Gravimetric Determination of Calcium as Calcium Oxalate Monohydrate

Introduction: Calcium ion can be analyzed by precipitation with oxalate in basic solution to form CaC_2O_4•H_2O. The precipitate is soluble in acidic solution because the oxalate anion is a weak base. Large, easily filtered, relatively pure crystals of product will be obtained if the precipitation is carried out slowly. This can be done by dissolving Ca^{2+} and C_2O_4^{2-} in acidic solution and gradually raising the pH by thermal decomposition of urea.

Before you come to class:

• Record the molar mass of calcium oxalate monohydrate CaC_2O_4•H_2O.
• Record the molar mass of calcium oxide, CaO.
• Write each of the three reactions (see procedure) in your lab notebook.
• Record the acid-base indicator that will be used in this experiment as well as the pH transition range and the color change that occurs at that pH (see p. 186 in your book).
• List all of the reagents (formulas and names) in your notebook. Familiarity with the reagents will help you avoid costly mistakes during the experiment.

Reagents: ammonium oxalate solution, (NH_4)_2C_2O_4
0.1 M HCl
methyl red indicator
urea
Calcium carbonate unknown

Perform the analysis in duplicate. All data, reactions, and calculations should be recorded directly into your lab notebook.

1. Record the number of your unknown in your lab notebook. Transfer unknown to weighing bottle. You may label your weighing bottle with your initials and its contents using a Sharpie (this can be removed later using methanol or acetone). Put the bottle and its lid (apart) into a 250 mL beaker and place a small ribbed watch glass on top. Using a Sharpie, label the beaker with your initials and place it in the oven for one hour. (The oven is set at 120+ °C.) Move on to step 2 while you wait. After an hour, put the weighing bottle and lid into a dessicator immediately after removing from oven, in order to keep it dry as it cools. Once it is cool you may put the lid on the bottle.

2. Put your water bottle into the ice bath so you’ll have cold water for step 10.

3. Write your initials in Sharpie on two medium-porosity, sintered-glass funnels. Place them in a large beaker, covered with a large watch glass. Place the beaker in the oven to dry for 1 hour at 110+ °C; cool them in a desiccator for 15 minutes and weigh them. Put back in the oven for 15 minutes, cool and weigh. Repeat the procedure with 15-minute heating periods until successive weighings of the same funnel agree to within ±0.0003 g. Use the last weight of each funnel for all future calculations.

4. Accurately weigh out approximately 0.35-0.38 g of your CaCO_3 unknown into a 400 mL beaker. Do this and all subsequent steps in duplicate.

5. Dissolve the unknown in a minimal amount of 0.1 M HCl, avoiding splattering. Start with about 50 mL. All of the calcium unknown should dissolve with effervescence. If necessary, add 10-20 mL of 0.1 M HCl to complete the dissolution of the calcium carbonate. Some samples may have a trace of fine insoluble silica (sand) that appears transparent upon close observation.
**Reaction #1:** Write the balanced reaction between CaO and HCl to produce Ca\(^{2+}\), Cl\(^-\) and H\(_2\)O in your lab notebook. What products remain dissolved in solution? The resulting solution is acidic, due to an excess of HCl.

6. After dissolution, add enough distilled water so that you have a total solution volume of approximately 100 mL.
7. Add 5 drops of methyl red indicator to each beaker.
8. Add 25 mL of the ammonium oxalate solution to each sample while stirring with a glass rod. Add 15 g of solid urea to each sample, cover with a watch glass, and boil gently for approximately 30 minutes or until the indicator turns yellow (the yellow color may be hard to see but the pink color will have disappeared.)

**Reaction #2:** The balanced reaction of the thermal decomposition of urea is:

\[
(H_2N)_2CO + 3 H_2O \underrightarrow{\text{heat}} CO_2 + 2 NH_4^+ + 2 OH^-
\]

**Reaction #3:** The balanced reaction of the precipitation of calcium oxalate monohydrate is:

\[
Ca^{2+} + C_2O_4^{2-} + H_2O \underrightarrow{} CaC_2O_4\cdot H_2O
\]

9. When both of your filters meet the criteria in step 3, you are ready to hot filter your solutions. Until this time, leave the solutions on the hot plate. Keep an eye on them so they do not boil dry.
10. Filter each hot solution through a weighed funnel at the vacuum station (be sure to empty the filtrate in the filter flask before it overflows into the vacuum system.) Rinse each beaker with a few mL of cold distilled water. Make sure that you quantitatively transfer every bit of precipitate into the funnel (any losses will be reflected in the accuracy of your result.). Draw air through the precipitate for about 1 minute.
11. Carefully place both funnels into a 400 mL beaker and cover with a large watch glass. Initial the beaker and put it in the oven at 105°C for at least two hours (you may wish to dry the sample overnight.)
12. After obtaining your final weights, clean out the precipitate and put your filter crucibles in the acid soak in the hood so that they will be available for the next laboratory section.

Report the result in terms of the percentage of calcium oxide %CaO in your unknown to the correct number of significant figures. The range on unknown values should be between 35% to 60%.

**SAVE YOUR UNKNOWN FOR A FUTURE EXPERIMENT.** Keep your capped weighing bottle in your drawer. Make sure it has the contents and your initials written on it in Sharpie.