Complexometric Titration of Calcium in Antacids

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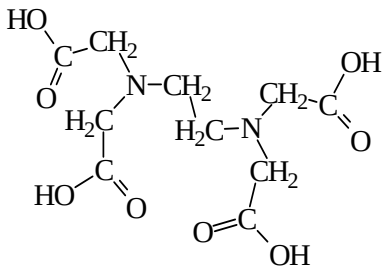
Purpose of this Exercise: To determine the amount of calcium ion in an antacid or diet supplement pill and unknown by complex formation with ethylenediaminetetraacetic acid (EDTA).

Background Information

Between 1.5 and 2% of your body weight comes from calcium, more than 95% of which is in your bones and teeth. In addition to being necessary for healthy bones and teeth, calcium is also essential in metabolism. Calcium ions present in blood serum participate in blood coagulation and neuromuscular activity. When the body's supply of available calcium runs low, it is replenished from and at the expense of the bones. Thus, long-term calcium deficiency is responsible for a bone-thinning process called osteoporosis which afflicts many elderly people.

Many adults do not receive enough calcium in their diets. According to one estimate, osteoporosis affects 20 million Americans, mostly women over the age of 45. The Recommended Dietary Allowance (RDA) of calcium for an adult is 800 mg per day (1500 mg for women after menopause). Many physicians consider this intake necessary to avoid osteoporosis. Foods such as dairy products, broccoli, kale, collard greens, tofu, and kidney beans are good dietary sources of calcium. However, dietary calcium alone may not suffice to prevent osteoporosis, and calcium supplement tablets are sometimes prescribed by physicians, especially for susceptible individuals and those allergic to dairy products. On the other hand, some nutritionists fear that over reliance on calcium supplements can lead to overdosing, which can result in formation of painful kidney stones. Some natural sources of calcium, such as dolomite and bone meal (available at "health food" stores) may also contain toxic elements, especially lead.

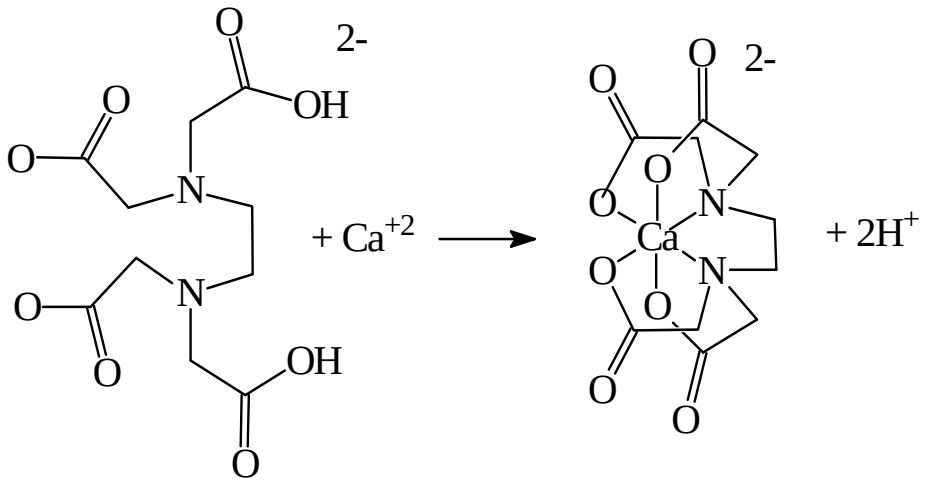
Most of the calcium supplements found as over-the-counter products contain calcium carbonate ($CaCO_3$) as the active ingredient. They are thus similar to antacids such as Tums, Rolaids, and Maalox caplets. Taking calcium carbonate may result in the generation of excess carbon dioxide gas in the stomach, leading to belching. As a result, some formulations now substitute calcium citrate for calcium carbonate. In addition to the active ingredient, pills usually include other ingredients, such as flavoring agents, coloring agents, fillers and binders, etc.



In this exercise, you will determine the amount of calcium in a calcium supplement or antacid. The method you will use involves titration with a solution of ethylenediaminetetraacetic acid (EDTA), which forms a coordination compound or "complex" with calcium ions. EDTA is a widely used complexing agent for cations. The structure of the neutral EDTA molecule is shown at the left. The molecule can be thought of as a diprotic acid, H_2EDTA. In the form normally used, EDTA has two negative charges resulting from the ionization of two of the organic acid groups (-COOH). We write this form of EDTA as $EDTA^{2-}$ There are six sites capable of acting as Lewis bases – the two nitrogen atoms and four of the oxygen atoms. It is able to wrap itself

around di- and trivalent cations to form very stable and *soluble* complexes. A three dimensional representation of a typical complex is shown at the right. In the home, EDTA is found in detergents and sink cleansers, where its ability to complex cations allows removal of rust stains caused by iron oxides. In medicine it is used in "chelation therapy" to remove toxic heavy metal ions, such as lead, Pb^{2+} from the body. Only simple monovalent cations such as Na^{+} are not complexed by EDTA.

