Experiment 12: Gravimetric Determination of Calcium as $CaC_2O_4 \cdot H_2O$

CH2250: Techniques in Laboratory Chemistry, Plymouth State University

Adapted from "2. Gravimetric Determination of Calcium as $CaC_2O_4 \cdot H_2O$," *Experiments To Accompany Exploring Chemical Analysis, 4th Edition*, Daniel C. Harris (2008), available at http://www.whfreeman.com/exploringchem4e. Originally from C. H. Hendrickson and P. R. Robinson, *J. Chem. Ed.*, **56**:341 (1979).

Suggested reading for background information: Ch 2.7-8, 6.4, 7.1-3, *Exploring Chemical Analysis, 4th Edition*, Daniel C. Harris (2008).

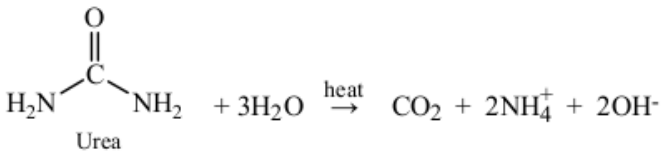
Introduction:

Mixtures of compounds in different phases (solid, liquid, gas) are perhaps the easiest to separate. Separating a liquid from a solid involves the commonplace technique of filtration. Thus, the conversion of an analyte dissolved in solution to a solid is often the first step in analyzing it.

Calcium ion can be analyzed by precipitation with oxalate in basic solution to form $CaC_2O_4 \cdot H_2O$:

$$Ca^{2+}\ (aq) + C_2O_4^{2-}\ (aq) + H_2O\ (l) \longrightarrow CaC_2O_4 \cdot H_2O\ (s)$$

Large, easily filtered, relatively pure crystals of product will be obtained if the precipitation is carried out slowly. It happens that the precipitate is soluble in acidic solution, because the oxalate anion is a weak base, which enables slow precipitation by dissolving Ca^{2+} and $C_2O_4^{2-}$ in acidic solution and gradually raising the pH by thermal decomposition of urea:



In the end, the mass of precipitate can be very accurately measured by using a glass funnel with a built-in glass frit (i.e., filter). Because the entire funnel and filter combination is glass, it can be vigorously dried in an oven before and after the filtration, removing water as a possible source of error in the mass.

Equipment: Read through the procedures and make a list of the equipment you will need.

Safety Considerations: Read through the procedures and note any safety considerations.

Procedure:

1. Three medium-porosity, sintered-glass funnels will have been dried at 105°C and cooled in a desiccator for your use prior to your arrival in lab. Note any labels or identifying marks on them. Weigh them, then return them to the oven for 30-min, cool them in a desiccator, and weigh them again to be sure they do not change mass (a change of 0.5 mg is acceptable). Repeat the heating, cooling, weighing cycle until successive weighings agree to within 0.5 mg. Record these masses in your notebook. Use a paper towel or tongs, not your fingers, to handle the funnels. Continue on to the follow steps while funnels dry.
2. Fill a plastic squirt bottle with distilled water and set it in ice.
3. Obtain an Unknown solution of Ca^{2+} from your instructor. Use a few small portions of unknown to rinse a 25-mL transfer pipet, and discard the washings. Transfer exactly 25.0 mL of unknown to each of three 250 beakers, and dilute each with ~75 mL of 0.1 M HCl. Add 5 drops of methyl red indicator solution to each beaker. This indicator is red below pH 4.8 and yellow above pH 6.0.

4. Add ~25 mL of ammonium oxalate solution to each beaker while stirring with a glass rod. *Remove the rod and rinse it into the beaker with small portions of distilled water.* Add ~15 g of solid urea to each sample, cover it with a watchglass, and boil gently for ~30 min until the indicator turns yellow.
5. Just before you are ready to remove the beakers from the heat, remove a filter funnel from the desiccator and set up a vacuum-assisted filtration.
6. Remove one beaker from the heat and filter the slurry through the weighed funnel, using suction (you may collect all the filtrates in the same vacuum flask). *It is advisable to pour the solution down a glass stirring rod into the funnel, but be sure to rinse the stirring rod into the funnel!* Add ~3 mL of ice-cold water to the beaker, quickly swirl to create a slurry, and transfer to the funnel. *You may wish to use a stirring rod to break up any solid, but be sure to rinse the stirring rod into the funnel.* Repeat this procedure with small portions of ice- cold water until all of the precipitate has been transferred to the funnel. Finally, use two 10-mL portions of ice-cold water to rinse the beaker, and pour the washings over the precipitate.
7. Dry the precipitate, first with aspirator suction for 1 min, then in an oven at 105°C for 30 min. Cool the filter in a desiccator and weigh. The product is somewhat hygroscopic, so only one filter at a time should be removed from the desiccator, and weighings should be done rapidly. Record the mass in your notebook.
8. Return the funnel to the oven for 30 minutes, followed by cooling and weighing. Ideally, this cycle would be repeated until the mass changed by less than 0.5 mg. However, you are limited by your ability to do this by the time length of the lab. Nonetheless, you must go through the cycle at least 3 times to complete the lab, even if this means leaving the samples in the oven and returning later in the day.
9. Repeat Steps 6-8 with the other two boiling beakers (step 4) and filtration funnels.

Analysis

1. Using the last mass measured (do not average the masses from all the heat/cool/weigh cycles!), calculate the moles of $CaC_2O_4 \cdot H_2O$ in each filtration funnel.
2. Calculate the average molarity of Ca^{2+} in the unknown solution. Report the standard deviation and relative standard deviation (s / x = standard deviation/average).

Conclusions

1. What would be the effect on your results if you did not rinse the stir bar in Step 4?
2. Consider some of the other techniques we have done this semester. Name one benefit and one downside of gravimetric analysis compared to another possible technique.

Homework Problems

The following problems from your book must be completed in your lab notebook (see the Syllabus for other suggested problems): Ch 2: **3**; Ch 6: **20**; Ch 7: **4**, **7**, **10a**