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Gravimetric Analysis of Calcium and Hard Water

AP* Chemistry Big Idea 1, Investigation 3
An Advanced Inquiry Lab

Introduction

In certain areas of the country, the presence of hard water poses significant problems in water supply systems. Various water softening techniques are used to remove the cations responsible for water hardness. This investigation involves the application of gravimetric analysis to test samples for the amount of water hardness and calcium ions.

Concepts

- Water hardness
- Gravimetric analysis
- Double replacement reactions
- Stoichiometry

Background

Water from natural sources may contain a number of dissolved substances. The amount and nature of these dissolved substances varies depending on the geography of the area and the journey the water has taken. As water travels through the ground or over the surface of the land, it can dissolve naturally occurring minerals. As minerals dissolve in the water, the compounds separate into their respective cations and anions. Common cations in water include Na^+, Ca^{2+}, Mg^{2+}, and Fe^{3+}, while the principal anions in water are Cl^-, HCO_3^-, NO_3^-, and SO_4^{2-}. The main ions contributing to water hardness are Ca^{2+}, Mg^{2+} and, to a lesser extent, Fe^{3+}. Their presence makes it difficult for soaps to lather and also causes a "scum" to form. Equation 1 (where R is a long hydrocarbon chain) shows the precipitation reaction between alkyl sulfate anions in a typical soap with calcium ions in hard water. The main problem due to water hardness in industrial pipes or boilers is the buildup of solid $CaCO_3$, which precipitates out and causes thick deposits to form in pipes and other appliances.

$$Ca^{2+}(aq) + \underset{\textit{Soap}}{2ROSO_3^-(aq)} \rightarrow \underset{\textit{Soap scum}}{Ca(ROSO_3)_2(s)} \qquad \textit{Equation 1}$$

There are many different ways to "soften" water. One of the most common ways to remove ions is by ion exchange. The *ion exchange* process uses a resin to replace some of the ions that cause hardness with ions that do not. Hardness is commonly measured in units of grains per gallon or milligrams per liter (also known as parts per million), and is classified by the U.S. Department of the Interior and the Water Quality Association as follows:

Classification	**mg/L or ppm**	**grains/gal**
Soft	0–17.1	0–1
Slightly hard	17.1–60	1–3.5
Moderately hard	60–120	3.5–7.0
Hard	120–180	7.0–10.5
Very Hard	180 and over	10.5 and over

Although several ions contribute to water hardness, the units of mg/L or ppm are defined in terms of the equivalent mass (milligrams) of $CaCO_3$ that would be present per liter of water. In this investigation, gravimetric analysis will be used to precipitate and isolate solid $CaCO_3$ from water samples and determine water hardness. Many municipal water treatment plants use soda ash (sodium carbonate, Na_2CO_3) and lime (calcium hydroxide, $Ca(OH)_2$) to chemically remove calcium and magnesium ions, respectively, from hard water.

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Experiment Overview

The purpose of this advanced inquiry lab is to investigate the suitability of gravimetric analysis for determining the amount of water hardness in the form of calcium carbonate, $CaCO_3$, in various water samples. Six samples, representing a wide range of potential water hardness, from 50 ppm to 500 ppm, will be analyzed by various student groups as part of a cooperative class investigation to determine the accuracy and sensitivity of gravimetric analysis for water hardness testing. Note that all water samples have been concentrated by a factor of 100 for the purpose of quantitative analysis. The lab begins with an introductory activity to develop skill in the calculations and techniques of gravimetric analysis, in particular, quantitative transfer and vacuum or gravity filtration. The precipitation reaction involves preparing and combining solutions of Na_2CO_3 and $CaCl_2$. The balanced chemical equation for this reaction predicts the amount of precipitate that will be formed. Careful isolation, drying and weighing of the precipitate will confirm the calculations and the percent yield. The procedure provides a model for guided-inquiry design of the cooperative class investigation described above. Antacid tablets are also provided as an opportunity for further inquiry—the use of gravimetric analysis to determine the amount of calcium in an over-the-counter medication.

