■ E x p e r i m e n t

4

Quantifying the Composition of Limestone

Lecture and Lab Skills Emphasized

- Determining the percent composition of a compound in a substance.
- Applying gravimetric analysis.

In the Lab

- Students will work in pairs.
- Parts must be completed in order.
- Record your procedure and original data in your lab notebook along with your calculations.
- Report data collected and subsequent calculations to **www.chem21labs.com**.
- *All equipment should be returned to the correct location after use*.

Waste

- Pour the solutions in the waste container.
- Solids can go into the trashcan.

Safety

- Gloves and safety goggles are mandatory when anyone is performing an experiment in the lab.
- Hydrochloric acid (HCl) is toxic by ingestion and inhalation and corrosive to skin and eyes; avoid contact with body tissues. You are using very concentrated HCl.
- Aqueous ammonia (NH_3) solution is corrosive and contact with skin or eyes should be avoided. Work in a well-ventilated area.
- Take care in handling solid reagents to avoid inhalation and eye exposure. Always use a brush to clean the balance.

- Long pants, closed-toed shoes, and shirts with sleeves must be worn at all times. Clothing is expected to reduce the exposure of bare skin to potential chemical splashes.
- Always wash your hands before leaving the laboratory.

Additional information can be found at **http://genchemlab.wordpress.com/4-empirical-formula**.

Your supervisor has been asked to have multiple samples of limestone studied to determine how much calcium carbonate is present in some samples collected by a local geologist. The geologist wants to use this data to see if she can determine where unknown samples came from.

Geochemistry of Limestone

Limestone comprises approximately 10% of all sedimentary rocks exposed on the earth's surface and is primarily biological in origin. Typically, limestone forms from the *lithification* (the process of turning loose sediments into rock) of marine organisms like shells, corals, and algae on the ocean floor. Limestone formation can also come from precipitation of dissolved calcium carbonate. This commonly occurs in clear, shallow, warm water. Limestone is common in many parts of the U.S. and makes up more than 50% of surface rocks in Kentucky.[1] What does that tell us about the state of Kentucky millions of years ago?

Limestone is composed of the mineral calcite, better known to chemists as calcium carbonate, small amounts of clay, silt, chert (silica, SiO_2), and dolomite (calcium-magnesium carbonate, $CaMg[CO_3]_2$).[2] To be called limestone, the rock has to have a composition of over 50% dolomite and calcite, though the exact percentages vary widely. The limestone available commercially is over 80% calcite and dolomite. Traditionally, the chalk in chalkboard was produced from limestone. However, the chalk used on chalkboards today is being replaced by gypsum (calcium sulfate, $CaSO_4$). Limestone is still used in AgLime and Lime, Portland Cement, and as stone used in construction projects. Quarries across the state and as nearby as the Lexington Quarry Company in Nicholasville and the Caldwell Stone Company in Danville have discovered calcite crystals along veins they were mining.[3]

Figure 4.1. Limestone.

When examining your rock samples, you may notice variation in color. The color of limestone can range from bright white to light gray, frequently an indication on the purity of calcium carbonate. Impurities found in limestone include iron oxides, the yellow and brown shades, and carbon impurities from plant material, dark gray to black colors. Magnesium, silicates (SiO_4^{-4}), manganese, iron, titanium, aluminum, sodium, potassium, and sulfur found within limestone generally came from the seawater present when the limestone was originally created.

Limestone fizzes (or effervesces) with the addition of acid due to the release of carbon dioxide gas. This occurs in a two-step process. Acids will react with the calcium carbonate producing carbonic acid (H_2CO_3). Then in the second step, carbonic acid rapidly decomposes to form carbon dioxide.

Step 1: $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2CO_3(aq)$

Step 2: $H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l)$

Net reaction:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Natural acids within ground water can dissolve limestone in the ground, resulting in caves commonly seen in Kentucky and around the U.S.

