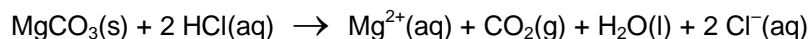
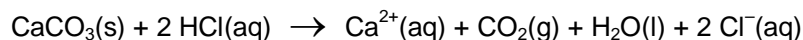


# ANALYSIS OF LIMESTONE

## INTRODUCTION

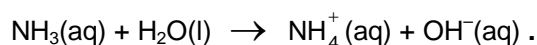
Limestone is usually described as rock made from calcium carbonate,  $\text{CaCO}_3$ , but in fact most limestone rock contains significant amounts of magnesium, silicates, manganese, iron, titanium, aluminum, sodium, potassium, sulphur (as sulphides or sulphates) and phosphorus. In this experiment, you will analyze a sample of limestone to find how much calcium it contains.

The reactions you will carry out are as follows. First, the carbonates present are reacted with hydrochloric acid. This procedure releases the calcium and magnesium ions present into solution. Any manganese, iron, titanium, aluminum, sodium, potassium and phosphates present will also go into solution.

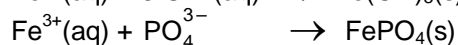
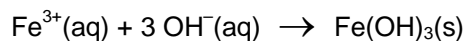


Some impurities, such as silicates, sulphides and sulphates, remain unreacted and do not go into solution.

Adding substantial amounts of both ammonia and ammonium ions to the solution creates a "buffer" solution which is slightly basic:

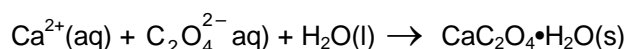


The resulting buffer solution does not contain sufficient concentrations of  $\text{OH}^{-}$  to precipitate the calcium, magnesium, sodium and potassium ions from solution. However, the concentration of  $\text{OH}^{-}$  is sufficient to precipitate all the iron, manganese, aluminum, titanium and phosphates from solution. For example:



Filtration at this point completes the removal of everything except the calcium, magnesium, sodium and potassium from the solution.

The solution containing the remaining ions is acidified with hydrochloric acid. The addition of oxalate ion, in the form of ammonium oxalate, prepares the solution to precipitate calcium oxalate. However, no precipitate forms because all oxalates are soluble in acidic solutions. By neutralizing the acid with ammonia the resulting solution becomes slightly basic and a precipitate of calcium oxalate monohydrate forms. Since magnesium, sodium and potassium oxalates are soluble in basic solutions, only calcium oxalate precipitates.



## PROCEDURE

**IMPORTANT:** Record all your observations as you work and record all data as required.

### DAY 1

1. Obtain a sample of limestone rock having a mass of about 2 g. Weigh the sample and **record its exact mass**. Place the limestone in a 250 mL beaker.

### Perform steps 2 and 3 in a fume hood.

2. Obtain 10 mL of 6 M hydrochloric acid (CARE: very corrosive!). Add the hydrochloric acid to the limestone and, using a hot plate which is pre-heated to medium-low heat, heat for 5 minutes or until the bubble-producing reaction ceases. CARE: If the mixture is almost dry before the bubbling stops, carefully add another 3 mL of 6 M hydrochloric acid to allow the reaction to go to completion.

**Get the following ready for step 3:**

- a) a single-flask vacuum filtration setup, and
- b) 50 mL of hot 2 %  $\text{NH}_4\text{Cl}$  solution (put this on your hot plate)

- Dilute the contents of the beaker to about 100 mL using distilled water. The remainder of this step can be performed at your bench.
  - Add about 5 g of ammonium chloride to the solution, then
  - heat the solution until it is nearly boiling, then
  - add 10 or 12 drops of methyl red indicator, then
  - add 7 M ammonia, with constant slow stirring, until the solution just turns pale yellow, then
  - boil for 2 minutes, then
  - filter the solution while still hot using a single-flask vacuum filtration apparatus, and finally
  - wash the precipitate with two 25 mL portions of hot 2 %  $\text{NH}_4\text{Cl}$  solutionSave the filtered solution in a 400 mL beaker for the next step and discard the precipitate. **Turn the hot plate up to high heat, in preparation for step 6.**
- Add another 10 drops of methyl red indicator and then add about 1 mL of 6 M hydrochloric acid to the solution. If the solution does not become pink, add another 1 mL of hydrochloric acid.
- Add 100 mL of 4% ammonium oxalate to the mixture in the beaker. Slowly add, with constant stirring, just enough 2 M ammonia solution (CAUTION: Check the concentration!) to turn the indicator's colour from pink to very pale yellow. When the indicator has turned yellow, add an extra 2 mL of 2 M ammonia solution to make the solution sufficiently basic. At this point, a precipitate should be present.
- Heat the mixture to  $90^\circ\text{C}$ , to clump the precipitate into larger particles. **CARE:** Keep a stirring rod in the beaker and stir frequently to avoid "bumping" of the mixture. The mixture can be filtered while still hot.
- Record the combined mass** of TWO filter papers. Then, set up a single-flask vacuum filtration apparatus, making sure to pre-wet the filter papers.
- Vacuum filter your solution through your pre-weighed filter papers. Wash every bit of the precipitate out of the beaker with three 50 mL portions of 0.1% ammonium oxalate solution.
- Label a 250 mL beaker with your name, using a grease pencil, and then **record the beaker's mass**. Carefully remove the filter papers from the filter funnel and place them in the beaker. If any of the precipitate remains on the funnel, scrape as much as possible of the solid into the beaker. Ideally, the precipitate and filter papers should be placed overnight in a drying oven at  $110^\circ\text{C}$  but if a drying oven is not available let the precipitate air-dry overnight. [CARE: Heating the precipitate above  $200^\circ\text{C}$  partially decomposes the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  to  $\text{CaC}_2\text{O}_4$  and extensive heating decomposes the oxalate to  $\text{CaCO}_3$ .]

## DAY 2

- Record the combined mass of the beaker, filter papers and dried precipitate.**

## CALCULATIONS AND ANALYSIS

- Calculate the mass of the dried precipitate,  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .
- Calculate the moles of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  you produced.
- Since each molecule of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  contains one atom of calcium, the moles of calcium contained in your sample of limestone equals the moles of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  produced. Use this fact to calculate the mass of calcium contained in your sample.
- Use the mass of calcium found in Calculation 3 and your mass of limestone to calculate the percentage of calcium present in your sample. This result is called the ACTUAL PERCENTAGE OF CALCIUM in your sample of limestone.
- Calculate the percentage composition of  $\text{CaCO}_3$ . The percentage of Ca found in your percentage composition is the THEORETICAL PERCENTAGE OF CALCIUM in pure limestone.
- Calculate the percentage purity of your limestone sample as follows.

$$\% \text{ purity} = \frac{\text{ACTUAL PERCENTAGE OF CALCIUM}}{\text{THEORETICAL PERCENTAGE OF CALCIUM}} \times 100\%$$