

Thermal Analysis

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TGA 8000 with Variable Rate TGA Software

Introduction

The technique of TGA is often used to determine the relative amounts of different components in a mixture based on their relative thermal stability. A better separation is favored by a thermal program using a slow heating rate, or one that essentially stops at the optimum temperature to allow the less stable component to decompose while the more stable one does not.

If time is available, one can heat the sample at a very low heating rate, e.g., 1 °C/min, to get the best possible resolution of the thermal events. If one knew exactly what temperature vs. time program provided the best separation, one could enter it into the Method Editor using a series of different heating rates and isotherms. Finding this out, however, may take trial and error testing, and the optimum separation program might be dependent on sample size or even on the surface area of the sample specimen.

These approaches are time consuming and not practical in today's laboratory work environment. A measurement from 30 °C to 850 °C would take 820 minutes.

Since time is money, it is worthwhile to utilize every resource to make analyses efficient. AutoStepwise™ TGA (1-3), and now Variable Rate TGA (VRTGA), are programming tools to optimize this thermal separation process. VRTGA has been requested by thermal analysis users and is now available in Pyris™ software.

How Variable Rate Analysis Works

Most weight loss processes are exponential in character, that is, they start off slowly, increase exponentially with increasing temperature, and then decay exponentially as the last remnants of material are transformed from solid to gas. The variable rate program takes advantage of this and works inversely; that is, as the weight loss reaction accelerates, the heating rate exponentially decelerates to allow more time for that weight loss process to go to completion. Then when the weight loss reaction comes to an end the heating rate returns to the original heating rate in an exponential fashion. Therefore, while the sample is losing weight the heating rate can be very slow, tenths of a degree per minute, to allow optimum resolution. This removes the requirement for the user to know in advance at what temperature the reaction starts and ends.

Variable Rate TGA Parameters

There are three parameters that define a VRTGA analysis: a threshold factor that determines how sensitive the algorithm is to a change in weight loss, a resolution factor that controls how steep the scan rate change is for a change in mass loss, and the initial heating rate, which also becomes the heating rate after the weight loss process completes.

Selecting the Threshold

For a quick survey scan the user can pick a fast initial scan rate (e.g., 40 °C/min or 50 °C/min), a moderate threshold (e.g., 5% weight loss per minute), and a resolution factor of 5 out of 10.

For many samples the result is a separation roughly equivalent to what would be obtained at a normal scan rate, such as 20 °C/min, but in a shorter period of time. For running a sample with a weight loss step that is a small percentage of the total weight, the threshold factor would be selected to be smaller to boost the sensitivity. Analyzing a sample with one weight loss that occurs over a few tens of degrees, one would pick a larger threshold parameter value since high sensitivity is not required. To optimize for an analysis having both weak and strong weight loss events, one can program two variable rate method steps that result in a switch from one set of VR parameters to another, better suited set.

Selecting the Resolution Factor

To effectively lengthen the time which the program spends at a slower scan rate, the resolution factor is increased to obtain a separation equivalent to that from a very slow scan rate. (See Figures 3 and 4).

When the weight loss event is over, the heating rate resumes gradually when a low value is selected for the resolution parameter, or quickly in the case of a higher resolution

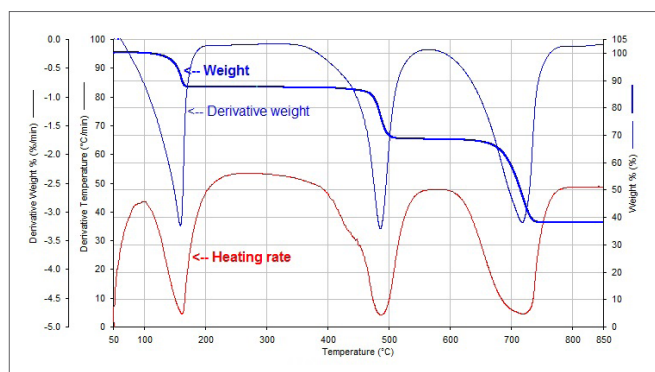


Figure 1. Variable Rate TGA: showing weight loss, rate of weight loss and heating rate versus temperature.

