **Solubilizing:** Add 25.0 mL of deionized (DI) water to the beaker.
   - **Acidification:** Slowly add approximately 10 drops of 6.0 M HCl.
   - **Reaction Control:** Cover the beaker with a watch glass and allow the solid to dissolve completely.

4. Experimental Procedures

2. Removal of Carbon Dioxide
   - **Rinsing:** Use a dropper and DI water to rinse any splashes from the beaker walls.
   - **Heating:** Heat the solution until it is just before boiling.
   - **Degassing:** Observe the evolution of CO_2 bubbles and continue heating until the gas is expelled.
   - **Cooling:** Remove from heat and allow the solution to reach room temperature.

4. Experimental Procedures

3. Quantitative Transfer and Dilution
   - **Transfer:** Add 50.0 mL of DI water to the cooled solution, then carefully pour the entire contents into a 100 mL volumetric flask.
   - **Bringing to Volume:** Add small increments of DI water multiple times to reach the horizontal graduation line (meniscus) of the flask
   - **Homogenization:** Secure the stopper (plug) on the flask and shake or invert for at least five minutes to ensure the solution is completely uniform.

4. Experimental Procedures

4. EDTA Calibration (Titration)
   - **Preparation:** Rinse the burette with 15 mL EDTA and fill it to the starting mark.
   - **Aliquot:** Pipette exactly 5.0 mL of the prepared Ca^{2+} solution into a 125 mL or 250 mL Erlenmeyer flask.
   - **Conditioning:** Add 6.0 mL of pH 10.0 buffer and 2 drops of Calmagite indicator.
   - **Titration:** Titrate with EDTA until the solution changes from burgundy/lilac to clear sky blue.
   - **Replication:** Repeat the titration twice more and average the results to calculate the final molarity of the EDTA.

① 0.040 g $CaCO_3$
② 25.0 mL DI water
③ 10 drops 6.0M $HCl_{(aq)}$

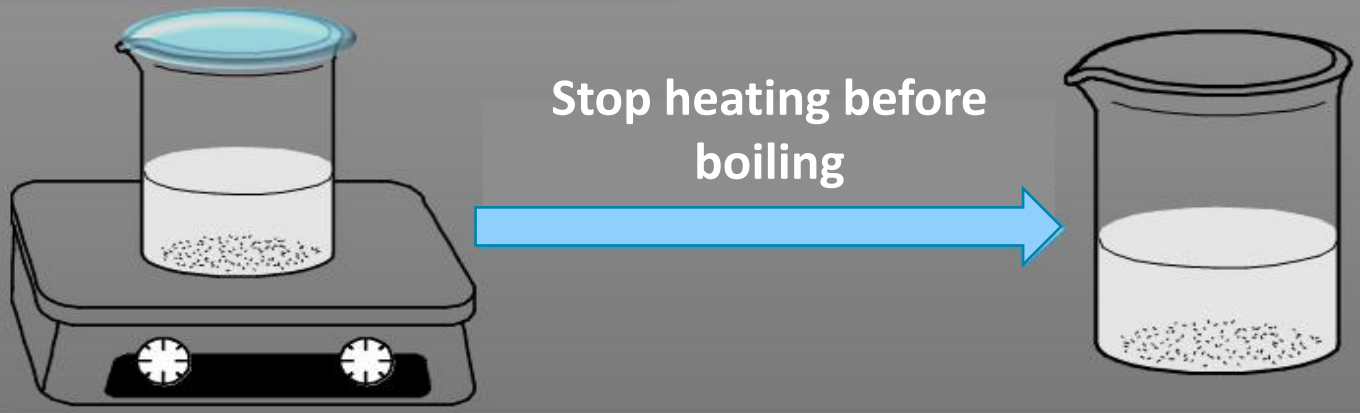


Figure 2. Explanation of Steps 1-1 ~ 1-2.