Pre-Lab Questions

1. Define the term gravimetric analysis. Describe the procedure used in this activity, and identify two other common examples of gravimetric analysis.
2. Write the balanced chemical equation for the reaction between calcium chloride and sodium carbonate.
3. Calculate the number of moles of each reactant in the *Introductory Activity* (see steps 1 and 2). Identify the limiting reactant in the reaction and determine the theoretical amount of $CaCO_3$ that should be produced.
4. As noted in the *Background* section, hardness levels are calculated by assuming that all the "hard" metal ions come from dissolved calcium carbonate and are reported in mg $CaCO_3$/L. Calculate the equivalent water hardness in mg $CaCO_3$/L for a calcium chloride solution containing 0.1 M Ca^{2+} ions.

Materials (for each lab group)

Calcium chloride, anhydrous, $CaCl_2$, 2 g
Hard water samples, 20 mL, 2
Sodium carbonate solution, Na_2CO_3, 0.5 M
Sodium carbonate, anhydrous, Na_2CO_3, 2 g
Water, deionized or distilled
Antacid tablets (optional)
Balance, 0.001-g precision (shared)
Beakers, 150-mL, 3
Drying oven (shared)
Filter flask, 250-mL
Filter paper, 3
Funnel, Büchner and rubber adapter
Graduated cylinder, 50-mL
Spatula
Vacuum filtration apparatus setup
Wash bottle
Watch glasses, 2
Weighing dishes, 2

Safety Precautions

Sodium carbonate is irritating to body tissues. Anhydrous calcium chloride is moderately toxic by ingestion and generates a great deal of heat when dissolved in water. Avoid contact of all chemicals with eyes and skin. Antacid tablets used in the lab are considered laboratory chemicals and may not be removed from the lab. Do not taste or ingest any materials in the chemistry lab. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the laboratory. Please follow all laboratory safety guidelines.

Introductory Activity

Precipitation Reaction and Vacuum Filtration

1. Weigh 2.5 g of sodium carbonate and place in a clean, dry 150-mL beaker. Record the precise mass and dissolve the solid in 20 mL of deionized or distilled water.
2. Weigh 2.0 g of calcium chloride and place in a clean, dry 150-mL beaker. Record the precise mass and dissolve the solid in 20 mL of deionized or distilled water.
3. Combine the two solutions by slowly adding the sodium carbonate solution to the calcium chloride solution. Record all observations about the reaction.
4. Separately weigh a piece of filter paper and a watch glass and record their masses.
5. Set up a vacuum filtration apparatus as shown in Figure 1. The second filter flask is used to prevent back-up of water from the aspirator to the filter flask when the vacuum is released.

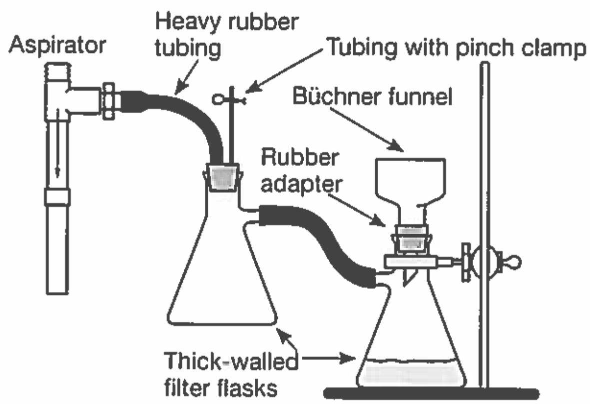

Figure 1. How to Set Up a Vacuum Filtration

For help in setting up a vacuum filtration and tips for carrying out the procedure, please see the following How-To Videos on the Flinn Scientific website under Teacher Resources: "How to Set Up a Vacuum Filtration" and "How to Perform a Vacuum Filtration." (flinnsci.com)

6. Isolate the precipitate by vacuum filtration. Careful transfer techniques are essential for accurate results! Precipitate may also be collected by gravity filtration.
7. Place the watch glass and filter paper containing precipitate in a lab oven to dry at 100 °C for 10–20 minutes. Monitor and carefully break up the solid with a spatula to ensure complete drying.
8. Calculate the percent yield of calcium carbonate.

Guided-Inquiry Design and Procedure

Accuracy and Sensitivity of Gravimetric Analysis to Determine Water Hardness

Form a working group with other students and discuss the following questions.