Using stoichiometry and these balanced reactions, we can determine the amount of calcium carbonate in a sample of limestone. The carbon dioxide produced in Step 2 could only have come from the carbonic acid produced in Reaction 1. This allows us to relate the amount of carbon dioxide produced back to the original calcium carbonate (Reaction 3).

We can also quantify the calcium carbonate by determining how much calcium ion is present in the sample. To do this, we will react the solution we produced in the anion analysis (is the calcium still calcium carbonate at this point?) with ammonium sulfate to produce the mineral gypsum ($CaSO_4$) following:

$$CaCl_2(aq) + (NH_4)_2SO_4(aq) \rightarrow CaSO_4(s) + 2NH_4Cl(aq)$$

Using stoichiometry again, we can see that calcium sulfate has one calcium ion, the same as in calcium chloride and calcium carbonate. If we can determine how much calcium sulfate we produce through this reaction, we can work backwards and determine how much calcium ion was present in the original sample and thus the amount of calcium carbonate.

By comparing the percent compositions of the two methods, we can gain insight into our experimental technique, and you can determine things you did during the experimental procedure that would result in differences in the percent compositions. Keep in mind as you perform the experiment that you will be using the same rock sample throughout and selectively removing components for study while leaving others.

Percent Composition

Structure–property relationships are key to understanding how a chemical structure leads to the physical properties seen. In particular, an understanding of structure–property relationships has led to key advancements in the development of new drugs, polymers, materials, dyes, electronics, as well as many other things. Understanding these properties begins with determining the elemental composition of a substance. From knowing which elements, and how many of each element, are present in a substance, we can determine the chemical formula and the bonding arrangement.

Mass percent composition (or percent by mass) is used to determine how much of one component is present in a sample. For chemists, this means trying to determine how much of one element is present in a compound. This must be done in a laboratory setting in order to remove impurities and ensure that no new substances are introduced into the sample (i.e., like using dirty glassware or equipment!). Frequently, the percent composition (or mass percent) is used to determine the empirical formula of a substance, as it relates the mass of one element to the mass of the substance. Mass percent is calculated using the following formula:

$$\text{mass \% of A} = \frac{\text{mass of A}}{\text{total mass of substance}} \times 100$$

where A is one component of the substance. Because mass percent is an intensive property (independent of amount), we can compare mass percent values from multiple experiments if they are done on portions of a common sample.

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Safety Note

Do **not** wear gloves out of the laboratory. Any chemicals on your gloves will be spread to whatever you touch, such as the water fountain or the bathroom door. Anyone coming along behind you could then be unknowingly exposed to a chemical. You could also put yourself in contact with chemicals by touching your face when wearing gloves, even if the gloves appear to be clean.

Even if you have not yet started working in the lab, do **not** wear gloves out of the laboratory for any reason. Imagine walking into a restaurant and seeing an employee wearing gloves while taking out the trash. Then that same employee, still wearing gloves, prepares your food. How do you know they aren't wearing the same pair of gloves? Would you want them preparing your food?

Since it is not always possible to tell whether your gloves have been in contact with a chemical, it is assumed that all gloves have been in contact with a chemical once you put them on your hands.

Gravimetric Analysis

In order to determine what elements are present, chemists often combine the sample with a compound known as a **precipitating agent**. Precipitating agent combines selectively with the element of interest in the dissolved sample. Can you identify the precipitating agent used in this experiment? The precipitate is then isolated and weighed to quantify the substance of interest. This method is known as *gravimetric analysis*. Two different gravimetric analysis methods are used in this experiment; can you identify them?

Ideally when choosing a precipitating agent, the product would need to be insoluble, easily filterable, very pure, and with a known composition. While you may not be able to meet all of these criteria, it is important that you use good experimental technique to ensure solid results. Good technique in chemistry lab refers to your ability to perform basic laboratory skills, including cleaning and drying glassware, following safety protocol, accurately using glassware and other equipment, and completely transferring materials from one container to another. These are just a few of the techniques that you will use in the lab, all of which will affect the quality and quantity of the product you produce.