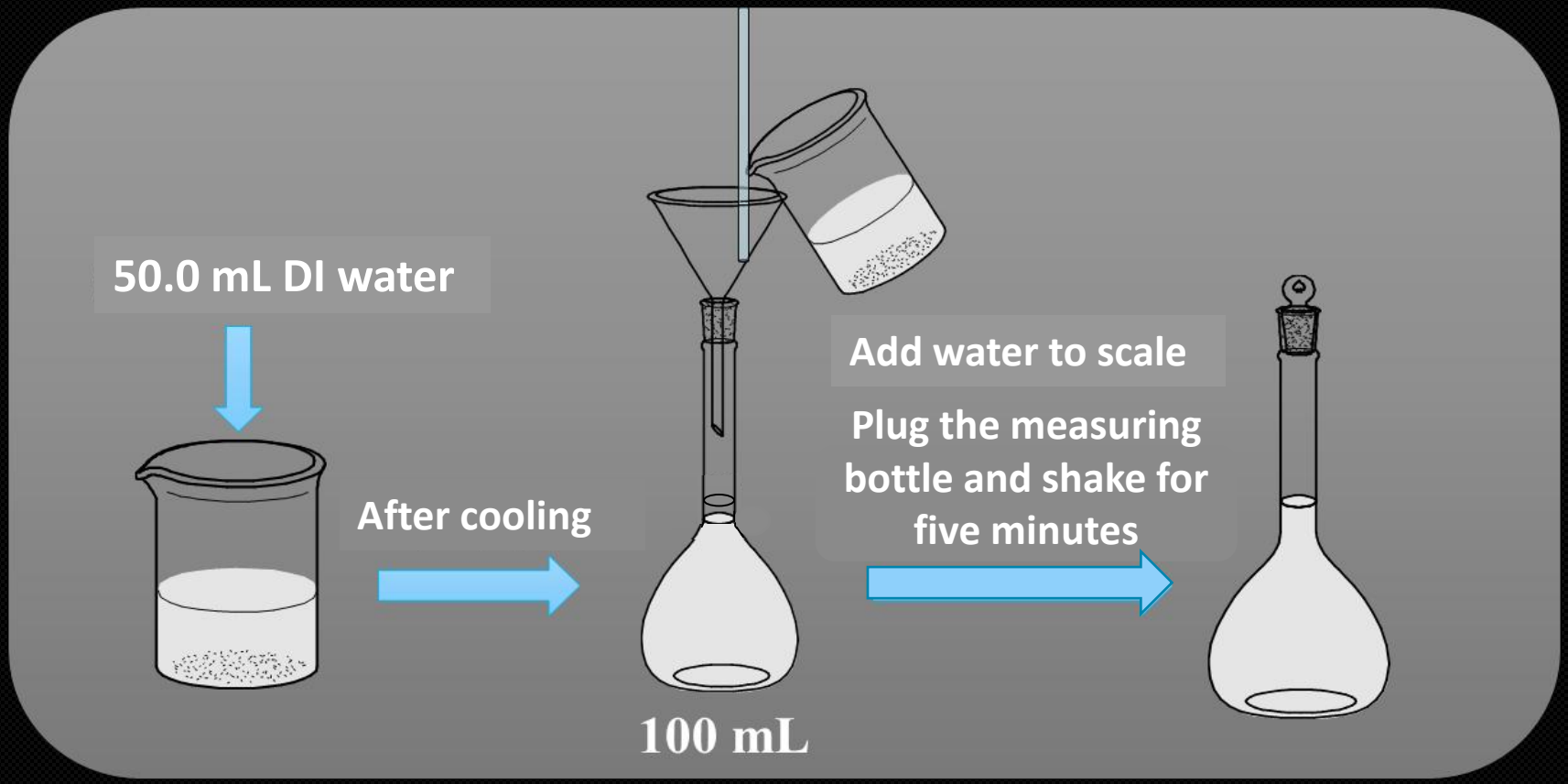
