

Calcium Carbonate Content of Limestone

01

OBJECTIVE

Prepared by Paul C. Smithson, Berea College

Using chips of limestone rocks, students prepare a powdered sample of limestone, react it with an excess of HCl, and determine calcium carbonate content of the limestone by back-titration of the unreacted HCl. A practical application of limiting reactant problems and a new technique of volumetric analysis are demonstrated. The same experiment may be performed exactly as written with agricultural limestone, and without significant alteration by replacing the limestone sample with a 500 mg antacid tablet whose active ingredient is CaCO_3 .

A P P A R A T U S

| | |
|-----------------------------------|-----------------------------------|
| Balance | 50-mL and 10-mL volumetric pipets |
| Mortar and pestle | 250 mL Erlenmeyer flasks |
| Hot plate | Lab scoop or spatula |
| Buret, buret clamp and ring stand | |

APPARATUS AND CHEMICALS

C H E M I C A L S

Limestone chips (or agricultural lime, or 500-mg antacid tablets)
HCl, about 0.25 M (may need to standardize—consult instructor)
Standardized NaOH, about 0.1 M (from Experiment 18)
Phenolphthalein indicator solution

The chemistry of acids and bases, and details of acid-base titration analysis were covered in Experiment 18. You should also have your standardized NaOH saved from that lab.

DISCUSSION

Today we consider the chemistry of calcium carbonate, the main component of limestone rocks. Actually, limestone usually contains a mixture of calcium carbonate and magnesium carbonate, which is called dolomitic limestone. For today, however, we will ignore that fact and assume our limestone contains only calcium carbonate. This will introduce some error into our mass percent calculations, but the basic principles of the analysis and calculations are the same. Calcium carbonate is the main ingredient of agricultural lime, which is just

Calcium Carbonate Content of Limestone

powdered limestone, and also of many antacid tablets. Agricultural lime and antacid tablets both neutralize acid, whether in soil or stomach, and therefore must be bases. This simple acid/base reaction provides for better soil conditions and improved crop yields, or stomach relief for weary students as they prepare for exams.

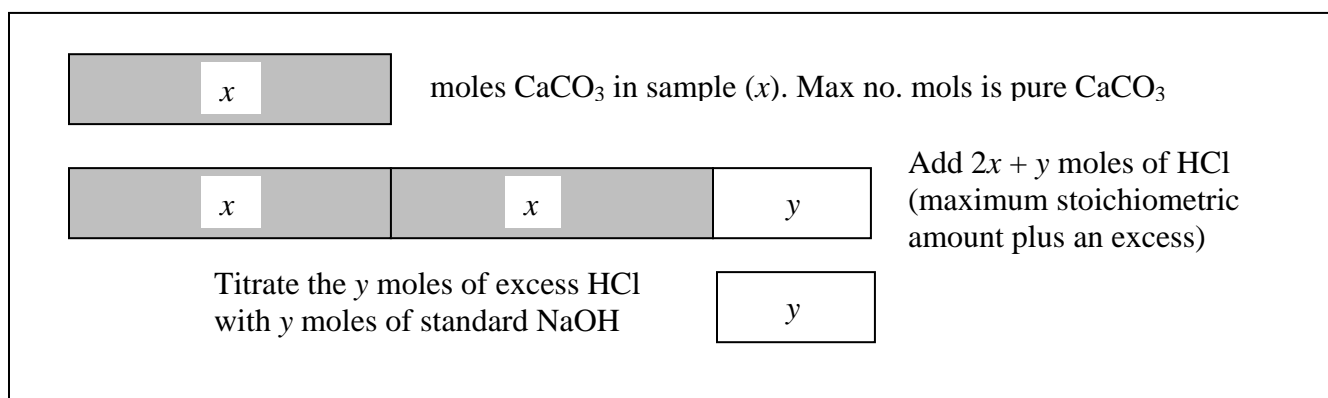
This experiment is slightly more complicated than the determination of acetic acid in vinegar that you did in Experiment 18. In this procedure we add an excess amount of acid of known concentration, allow it to react with a sample of powdered limestone and then titrate the excess unreacted acid. The complication is mainly mathematical, in that you need to do an extra calculation. This type of analysis is known as a *back titration*: you add an excess amount of acid to the unknown basic substance, then *titrate back* to the phenolphthalein endpoint with your standardized NaOH.