Filtration

To perform a gravimetric analysis, you will need to be able to filter the solids formed in your reaction out of solution. **Filtration** is used to separate components which are soluble (dissolve in a solvent) and insoluble (do not dissolve in a solvent). A solvent can be just about anything, regardless of the phase. We tend to think of solvents as liquids, such as water, but solvents and solutes (the species which dissolve in the solvent) can be in any phase and it is not necessary for them to be in the same phase. Filters in chemistry lab work like filters in cars or your house, or the colanders in your kitchen. When cooking pasta, we pour the pasta and water through a colander, which is our filter. The holes are large enough for the water to go through but too small for the pasta. In chemistry, we are usually talking about much smaller things so we use filter paper which has holes like a colander, only they are much, much smaller.

To filter out the solids of the solution you produce in this lab, you will use two different techniques. The simplest technique uses gravity to filter the solution through filter paper (Figure 4.2). This system works well when the solids are large and you are interested in the solution. When you have small crystals that you want to keep, **vacuum filtration** would be more appropriate, as it uses a vacuum to pull suction on a special piece of glassware known as a filter flask with a Büchner (pronounced Byook-ner) funnel to hold the filter paper (Figure 4.3). The difference between the two methods is like the difference between picking up a large bag of peas spilt on the floor by hand or by using a vacuum cleaner. We are using the power of suction to pick up the peas, just like we'll be using the suction to pull the liquid through the filter paper. In the lab, suction can be generated by a vacuum pump (think of a really powerful vacuum cleaner) or a water aspirator. The aspirator is easy to use and readily available since all it requires is an adaptor and a water faucet. The aspirator is connected to a filter flask with a rubber vacuum hose and a Büchner funnel attached.

The rubber stopper on the bottom of the funnel seals the filtration flask so outside air is not pulled in from the top and the suction from the aspirator is concentrated on the contents of the Büchner funnel. As the water runs down through the faucet, it creates a suction in the side arm of the adaptor which pulls air from the connected filtration flask, creating a vacuum in the flask.

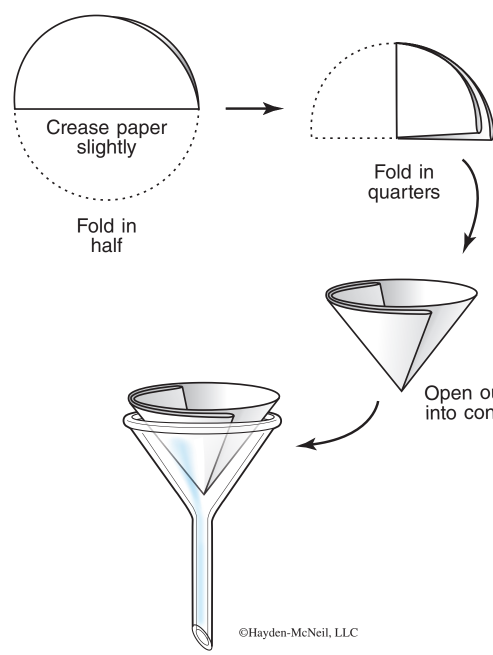


Figure 4.2. Gravity filtration.

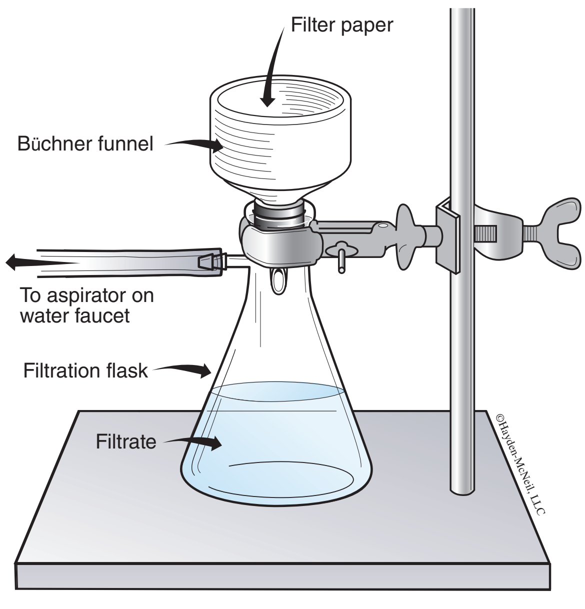


Figure 4.3. Separation technique: Suction filtration.