1. The ideal precipitate in a gravimetric analysis procedure should be insoluble and have a known composition. Using reference texts such as *The Merck Index* or the *Handbook of Chemistry and Physics*, look up the properties of calcium carbonate and discuss its advantages and possible disadvantages for gravimetric analysis of calcium.
2. Based on solubility rules, what ions in water might interfere with the analysis of calcium ions by precipitation of calcium carbonate?
3. Precipitate particles in gravimetric analysis must be large enough to be collected by filtration—smaller particles may pass through or clog the filter. Discuss how the following techniques will help prevent product loss and ensure product purity in a gravimetric procedure.
   - Add the precipitant slowly with vigorous mixing.
   - "Digest" the precipitate by allowing it to stand in contact with the solution and/or heating the mixture for 10–15 minutes.
   - Rinse the precipitate with a small amount of water after filtration.

Six water samples containing known concentrations of calcium chloride are available for analysis as part of a cooperative class activity. Each student group should analyze two different samples. The recommended sample volume for the precipitation reaction is 20 mL. Complete the table below with the results of the calculations from Questions 4–6 below.

Sample	[$CaCl_2$], M	Moles of Ca^{2+} in 20 mL of Solution	Theoretical Amount of $CaCO_3$ Precipitate	Volume of 0.5 M Na_2CO_3 (20% excess)	Theoretical Water Hardness, mg/L
1	0.400	0.008	0.801 g	19.2 mL (20)	400 mg/L
2	0.200				
3	0.500				
4	0.100				
5	0.050				
6	0.300				

4. Calculate the number of moles of Ca^{2+} ion in 20 mL of each solution and the theoretical amount of $CaCO_3$ that can be obtained by reacting 20 mL of each solution with excess sodium carbonate. Enter the results in the table.

5. Excess sodium carbonate solution (precipitant) is recommended to ensure that all of the calcium ions in solution are converted to product. For each sample, determine the volume of 0.5 M sodium carbonate solution that provides the stoichiometric number of moles of Na_2CO_3 needed to react completely with the $CaCl_2$ solution. Multiply the result by 1.2 to provide a 20% excess, and enter the results in the table.

6. Calculate the theoretical water hardness in mg $CaCO_3$/L for each water sample. Recall that each sample has been concentrated by a factor of 100 to provide the solution shown in column 2. The calculation for sample 1 is shown below as a guide.

   Sample Calculation (Sample 1): (0.801 g $CaCO_3$/0.020 L) × (1000 mg/g) × (1/100) = 400 mg $CaCO_3$/L

   Note that the factor 1/100 accounts for the concentration of the original water sample to the final analyzed volume of 20 mL.

7. Write a detailed, step-by-step procedure for analyzing the concentration of calcium in the water samples. Include the reagents needed, the glassware and equipment that will be used, and the appropriate measurements and observations that must be made.

8. Review the hazards of the chemicals used in the procedure and write appropriate safety precautions that must be followed during the experiment.

9. Carry out the procedure and record the results in an appropriate data table.

10. Repeat the analysis as needed to check for reproducibility.

Analyze the Results

Calculate the percent yield of calcium carbonate and determine the experimental water hardness in mg/L for each sample. Classify the water hardness of each sample according to the criteria established by the U.S. Department of the Interior and the Water Quality Association (see the *Background* section). Compile the class data for all the samples that were analyzed and compare the accuracy and sensitivity of the gravimetric analysis procedure over the range of possible water hardness from 50 to 500 mg/L.

Opportunities for Inquiry

Gravimetric Analysis to Determine the Mass of Calcium Ion in an Antacid Tablet

The amount of calcium in an antacid tablet may also be determined using gravimetric analysis. Note that antacid tablets contain binders and other inert ingredients or additives. Design a procedure to dissolve and separate the calcium carbonate from the binders in the tablet and analyze the amount of calcium.

AP Chemistry Review Questions

Integrating Content, Inquiry and Reasoning

Copper(II) chloride ($CuCl_2$; 0.98 g) was dissolved in water and a piece of aluminum wire (Al; 0.56 g) was placed in the solution. The blue color due to copper(II) chloride soon faded and a red precipitate of solid copper was observed. After the blue color had disappeared completely, the leftover aluminum wire was removed from the solution and weighed. The mass of the leftover aluminum wire was 0.43 g.

1. Calculate the number of moles of (a) copper(II) chloride and (b) aluminum that reacted.

2. What is the mole ratio of copper(II) chloride to aluminum metal? Express this to the nearest whole number ratio.

3. What happened to the aluminum metal that was consumed in this reaction? Write the formula of the most probable aluminum-containing product.

4. Write a balanced chemical equation for the single replacement reaction of copper(II) chloride with aluminum.