A back titration is really just a practical application of a limiting reactant problem. We calculate the maximum amount of CaCO_3 that could possibly be present in our sample, then add a known amount of acid that is somewhat in excess of the maximum stoichiometric amount needed to dissolve the maximum possible amount of CaCO_3 . Why do we add an excess? We do that because the reaction of HCl with CaCO_3 is not instantaneous, and as acid is consumed in the reaction, its concentration decreases, so the rate of reaction slows dramatically. It would be difficult or impossible to accurately determine the endpoint of the titration if we tried to add only the stoichiometric amount of acid needed.

With the back titration, however, we avoid that problem. A simple graphic may help explain the process. First the reaction:



Next draw a figure showing relative amounts of the reactants:



In summary: We add a known amount of HCl, equal to $2x + y$ moles, to x moles of CaCO_3 . $2x$ moles of HCl react with the CaCO_3 , leaving y moles of unreacted HCl in the flask. We titrate the excess HCl with y moles of NaOH. Therefore, we

Calcium Carbonate Content of Limestone

know $(2x + y)$, and we know y , so we can calculate x from our measured quantities.

Example Calculation 1.1

A 0.504 g sample of finely ground limestone was placed in an Erlenmeyer flask, and 50.00 mL of 0.250 M HCl was added using a volumetric pipet. The mixture was heated and stirred until all the CaCO_3 was dissolved (no more bubbles of CO_2 being evolved). The unreacted acid in the flask was titrated to a phenolphthalein endpoint with 0.104 M NaOH, taking 28.09 mL of NaOH to reach the endpoint. What is the mass% of CaCO_3 in the limestone?

Step 1—Calculate moles of HCl added ($2x + y$)

$$50.00 \text{ mL HCl} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.250 \text{ mol HCl}}{\text{L}} = 1.25 \times 10^{-2} \text{ mol HCl added} \quad \text{Equation 2}$$

Step 2—Calculate moles of unreacted HCl (y)

$$28.09 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.104 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 2.92 \times 10^{-3} \text{ mol HCl unreacted} \quad \text{Equation 3}$$

Step 3—Calculate moles of CaCO_3 (x)

$$(1.25 \times 10^{-2} \text{ mol HCl added} - 2.92 \times 10^{-3} \text{ mol HCl unreacted}) \times \frac{1 \text{ mol CaCO}_3}{2 \text{ mol HCl}} = 4.79 \times 10^{-3} \text{ mol CaCO}_3 \quad \text{Equation 4}$$

Step 4—Calculate mass percent CaCO_3

$$\frac{4.79 \times 10^{-3} \text{ mol CaCO}_3 \times \frac{100.09 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3}}{0.504 \text{ g limestone}} \times 100 = 95.1 \text{ mass\% CaCO}_3 \quad \text{Equation 5}$$

Calcium carbonate (CaCO_3) content of limestone

PROCEDURE

1. Preparation and standardization of HCl. (Your instructor may provide HCl of known molarity. If so, skip this step and proceed to step 2.)
 - a. Add between 8.0 and 8.5 mL 6 M HCl to about 100 mL deionized water and dilute to a total volume of 200 mL. Mix well. This is approximately 0.25 M HCl.
 - b. Pipet triplicate 10.00-mL subsamples of the ~0.25 M HCl into 3 clean, labelled Erlenmeyer flasks. Add about 25 mL deionized water to each flask. Record the volume of HCl used [Data Sheet Q1].