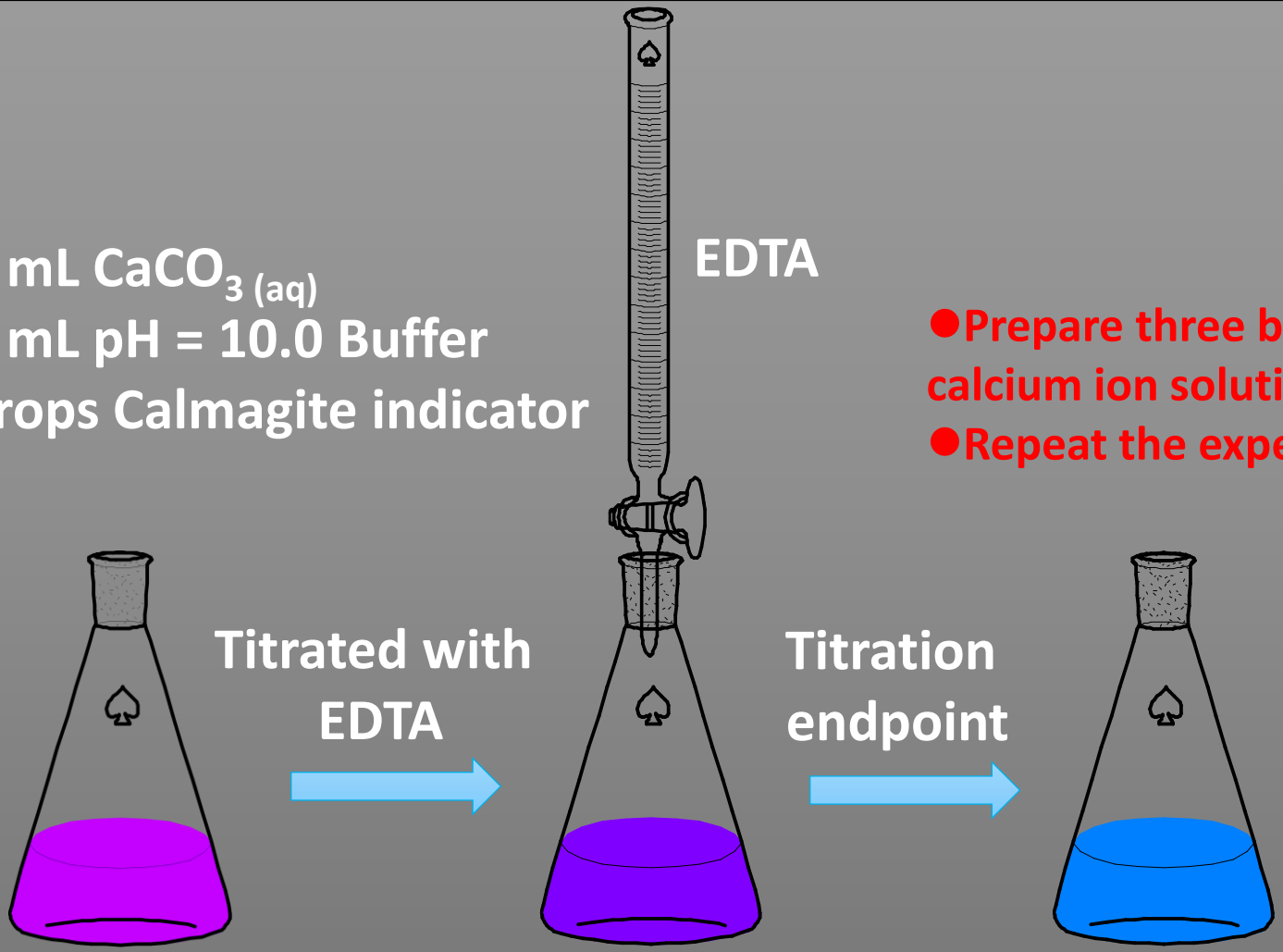