pH and Indicators

pH is the change in the concentration of H^+ ions in a solution. This change in concentration can be monitored in a number of different ways, including using a probe which constantly monitors pH or by using an indicator that changes color in a particular pH range. **pH indicators** are molecules that react to specific and small changes in pH by physically changing color with their protonation or deprotonation (addition or removal of a H^+ ion). Many indicators are known, with phenolphthalein, methyl red, and bromophenol blue being some of the most commonly used. You will learn more about changes in pH and acid–base titrations in a later lab. However, you will be using a pH indicator in this experiment, methyl red.

Methyl red indicator, or simply methyl red, changes color when the pH changes between 4.4 and 6.4. Initially with acidic solutions (those around pH 4 or less) methyl red will be red colored, and pink the closer to pH 4.4 the solution is. As the pH rises with the addition of base, the solution will turn yellow, as methyl red reacts to the change in pH. What is happening structurally to the methyl red when this occurs?

Materials and Procedures

Limestone

3.00 M HCl

2—50 mL Erlenmeyer flask

150 mL Erlenmeyer flask

Methyl red indicator

Ammonium sulfate

2.00 M aqueous ammonia

Droppers

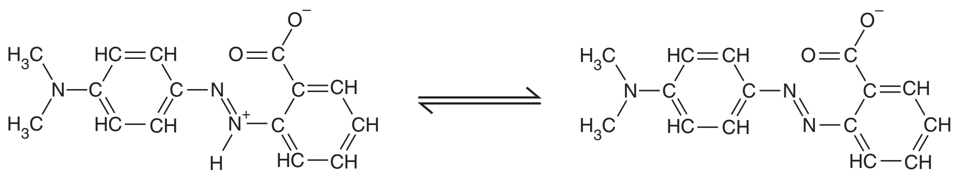
Glass stir rods

Oven

Procedure

Carbonate in Limestone

1. Obtain enough pieces of limestone so that you have two separate rock samples weighing ~0.70 grams to 0.80 grams and record the exact mass. See Chapter 3 for instructions on how to use an electronic balance. You will want to choose small pieces. If necessary, carefully use a hammer to further crush the limestone.



Acid form (red colored) Basic form (yellow colored)

Figure 4.4. Methyl red.

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Complete each of the remaining steps on each sample separately. You may want to work on one sample while your lab partner works with the other sample.

2. Add approximately 15 mL of 3.00 M HCl to a clean and dry (**important**!) 50 mL Erlenmeyer flask. Record the total mass of the container with the HCl.

3. Add the limestone to the flask with the HCl. Swirl gently to mix the solution. Record your observations of the reaction in your lab notebook.

4. Allow the reaction to proceed for approximately 15 minutes or until the bubbling has stopped while mixing.

5. Record the final mass.

6. Keep this solution as you will use it in the next part.

Calcium in Limestone

7. If your sample has any undissolved solids, carefully filter the solution using gravity filtration. See Figure 4.2. If your sample completely dissolved, continue to the next step.

   a. Following Figure 4.2, set up your filter paper and place it in the funnel. Place the funnel in the 150 mL Erlenmeyer flask.

   b. Completely wet the filter paper with distilled water.

   c. Filter the solid from the solution. It may be necessary to pour the solution into the funnel in portions so that you do not overfill the filter paper. Use your wash bottle with distilled water to remove all of the solids from the flask.

   d. Clean and dry your 50 mL Erlenmeyer flask before continuing.

   e. Pour the filtrate (solution) into a clean 50 mL Erlenmeyer flask for use in the rest of the lab.