Calcium Carbonate Content of Limestone

- c. Add 3 drops of phenolphthalein to each flask and titrate to the first permanent pink endpoint with your standardized NaOH (from Experiment 18). Record starting and ending buret readings **[Data Sheet Q2 and Q3]**.
 - d. Calculate the NaOH titre volume **[Online Report Sheet Q4]**.
 - e. Calculate the molarity of the HCl. **[Online Report Sheet Q5]**. Use the molarity for the NaOH that you determined in Experiment 18.
 - f. Calculate the average molarity of the HCl **[Online Report Sheet Q6]**.
2. Back-titration method of CaCO₃ determination in limestone
- a. Grind a few limestone chips to a fine powder with a mortar and pestle. Make sure you have a finely powdered sample so that the next step will proceed more rapidly. Weigh to 3 decimal places duplicate 0.5 ± 0.03 g subsamples into two 250-mL Erlenmeyer flasks. Record the mass of your subsamples **[Data Sheet Q7]**.
 - b. Using the 50.00 mL volumetric pipet, add 50.00 mL of HCl to the Erlenmeyer flasks containing the powdered limestone. Record the volume **[Data Sheet Q8]**. If the HCl has been prepared for you, be sure to record the molarity of the HCl listed on the bottle. Stir the solution vigorously with a stirring rod and heat on a hotplate with regular stirring (DO NOT boil) to speed the dissolution of the limestone powder. The solution may remain somewhat cloudy due to the insoluble constituents of limestone, but this will not affect the titration.
 - c. It will take some time—maybe 10-15 minutes with vigorous heating and stirring—for the limestone to dissolve. Be patient and be sure all soluble matter has in fact dissolved. When the limestone has dissolved completely (no more CO₂ bubbles are coming from any remaining solid), cool to near room temperature in an ice bath.
 - d. Add 3 drops of phenolphthalein solution and titrate with the standardized NaOH to a faint permanent pink endpoint. Record the starting and ending buret readings **[Data Sheet Q9]**. Use the NaOH molarity you determined in Experiment 18 for the following calculations.
 - e. Calculate the number of moles of CaCO₃ in your limestone samples, and the average **[Online Report Sheet Q10 and Q11]**.
 - f. Calculate the mass percent of CaCO₃ in your limestone samples, and the average **[Online Report Sheet Q12 and Q13]**.

Laboratory Clean-up and Chemical Disposal

Calcium Carbonate Content of Limestone

3. All solutions may go down the sink.
4. Be sure that any dirty glassware is cleaned and returned neatly to your drawer after each laboratory. Also, wipe out your work area with a wet sponge before you leave the laboratory. Rinse your burets out with water and return them to their proper place.

Post-Lab Questions: The questions for this lab can be found at <http://www.Chem21Labs.com>. **Do Not Wait Until The Last Minute!!!! Computer Problems and Internet Unavailability Happen, But Deadlines Will Not Be Extended!!** On the Internet, complete any Post Lab Questions for Laboratory 9. The computer program will check your answer to see if it is correct. If there is an error, you will be given additional submissions (the number and penalty to be determined by your instructor) to correct your answer.

Late Submission: Late submission of the lab data / calculations is permitted with the following penalties: **- 10 points** for submissions up to 1 day late, **- 20 points** for submissions up to 2 days late.

Laboratory 1

Student Data Sheet

Standardization of HCl

| | <i>Trial 1</i> | <i>Trial 2</i> | <i>Trial 3</i> |
|---------------------------------|----------------|----------------|----------------|
| 1. Volume of HCl used (10 mL) | _____ mL | _____ mL | _____ mL |
| 2. Initial buret reading (NaOH) | _____ mL | _____ mL | _____ mL |
| 3. Final buret reading (NaOH) | _____ mL | _____ mL | _____ mL |

Back-titration of limestone

| | <i>Trial 1</i> | <i>Trial 2</i> |
|---------------------------------|----------------|----------------|
| 7. Mass of limestone | _____ g | _____ g |
| 8. Volume of HCl added (50 mL) | _____ mL | _____ mL |
| 9. Initial buret reading (NaOH) | _____ mL | _____ mL |
| 10. Final buret reading (NaOH) | _____ mL | _____ mL |



Laboratory 1

Instructor Data Sheet

Name: _____

Standardization of HCl

| | <i>Trial 1</i> | <i>Trial 2</i> | <i>Trial 3</i> |
|---------------------------------|----------------|----------------|----------------|
| 1. Volume of HCl used (10 mL) | _____ mL | _____ mL | _____ mL |
| 2. Initial buret reading (NaOH) | _____ mL | _____ mL | _____ mL |
| 3. Final buret reading (NaOH) | _____ mL | _____ mL | _____ mL |

Back-titration of limestone

| | <i>Trial 1</i> | <i>Trial 2</i> |
|---------------------------------|----------------|----------------|
| 7. Mass of limestone | _____ g | _____ g |
| 8. Volume of HCl added (50 mL) | _____ mL | _____ mL |
| 9. Initial buret reading (NaOH) | _____ mL | _____ mL |
| 10. Final buret reading (NaOH) | _____ mL | _____ mL |