Figure 3. Explanation of Steps 1-3.

Calibrate EDTA

① 5.0 mL $CaCO_{3\,(aq)}$
② 6.0 mL pH = 10.0 Buffer
③ 2 drops Calmagite indicator



- Prepare three bottles of calcium ion solution
- Repeat the experiment

Figure 4. step 1-4 EDTA calibration diagram.

Step 2 : Determination of Tap Water Hardness

Using the calibrated EDTA to measure local Tap water samples.

1. **Preparation:** Take 5.0 mL of tap water, add 6.0 mL of pH 10 buffer, and 2 drops of Calmagite indicator.
2. **Titration:** Titrate with the standardized EDTA solution and record the volume consumed at the blue endpoint.
3. **Replication:** Repeat the titration twice more (three times total) to calculate the average water hardness in ppm.

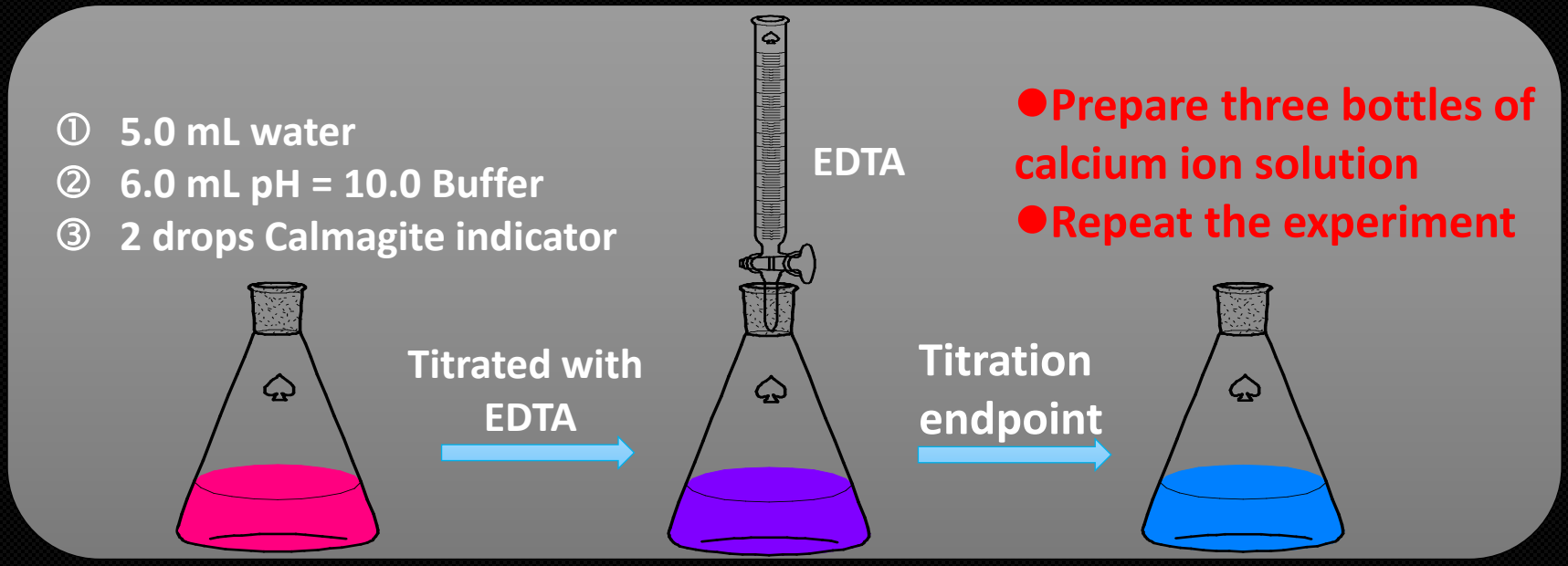


Figure 5. step 2 explanation diagram.

5. Titration Processes - I

$CaCO_3$ is standardized using EDTA.

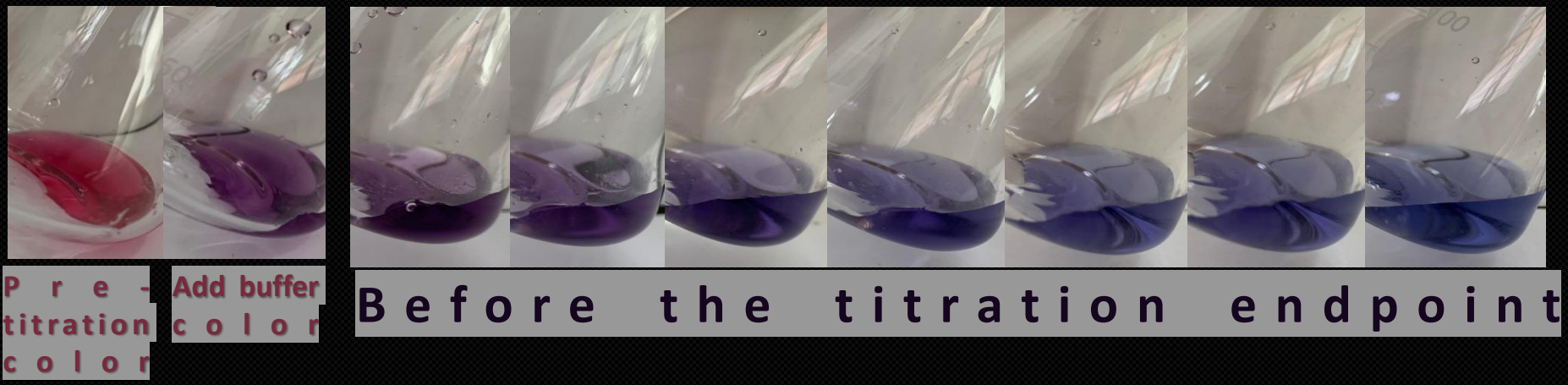


Figure 6. Color Change During Titration Process.

Figure 7. Titration endpoint color and titration excess color change.

5. Titration Processes - II
water hardness

Figure 8. Color change before and after titration.