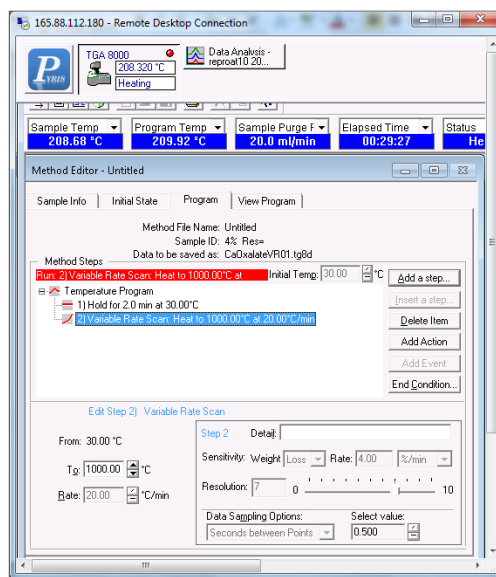


Figure 2. Input dialog for a Variable Rate TGA method step.

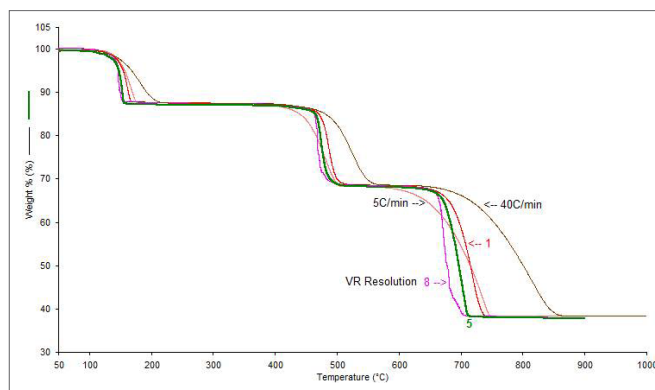


Figure 3. Calcium oxalate monohydrate showing effect of changing the resolution parameter, and also showing two fixed rate analyses.

parameter setting. In either case this avoids the unnecessary time taken up by slow scanning in a temperature region where there is little or no weight loss activity. However, notice that the higher value of the resolution parameter reduces the heating rate during weight loss regions and lengthens the overall test time. In the example of calcium oxalate there is a good resolution of the weight loss events under all the selected conditions. (This well characterized thermal decomposition sample was selected just to show the effect of changing method parameters.)

Applications

Copolymer and Polymer Blend Separation

Usually, the reason for selecting the use of a variable rate step is to better separate two weight loss components that are difficult to separate. For instance, the two weight-loss processes overlap because they each consist of a distribution of components having a range of thermal stabilities, and these two distributions overlap. Variable Rate TGA enhances the separation by letting the kinetics of the weight loss processes determine the temperature separation profile. For example, in the case of copolymers, such as ethylene vinyl acetate polyethylene copolymer, the polymer chain consists of alternating blocks of two polymers having different thermal stabilities. As the less stable polymer breaks down, the polymer chain is broken up, and this destabilizes the more stable component.

Figure 5 shows the example of an ethylene vinyl acetate copolymer run at 20 °C/min, and also using a variable rate scan (initial rate = 40 °C/min, Threshold = 2 %, and Resolution = 8.) The variable rate scan yields a more definitive separation by slowing the heat rate from 40 °C/min to less than 1 °C/min until the rate of the initial weight loss subsides.

Rubber Separation

TGA has long been used to quantify the essential components of rubber, namely softener, elastomer, carbon black, and inert filler, Figure 4. The first two components are determined in an inert atmosphere, then air or oxygen is introduced to burn the carbon and measure the remaining filler. The data in Figure 6 were obtained using two back-to-back variable rate programming steps. The first step utilizes a threshold of 3 % in order to capture the relatively slow weight change of the oil-extender weight loss, and the second step utilizes a threshold of 7 % and a resolution parameter of 3 to control the rate of oxidation of the carbon oxidation and to allow completion of this combustion step before the loss of CO₂ from carbonate in the filler. By using the variable rate step to slow the rate of combustion this approach can also improve sensitivity by allowing a larger sample to be used without concern that the combustion step will run away which can cause loss of ash. Figure 6 shows the results of two samples of differing mass which were run using the same method to show that although the temperature profile is somewhat different, the separation is similar.

Copper Sulfate Pentahydrate

Variable rate TGA is able to easily resolve three dehydration steps whereas a constant 5 °C/min scan only resolves two of the dehydration steps, in Figure 7. It should be noted that using a high value for the resolution parameter and a low sensitivity threshold makes the temperature program extremely sensitive to small changes in the weight loss. This can be used to amplify small changes in weight and thus produce a signature of the derivative weight loss of a mixture of hydrated materials in a mixture.

