The percentage of calcium in an unknown sample will be determined using a gravimetric method. In this particular gravimetric method, calcium ion in solution is homogeneously precipitated in the presence of oxalate anion to form a fine crystalline precipitate of calcium oxalate-monohydrate.

Solutions and Chemicals Required:
- unknown calcium sample dried at 110° C
- concentrated HCl (found in various hoods)
- methyl red indicator
- 5 M NaOH
- 1 M HCl
- 5% (NH₄)₂C₂O₄ solution
- urea
- acetone provided in wash bottles

Special Equipment:
- three, medium-porosity sinter glass funnels
- special boiling rods (three)
- filter traps (one)

INTRODUCTION

A successful gravimetric determination depends on the ability to obtain large, pure crystals which are in an easily weighable form. One of the ways to obtain such crystal is by generating the precipitating agent slowly, *in situ*, which assures that its concentration will never be very high. Accordingly, supersaturation in the solution will be minimized, which according to the von Wiemann’s ratio, should lead to larger, purer crystals. Other factors which affect crystal size are temperature and stirring (or lack thereof). This experiment is designed to optimize the conditions of crystallization by avoiding local areas of precipitate supersaturation.

As shown in eq. 3, the precipitating agent for Ca²⁺ is the oxalate anion, C₂O₄²⁻. A series of reactions, starting with eq. 1, occurs. The solution starts off being acidic with undissociated oxalic acid, H₂C₂O₄. In this form, the calcium ion will not be precipitated. However, upon heating, the urea, (NH₂)₂CO, slowly decomposes to form −OH, which in turn, neutralizes the oxalic acid to liberate the oxalate anion. Precipitation occurs slowly allowing for slow crystal growth, hence larger and purer crystals develop.

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\begin{align*}
(NH_2)_2CO + 3H_2O & \rightarrow 2NH_4^+ + CO_2 + 2-\text{OH} \quad \text{eq. 1} \\
2-\text{OH} + H_2C_2O_4 & \rightarrow C_2O_4^{2-} + 2H_2O \quad \text{eq. 2} \\
Ca^{2+} + C_2O_4^{2-} & \rightarrow CaC_2O_4 \cdot H_2O \text{ (precipitate)} \quad \text{eq. 3}
\end{align*}
\]

PROCEDURE

Drying the Sample

Transfer about 1.5 grams of the combined calcium unknown from the vial to a weighing bottle. Place the weighing bottle in a 150 ml. beaker. Cover the beaker with a watch glass and place
them in the oven at 110° C for at least an hour to dry (it won't hurt if the sample is in the oven more
than an hour). Be sure to mark the beaker or the weighing bottle in order to identify the sample.
When the sample has dried for a sufficient period of time, remove it from the oven and let it cool in
the dessicator. Remember to keep the dessicator’s lid ajar until the sample is near room
temperature. Slide the dessicator top shut and allow the sample to equilibrate in the desiccator for at
least a half hour.

Determining the Constant Weight of Three Empty Filtering Funnels

Sign-out from the stockroom, three, medium porosity, sintered glass funnels. Number the
funnels with pencil on the ground glass patch. Set up a filtering system using a 500 ml filter flask,
a Gooch crucible holder, and the sintered glass funnel. Attach the filter system to a water aspirator
by way of a trap which may be found on one of the laboratory benches.

Prepare about 50 ml of 1:1 HCl by adding 25 ml of concentrated HCl to 25 ml of distilled
water. (ALWAYS ADD ACID TO WATER). Rinse the funnel with a total of 10-15 ml of 1:1
HCl, drawing small volume of the acid through the funnel by suction. Discard the HCl rinsings in
the collection flask. Rinse the funnel at least three times with deionized water, drawing a reasonable
amount of deionized water through the funnel. Slowly break the suction of the filtering flask.
Discard the water rinsings in the filter flask. Next, wash each funnel one at a time, with acetone
from an acetone-washing bottle. Rinse the funnel several times with a stream of acetone and draw
air through the funnel for about five minutes. Allow the funnel to stand in the air about twenty
minutes and obtain its weigh to the nearest 0.1 mg. Rinse the funnel with acetone a second time, let
it air dry and weigh it again. Repeat this procedure until you have a reproducible (constant) weight
within 0.4 mg.

The funnels should be stored in air, and not in a dessicator. It is best to store the funnels
in a beaker with a watch glass on top, inside your cabinet to avoid them becoming contaminated
by dirt and dust particles. Since the final precipitate cannot be stored in the desiccator, neither
should the empty funnels.

Dissolving the Sample

The analysis should be carried out in triplicate. Number three, 400 ml. beakers with pencil
on the ground glass patch. Into each beaker, weigh to the nearest 0.1 mg., by difference, 0.4-0.5
grams of the unknown calcium sample.

Solubilize each sample in the following way: to the beaker containing the known weight of
the unknown calcium sample, add about 20 ml. of deionized water from a graduated cylinder.
Using a medicine dropper, carefully add concentrated HCl dropwise until the effervescence (loss of
CO₂) ceases indicating that all of the sample has been converted to CaCl₂ and has gone into
solution. Do this carefully so that the sample does not spatter-out of the beaker. Stir the beaker
and use a hot plate to gently boil the solution to expel CO₂. Slowly boil the solution reducing its
total volume to about one fourth of its original volume. Do not heat to dryness. Then add enough
distilled water so that the total volume is about 150 ml.