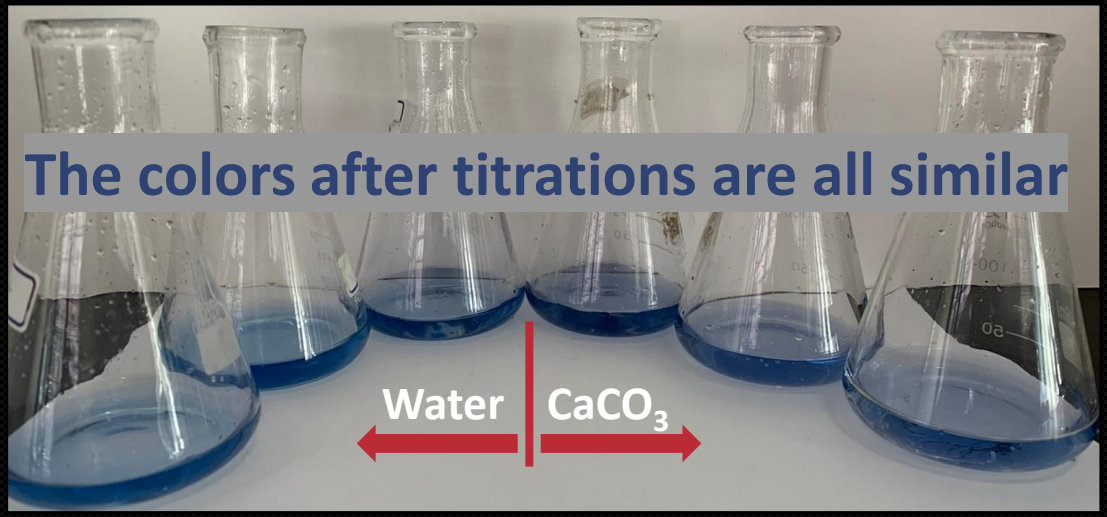


Figure 9. Titration end point color.

6. Safety and Precautions (1/2)

1. **Safety:** Standard PPE (lab coat, goggles, and gloves) is mandatory at all times.
2. **Chemical Handling:** 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.
3. **Prohibited Actions:** Removal of any chemicals or laboratory equipment from the lab is strictly prohibited.
4. **Endpoint Judgment:** The EDTA endpoint blue is difficult to judge; ensure all titrations reach a similar shade to minimize error.

6. Safety and Precautions (2/2)

5. **pH Importance:** Titration must occur at pH 10 because EDTA binds Ca^{2+} more effectively at high pH, and Calmagite becomes protonated at lower pH, interfering with the color change.
6. **Solubility Risks:** If the pH is too high, Mg^{2+} reacts with OH^- to form $Mg(OH)_2$ precipitate, leading to an underestimation of water hardness.

7. Experimental Data

- **Calcium carbonate is calibrated with EDTA**

1. Weight of calcium carbonate：
2. Calcium carbonate (calcium ion) mole ：
3. Calcium ion concentration：
4. The number of moles of the calcium ions contained in each titration：
5. Volume of EDTA：
6. Concentration of EDTA：

• The hardness of water is determined

1. Volume of water：
2. Volume of EDTA：
3. The volume of EDTA required to titrate 1 liter of water：
4. The number of moles of EDTA required to titrate 1 liter of water equals the number of moles of calcium ions present in 1 liter of water：
5. The mass of calcium contained in 1 liter of water：
6. The hardness of water （1 ppm = 1 mg/L）：

The water hardness in the Minxiong Township area of Chiayi County: 207 ppm
Reference: https://data.gov.tw/dataset/36605 (Extract day:2026/02/03)

8. Questions

1. Dissolve 0.557 g of magnesium carbonate in 6.0 M HCl(aq) and dilute to 500 mL.

a. Moles of $MgCO_3$ in the sample?

b. Mg^{2+} concentration?

c. Moles of Mg^{2+}?

2. In this experiment, water hardness is the sum of calcium and magnesium ions.

a. How can Ca^{2+} and Mg^{2+} be measured separately?

b. Can this be done using the indicator from this experiment?

3. In Step 7, why is a pH 10.0 buffer solution added? Why must the titration of calcium ions be carried out under this pH condition?

4. If the titration solution's pH is too high, Mg^{2+} reacts with OH^- to form $Mg(OH)_2$ precipitate. According to solubility equilibrium, this decreases the free Mg^{2+} in solution, so less magnesium is detected during titration, leading to an underestimation of water hardness.

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