8. Add 10 drops of methyl red indicator to the sample. Record your observations.

9. While stirring, add 1.50 grams of $(NH_4)_2SO_4$ to the flask. Continue stirring until it completely dissolves. Record your observations.

10. While continuing to stir, slowly add 2.00 M NH_3 drop-wise until the color *just* shifts from pink to pale yellow. It is important not to overshoot this color change. The color change should be maintained with stirring or shaking.

11. Obtain a clean and dry watch glass and piece of filter paper. Use a marker to write your name on the watch glass.

12. Record the mass of the watch glass and the mass of your filter paper.

13. Set up a Büchner filtration system as shown in Figure 4.3.

14. Place the weighed filter paper in the Büchner funnel. **Wet the paper thoroughly with distilled water**. Turn the water on to allow the paper to be sucked onto the funnel. In order to ensure a good seal, you may want to add a small amount of water into the funnel.

15. Collect the crystals by pouring the solution onto the filter paper. Make sure that the water is fully open for maximum suction filtration. Do not disturb the crystals on the filter paper or you will break the filtration vacuum. Wash any product in the beaker into the funnel with **cold** distilled water; rinse your stirring rod as well. Remember, any product you lose here will affect your mass percent.

16. Wash the **precipitate** (solid) with distilled water and allow the vacuum to pull air through to try your sample for a few minutes.

17. Allow the filtration to continue until you see no more water droplets fall from the funnel. Turn the water off. Insert a spatula between the edge of the paper and the side of the funnel and lift the paper from the funnel.

18. Place the filter paper carefully on a watch glass so that you do not lose any of your solids. Note the color and texture of the solids in your lab notebook.

19. Put the watch glass into the oven to dry for 5 minutes. Then remove the filter paper from the oven and scrape the sample onto the watch glass. Place the watch glass in the oven. Leave the sample in the oven to dry for at least 20 minutes.

20. Remove the sample from the oven, allow it to cool for 5–10 minutes, and record its mass and any observations. Check that you have *your* sample.

Data Analysis

Make sure to show all of your calculations in your lab notebook as a record of how you completed your calculations. Don't forget to include your units and correct number of significant figures! Then, go onto Chem21 and report your results.

1. Determine the mass of the carbon dioxide released.

2. Determine the moles of carbonate in the limestone.

3. Based upon your anion analysis, what is the percent composition by mass of calcium carbonate in limestone?

4. Determine the mass of calcium sulfate that precipitated.

5. How many moles of calcium carbonate are in the limestone based upon the cation analysis?

6. Based upon your cation analysis, what is the percent composition of the calcium carbonate in limestone?

In your report, make sure you clearly identify the purpose of the experiment (are we testing a hypothesis or simply trying to accomplish something; what is the difference?). How will the purpose be met? How does the procedure fit what is stated in your introduction? Give specific support using your chemical understanding. Don't forget to include any appropriate chemical reactions or mathematical equations, if appropriate, and explain them.

References

1. Kentucky Geological Survey. *Carbonates*. **http://www.uky.edu/KGS/rocksmn/carbonates.htm#calcite** (accessed May 8).

2. Bliss, J. D.; Hayes, T. S.; Orris, G. J. *Limestone—A Crucial and Versatile Industrial Mineral Commodity*; 2008–3089; Denver, CO, 2008 revised 2012.

3. Kentucky Geological Survey. *Limestone*. **http://www.uky.edu/KGS/rocksmn/limestone.htm** (accessed May 8).

Lab is adapted from Gregg Dieckmann and John Sibert's "Percent Composition from Gravimetric Analysis: Calcium Carbonate in Texas Limestone." *An Atoms First Approach to the General Chemistry Laboratory*. New York: McGraw-Hill. 2012.