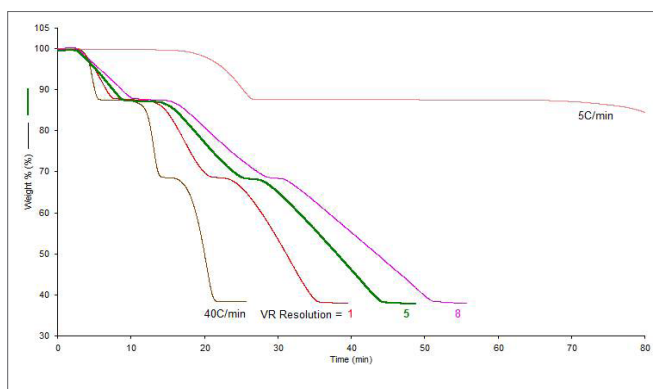


Figure 4. Same data as Figure 3 displayed versus time.

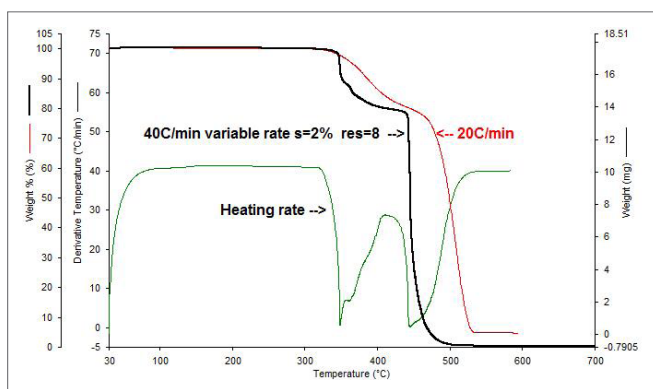


Figure 5. EVA/PE copolymer heated at 20 °C/min and at 40 °C/min variable rate, showing the variable scan rate.

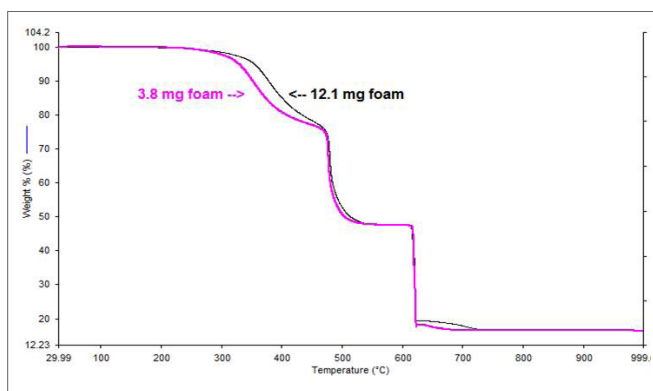


Figure 6. Rubber automotive foam (VRTGA threshold 3%; resolution, 7) .

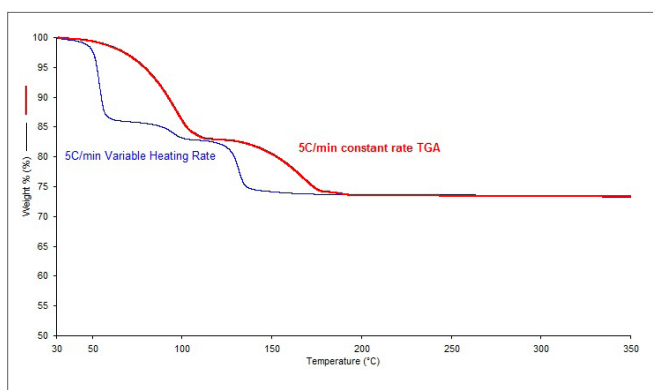


Figure 7. Copper Sulfate pentahydrate at 5 °C/min constant rate and 5 °C/min variable rate.

Summary

Variable Rate TGA is an analytical method that reduces the heating rate over weight-loss temperature regions. It has been implemented as a method step that can be used alone as a simple exploratory technique to ascertain the kinetically optimum temperatures to perform a stepwise separation. It can also be used as one of several steps, each optimally fine-tuned, to achieve a reliable, routine separation. As such, it is more than just a time-saving technique, it is a tool for improving and optimizing thermal separations.

ADVANTAGES OF VARIABLE RATE TGA

- Improves separation of thermal processes
- Relieves need to know temperature range of the weight loss process
- No time wasted in regions of no thermal activity
- Reduces violent weight loss events that might lose sample
- It improves weight loss sensitivity by allowing larger samples to be run
- VR-TGA Survey scan provides input for a stepwise method
- Variable rate analysis can produce a diagnostic fingerprint to characterize a mixture of components