Adjustment of pH

In order for the calcium to precipitate homogeneously, the pH must be carefully adjusted so
that it will gradually become basic as the urea decomposes. Place a special boiling rod with the
dimpled end (distributed by the teaching assistant) into each beaker. Add two drops of methyl red
indicator and stir; the solution should be red. (It is advisable that you carefully clean and rinse
these special boiling rods, since you do not know their previous history!) Add 5 M NaOH
dropwise from the dropping bottle provided until the solution just turns from red to yellow. Then
add a few drops of 1 M HCl until the solution just turns red again. Now add 4 ml concentrated
HCl and enough distilled water to bring the total volume to 200 ml as indicated by the marking on the beaker.

**Precipitation of CaC$_2$O$_4$·H$_2$O**

Heat the pH adjusted calcium solution almost to boiling using a hot plate. At the same time, heat 60 ml of 5% (NH$_4$)$_2$C$_2$O$_4$ almost to boiling in a small beaker using a different Bunsen burner. Slowly, and with stirring, add about 20 ml of the ammonium oxalate solution to each of the calcium solutions. Place the beaker containing the sample on a heat-proof mat and transfer it to a hot plate with the help of tongs. DO NOT CARRY A HOT BEAKER WITH TONGS UNSUPPORTED ON THE HEAT-PROOF MAT.

The temperature of the hot plate will be adjusted by the instructor. At this point, there will probably be no precipitate. If there is, see the instructor. A slight cloudiness may occur, however, and is normal. With the beaker on the hot plate and its solution warmed to about 50 °C, add about 6.0 grams of reagent grade urea and stir to dissolve completely. Leave the stirring rod in the beaker and cover it with a watch glass. The calcium oxalate will probably start to precipitate within a few minutes after the addition of urea. Leave the beaker on the hot plate to digest overnight. The instructor and/or teaching assistant will check the temperature and remove the beakers the following day. If on the second day, your solutions are still pink and are not yellow or colorless and do not contain a nice white precipitate consult the lab instructor.

Before beginning the filtration step, test for complete precipitation by adding a few drops of 5% (NH$_4$)$_2$C$_2$O$_4$ to the beaker from the dropper bottle provided. Look carefully for any cloudiness which would indicate that not all the calcium has been precipitated. Check with the instructor for the procedure to follow in the event of incomplete precipitation.

**Filtration and Weighing of Calcium Oxalate Precipitate**

When a constant weight for the funnel has been obtained, the precipitate can be filtered. First, cool a wash bottle filled with deionized water in ice; ice-cold water will be needed later to wash the precipitate. Then set up the filter assembly and start the suction. First, decant the clear supernatant solution into the funnel using the stirring rod to direct the flow of solution onto the filter funnel. This procedure assures that the filter’s pores do not immediately become clogged with precipitate hence slowing down the filtration step. Next, wash the precipitate in the beaker with several portions of ice-cold deionized water and decant the wash into the funnel. Next, transfer the bulk of the precipitate quantitatively into the funnel using the glass rod or a rubber policeman and, with the aid of squirts of the ice-cold, deionized water from the wash bottle.

After all of the calcium oxalate has been transferred into the funnel, wash the precipitate with small portions of ice-cold, deionized water until a few milliliters of filtrate gives a negative test for chloride when treated with two drops of acidified AgNO$_3$ solution. Avoid overwashing the precipitate as this will lead to solubility losses. (Note that oxalate ion also forms a precipitate with silver ion in the receiving portion of the filtering flask). (All rinse solutions may be disposed down the sink). When the precipitate has been sufficiently washed with deionized water, rinse it with a few squirts of acetone. Be sure to rinse away any droplets of deionized water from the glass funnel.

Draw air through the acetone-rinsed precipitate and funnel for no more than five minutes. Allow the funnel to stand in the air for about twenty minutes and weigh. Rinse the funnel and precipitate again with acetone and re-weigh. Repeat until weights are constant to within 0.4 mg. Obtain the weight of the precipitate by determining the weight gain of a particular filtering funnel.

**Microscopy**

Examine some of your homogeneously precipitated crystals under the microscopes set-up in the lab. Compare them with a sample of conventionally precipitated calcium oxalate provided by
the laboratory instructor. Make a rough sketch in your lab notebook of the size and shape of the two types of crystals. Comment in your laboratory report about your observations.

Upon completion of the experiment, discard the solid precipitate in a chemical waste bottle and wash out the sintered glass funnels with 1:1 dilute HCl as done at the beginning of the experiment.

**CALCULATIONS**

1. Assuming that all of the calcium has precipitated as CaC$_2$O$_4$ · H$_2$O, calculate the percentage of Ca in the unknown sample for each trial. The equation needed for these calculations will be presented in the lab briefing.

2. Calculate the standard deviation of your three trials.