Calcium ions react with EDTA to form a 1:1 complex as shown:



The reaction is rapid and quantitative. However, none of the components shown in the equation is colored, so something needs to be done to generate a visible endpoint in a titration. What is done is to add to the solution an indicator, "Eriochrome Black T," EBT. EBT is a blue dye which forms a weak red-colored complex with free calcium ions at a pH of 10 or so. When we add the EBT to the solution containing calcium ions, we see a red color due to the Ca(EBT) complex. As we add EDTA, the free calcium ions react first with the EDTA, generating no visible change. However, when all of the free calcium ions have reacted, the next drop of EDTA solution will extract the remaining calcium ions from the Ca(EBT) complex to form the more stable $Ca(EDTA)^{2-}$ complex. This releases the free EBT, so that the color of the solution changes at the endpoint from red to blue.

$$\underset{\text{red}}{Ca(EBT)} + H_2(EDTA)^{2-} \rightarrow Ca(EDTA)^{2-} + \underset{\text{blue}}{H(EBT)^{-}} + H^{+}$$

You will use this method to determine the amount of calcium present in antacids or calcium supplements. As an alternative, you can analyze seashells or eggshells, which are also composed primarily of calcium carbonate. You will also use the EDTA method to determine the amount of calcium carbonate in an unknown provided by your TA.

Procedures

Pill

1. Record the calcium content and other identifying characteristics of the pill from the label on the container. Weigh the entire pill on the analytical balance. Using a mortar and pestle, grind the pill until you are sure that the ground sample is of uniform composition. Place the entire ground sample in a clean dry 10 mL beaker. Record the concentration of the stock EDTA solution. From the information on the label, the weight of the pill and the concentration of the EDTA, calculate what weight of the ground pill sample will be necessary to consume 25 mL of the EDTA solution. Record this number in your notebook and on the data sheet.

Accurately weigh out **by difference,** *using the analytical balance*, a sample of approximately the weight that you calculated above into a 250-mL Erlenmeyer flask. The sample you weigh should be within 20% of the weight you calculated above. E.g.,

Suppose the pill contains 650 mg of $CaCO_3$ and weighs 1.5000 g (1500 mg), and the concentration of the EDTA is 0.05000 M.

- *We wish to consume 25.0 mL of the EDTA, or 25 x 0.05000 = 1.25 mmoles*
- *The Ca-EDTA complex is 1 : 1, so that will require 1.25 mmoles of Ca which are contained in 1.25 mmoles of $CaCO_3$*
- *1.25 mmoles of $CaCO_3$ weighs 1.25 x 100.1 = 125 mg*
- *1500 mg of the pill contains 650 mg of $CaCO_3$*
- *Therefore, (125 / 650) x 1500 = 288 mg of the pill will contain 125 mg $CaCO_3$*
- *We can use a sample weighing (1.00 ± 0.20) x 288, or between 230 mg and 345 mg*

(If you do not know the approximate composition of the sample (e.g., a sample of unknown calcium content that you may have brought in yourself, weigh out about 100 mg, accurately. In this case, you should adjust the weight in the second titration to consume about 25 mL based on the first titration.)

2. Add 5 mL of 6 M hydrochloric acid (***CAUTION***), measured using a 10 mL graduated cylinder, to the Erlenmeyer flask to dissolve the sample.

3. Once the sample has dissolved, add about 25 mL of distilled water to dilute the sample.

4. Add 10 mL of pH 10 buffer solution to the sample.

5. Add a small spatula tip-ful of Eriochrome Black T indicator. The end point is most easily detected if a small amount of indicator is used.

6. Rinse a clean buret with two small portions of standardized (*ca.* 0.05 M.) EDTA solution. Fill the buret with standardized EDTA solution, being sure that the buret tip has no air bubble trapped. **Record the exact concentration of the EDTA stock solution**.

7. Record the initial reading of the buret. Then titrate the calcium-EBT solution from Step 5 by carefully adding EDTA solution, with constant stirring or swirling. A permanent color change

from wine red to blue will indicate the endpoint. It is helpful to look at the solution by transmitted daylight, if possible, to detect the presence of any red coloration at the end point. Record the final buret reading,

8. Repeat in order to obtain a reliable average result. Report as Trials 1 and 2 on the Data Sheet 1. Calculate the mass percent CaCO3 content of the samples, the average mass percent, the average deviation of the mass percent and the percent deviation of the results.

