Thermogravimetric analysis (TGA) analysis of Calcium Oxalate monohydrate

Method

Thermogravimetric analysis (TGA) is an advanced application of the analytical balance. The instrument consists of such a balance and an oven. The temperature in the oven can be scanned under computer control up to about 1000 ^{o} C. In addition, it is possible to flush the sample space with a gas of choice. We have currently both nitrogen and air available. The sample is typically suspended in a small basket. Platinum, Alumina, or aluminum can be used depending on the sample. Alumina basket will be used for this lab (should not use Aluminum for heating to temperatures above 600 degrees). The weight of the sample is recorded as a function of time and/or as a function of temperature if the latter is ramped at constant speed. The resulting data are a 1D data set of W(t) or W(T).

Most materials will decompose stepwise when heated in an inert atmosphere. It is possible to combine the technique with mass spectrometry or infrared spectroscopy to identify the gaseous products but often we can also do that from gravimetric considerations and stoichiometry. The compound you will study is calcium oxalate monohydrate then you will collect and analyze the thermogram of a dried and ground egg-shell sample.

Calcium oxalate monohydrate decomposes in three clearly separated steps that involve the successive release of water, carbon monoxide and carbon dioxide.

Experiment

Make sure the nitrogen tank attached to the instrument has enough gas by checking the regulator. Ensure that the regulator is open. The pressure provided to flush the TGA needs to be about 20 psi.

Let the instructor show you how to load the TGA. The wire from which the sample hangs is very fragile and once it is bent cannot be straightened. Therefore, always let the built-in sample robot suspend the basket from the wire.

First load the empty basket and *tare* the instrument. You only need a small amount (ca. 20 mg, spatula tip) of sample and the TGA will weigh it for you.

Program the Q50 software to ramp under nitrogen from room temperature to 950 ^{o}C at 20^{o} per minute. Check the data in the Analysis pack on the computer and go under File to export it to a memory stick as a spreadsheet file.

During the run determine the percentage weight loss of the first two events in the Data Analysis pack. You can click on the curve and then on the Δ icon. Then double click on the flat part before an event and double click on the plateau after it. Move mouse to open space and right-click. Opt for accept.

Calculate what percentage weight loss you would expect for the losses at the individual steps.

Carefully remove the final product from the TGA sample pan and label and set aside for FTIR analysis. Base on this first run and the obtained thermogram, determine the approximate temperatures at which subsequent runs should be stopped in order to generate and isolate the two decomposition intermediates.

Perform a TGA run on two more calcium oxalate samples using the same initial and ramp rate temperatures but program a 10 min hold at the end of each identified stopping temperatures to isolate the intermediates.
After each run, collect the intermediate, remove from the pan and set aside for FTIR analysis.

Note that TGA pans can be very hot and should be handled very carefully with tweezers because they can burn your skin and the oils from the skin can affect the performance of the instrument. Also be very careful not to damage the sample basket.

Data work up

Open your data file (full run) in Excel; it is space delimited. First make a graph of the weight against temperature. There should be four flat parts in the curve. For each flat part, select a range of values in the weight column, corresponding to a flat part in the curve and use the RLS macro to determine its robust average and its standard error by doing a 1D RLS procedure (Values should be reported in 2&15 format). If the RLS cannot handle the number of points, use Alt+F11 to go to the VBA editor and inspect the top of the RLS module Change the dimension statement Dim rres(1000), abrres(1000) to e.g. 3000 to accommodate more points.

Write three balanced equations for the three consecutive decomposition reactions.
For each decomposition step, calculate the extrapolated onset temperature (denotes the temperature at which the weight loss begins -see figure 1 for determining the onset temperature) and the temperature of peak weight rate change (this can be obtained from the 1st derivative curve which is easily displayed by selecting that option under the MATH drop-down list).

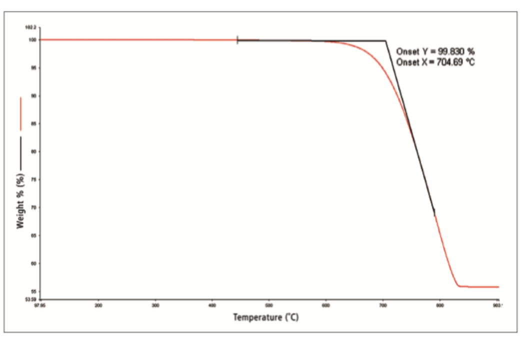

Figure 1. Graphical illustration of how to determine the onset temperature for each decomposition step.

Finally calculate the molar masses of the four solid compounds involved in the run and do a linear regression of the four masses against the molar masses. Is the intercept significant? How many moles of calcium did the sample contain?

Using the slope and intercept compute an estimated weight for each compound and determine the absolute value of the residual from the regression line. To get a better feeling for how important the residuals for each point (i.e. sqrt($(y_i-\langle y \rangle)^2$), you could divide the residual by the standard deviation for the straight line fit. Make a plot of the residuals against the molar mass. What does the result say about the chemistry? i.e. which determined weight shows the largest residual? Is this consistent with the chemical identity driven off by heating and the ease (energetically) of its removal?

Compare the IR spectrum of the eggshell sample to spectra generated from the calcium oxalate decomposition runs. Also determine from the eggshell thermogram the onset and peak temperature of the main decomposition step. Use this information to determine the identity of the key component in eggshell.

References:

Blazejowski, J.; Zadykowicz, B. Computational prediction of the pattern of thermal gravimetry data for the thermal decomposition of calcium oxalate monohydrate *J Therm Anal Calorim* **2013**, 113, 1497–1503

Pre-class Reading Links: TA instrument video resources for TGA Q50

TGA quick start:
https://www.tainstruments.com/tga-quickstart/

Universal analysis advanced e-training:
https://www.tainstruments.com/universal-analysis-advanced-e-training/

universal analysis quick start course:
https://www.tainstruments.com/universal-analysis-quickstart-course/