Unknown

9. Since the composition is unknown, the first sample of unknown should weigh approximately 100 mg. We call this a trial run. Based on the results of the trial run, adjust the subsequent weights of unknown so as to consume about 25 ml of EDTA.

Follow steps 2 – 7 above.

Repeat with a second and third titration of an appropriate mass of the unknown.

Transfer the label identifying the unknown to the data sheet in the usual manner. The results you report on the unknown should have an average deviation of 1% or less. You must report at least two results in addition to the trial run. (If the trial run of the unknown required between 20 and 35 mL of EDTA, you may use that as one of the results in the computation of the average, etc. If you do, indicate it on the data sheet.)

Report the unknown results on which you wish to be graded on Data Sheet 2. (It is a good idea to wait until after you have performed all of the required titrations and done your calculations before entering results on your data sheet.)

Notebook Grade: _____

Safety Grade: _____

SUSB-017 Data Sheet - 1

Name Section Date

Concentration of standard EDTA solution: _____ M

Weight of tablet _____ g

Calcium Carbonate content of the tablet (nominal) _____ mg

Weight of tablet for 25 mL of EDTA _____ mg

Tablet

	Trial 1	**Trial 2**
Init. Mass of container + sample (g)	_____	_____
Mass of container + sample left over (g)	_____	_____
Mass of sample to be titrated (g)	_____	_____
Final buret reading (mL)	_____	_____
Initial buret reading (mL)	_____	_____
Net volume EDTA solution (mL)	_____	_____
mmoles EDTA (mmol)	_____	_____
mmoles Ca^{2+} in weighed sample (mmol)	_____	_____
mmoles $CaCO_3$ in weighed sample (mmol)	_____	_____
Mass of $CaCO_3$ in weighed sample (g)	_____	_____
Mass of $CaCO_3$ in weighed sample (mg)	_____	_____
Mass percent $CaCO_3$	_____	_____
$CaCO_3$ content of entire tablet (mg)	_____	_____

Average mass percent $CaCO_3$ in tablet _____ %

Average deviation of mass percent _____ %

Percent deviation of mass percent _____ %

SUSB-017 Data Sheet - 2

Name Section Date

Concentration of standard EDTA solution: _____

Unknown Identifier Label:

		Unknown	
	Trial Run	**Run 1**	**Run 2**
Init. Mass of container + sample (g)	_____	_____	_____
Mass of container + sample left over (g)	_____	_____	_____
Mass of sample (g)	_____	_____	_____
Mass of sample (mg)	_____	_____	_____
Final buret reading (mL)	_____	_____	_____
Initial buret reading (mL)	_____	_____	_____
Net volume EDTA solution (mL)	_____	_____	_____
mmoles EDTA (mmol)	_____	_____	_____
mmoles Ca^{2+} in weighed sample (mmol)	_____	_____	_____
mmoles $CaCO_3$ in weighed sample (mmol)	_____	_____	_____
Mass of $CaCO_3$ in weighed sample (mg)	_____	_____	_____
Mass percent $CaCO_3$ (%)	_____	_____	_____

Average mass percent _____ %

Average deviation of mass percent _____ %

Percent deviation of mass percent _____ %

SUSB-017 Pre-Laboratory Assignment

Name Section Date

EDTA titration can be used to determine the "hardness" of water. "Hardness" is due principally to the presence of calcium and magnesium ions in water. Their presence leads to precipitation of soap scums from soaps, and precipitation of calcium carbonate on heating the water, as in tea kettles or industrial boilers through the reaction:

$$Ca^{2+} + 2\ HCO_3^- \rightarrow CaCO_3\ (s) + H_2O\ (l)\ CO_2\ (g)$$

In order to determine the concentration of calcium ion in tap water, Spring Wawda titrated a 250.0 mL sample of tap water with 0.0500 M. EDTA solution, following the procedure of SUSB-017. The volume of solution required to reach the endpoint was 25.84 mL.

1. How many mmoles of EDTA were used in this titration?

2. How many mmoles of calcium ion [Ca^{2+}] were present in the water sample?

3. How many mmoles of $CaCO_3$ would precipitate upon heating a 500 mL sample of this water?

4. How many grams of calcium carbonate is this?

5. Marble is essentially pure calcium carbonate. What will happen if you spill vinegar on a marble countertop?

(Over)

6. The label of an antacid tablet bottle states that each tablet contains 480 mg of $CaCO_3$. A tablet weighs 1.40 g.

a.) What weight of the tablet will be required to use 20 mL of 0.050 M EDTA?

b.) What weight of the tablet will be required to use 30 mL of 0.050 M EDTA?

c.) What is the range in weight of a tablet sample that will require 25 ± 5mL of EDTA?