TGA
Hi-Res™ Option

Operator's Guide

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Overview

This document describes how to use the High Resolution option for the Discovery TGA instrument.

Some of the benefits provided by the Hi-Res™ option are:

- Improved Transition Resolution
- Faster Survey Scans
- Enhanced Signature Analysis Capability
- Transition Temperatures Closer to Isothermal Values
- Increased Method Programming Versatility

The Hi-Res option provides three method programming steps (segments) which are used for the high resolution TGA capability. The new method segments are:

- High Resolution Ramp
- High Resolution Sensitivity
- Abort Next Segment

With the addition of these segments, method programming becomes more versatile and powerful than ever before. The Hi-Res ramp can be used alone as a simple single-segment method, or the method segments can be combined with more traditional segments, such as constant heating rate ramps and timed isothermal periods, for maximum programming flexibility.

What these segments do and how to use them to control TGA experiments and improve transition resolution is described in the following sections. For further details regarding creating methods, refer to the online help and documentation.

Using Hi-Res™ TGA

Background

TGA is particularly useful for observing the thermal decomposition of compounds. When individual thermal decompositions occur at well separated temperatures, quantitative information about sample composition can be obtained from the percent weight change at each transition. However, many TGA decomposition transitions overlap or appear drawn out in temperature due to the time-dependent nature of the reactions taking place. This overlap substantially reduces the ability to obtain an accurate measurement of weight change and reaction temperature.

It has long been known that using very slow heating rates will improve the separation of some overlapping transitions and, thus, increase the resolution of the TGA scan. Another technique to increase resolution is to increase furnace temperature until the onset of decomposition and then hold temperature isothermally until the decomposition is complete. After which, the temperature is raised again until the next decomposition begins, and so on until the final temperature of interest is reached. A third technique to increase resolution is controlling the furnace temperature in such a way as to maintain a preselected constant reaction rate (%/minute). This results in slower or even negative heating rates during a transition which gives the reaction more time to reach completion before the next transition is encountered.

The major drawback to these techniques is that they increase substantially the total time required for a measurement, thereby reducing laboratory productivity. Moreover, increasing measurement time often reduces the accuracy and reliability of the analysis. This is due to exposing the sample to high temperatures for long periods of time which may cause slow time-dependent changes such as oxidation and absorption, or exposure to changing ambient conditions such as humidity and pressure.

The TA Instruments Hi-Res™ Technique

The TA Instruments Hi-Res technique, dynamic rate TGA (DRTGA), differs from previous control techniques in that the heating rate of the sample material is dynamically and continuously modified in response to changes in the rate of decomposition of the sample so as to maximize weight change resolution. This technique allows the use of very high maximum heating rates during Hi-Res ramp segments while avoiding transition temperature overshoot. Typical Hi-Res ramps often take the same or less time to complete than a comparable constant heating rate experiment run at a lower heating rate, while providing improved resolution.

The Hi-Res™ Ramp Segment

The new Hi-Res ramp segment varies the heating/cooling rate of the furnace in response to changes in the rate of decomposition of the sample so as to improve weight change resolution. The new segment has the following format:

Ramp <rate>˚C/min res <res_setting> to <temp>˚C

where:

<rate> is the maximum ramp heating rate (0.01 to 200˚C/minute)

<res_setting> is the resolution setting (-8.0 to +8.0)

<temp> is the ramp final temperature (-200 to 1000˚C)

example:

Ramp 50.00˚C/min res 4.0 to 800.00˚C

The Hi-Res ramp segment operates similarly to the traditional constant heating rate ramp segment, except that the heating rate is varied dynamically during the ramp in response to the derivative of weight change (%/minute). As percent/minute increases, heating rate is decreased. As percent/minute decreases, heating rate is increased. The heating rate is constrained to the range 0.001˚C/minute (minimum) to the maximum specified in the ramp segment. The resolution setting is a unitless number used to select the most useful band of percent/minute values for proportional heating rate control.

Higher resolution settings select lower percent/minute values, and generally result in increased resolution and longer experiment times. Lower settings have the opposite effect.

Resolution settings may be selected anywhere in the range of -8.0 to +8.0. Positive settings indicate that dynamic rate mode is to be used during the ramp. Negative settings indicate that constant reaction rate mode is to be used. More details on using each mode is covered in the Advanced Hi-Res Techniques section.
Positive resolution settings are the most universally useful settings and the least likely to have undesirable side effects. Although there are no hard and fast rules about which resolution setting to use for a given experiment, there are some general guidelines which will be helpful.

It has already been stated that higher resolution settings usually provide better resolution results and lower settings the reverse. The closer the setting is to zero the larger the derivative of weight change (%/minute) must be for a reduction in heating rate to occur. In fact, a resolution setting of exactly zero completely disables the application of the Hi-Res® technique, resulting in a normal constant heating rate ramp at the maximum rate specified.

A resolution setting of +1.0 will produce a TGA scan at 50˚C/minute that roughly approximates the resolution obtained by a constant heating rate scan at 20˚C/minute. In other words, you can zip through baseline sections of your scan at a higher heating rate while slowing down only for transitions and still get the resolution of the slower heating rate scan. For scans which contain a large amount of baseline this can result in very significant overall time savings with no loss of resolution. The same speed/resolution relationship applies to other heating rates as well.

Higher resolution settings apply the Hi-Res technique more aggressively by reacting to smaller percent/minute values. Some general rules-of-thumb for selecting resolution settings are as follows:

1. If you are uncertain what the resolution setting and heating rate should be, then try setting +3.0 and 50°C/minute. (Negative resolution settings are covered in the Advanced Hi-Res Techniques section.)

2. When trying to obtain better resolution, try progressively higher resolution settings, 1.0 at a time, while leaving the heating rate fixed.

3. The most useful resolution settings are 3.0 to 5.0 because they cover the most commonly encountered bands of percent/minute during typical decompositions. If your decompositions tend to be explosive in nature, with large percent/minute peaks (greater than 50 %/minute), or if you wish to minimize experiment time, then use settings less than 3.0. If your decompositions are very gradual (less than 0.5 %/minute peaks), or if it is important to limit the rate of decomposition, try settings greater than 5.0.

The most useful maximum heating rates are 10 to 50°C/minute for positive resolution settings. However, other values are perfectly acceptable when required by the needs of the experiment.

Use lower heating rates when transitions are very closely spaced in temperature, or if the sample material reacts very rapidly. A higher heating rate conventional ramp can be used to skip over baseline sections in order to shorten experiment time. Generally speaking, you no longer need to use very slow heating rates, less than 5°C/minute, because the dynamic rate Hi-Res™ technique automatically reduces heating rate with the accompanying improvement in resolution.

There are no special method programming constraints on Hi-Res™ ramp segments. They may appear anywhere in a method that a normal ramp could appear. The maximum ramp rate, resolution setting and final temperature of an executing Hi-Res ramp may be changed via the Modify Segment feature on the controller.

Selecting the resolution setting is covered in greater detail in the Advanced Hi-Res™ Techniques section.

Calcium Oxalate Example Scans

In this example, five TGA scans of calcium oxalate monohydrate ($CaC_2O_4.H_2O$) were run in nitrogen to compare the results using conventional TGA and Hi-Res™ TGA. In all cases a single ramp or Hi-Res ramp segment from ambient to 800°C was used for the method.

Figures 1 and 2 show the results of constant heating rate scans at 20°C/minute and 1°C/minute. Figures 3, 4 and 5 show the results of Hi-Res scans at 50°C/minute with resolution settings 3.0, 4.0 and 5.0 respectively. Figure 6 shows a composite plot of the derivative of weight loss for each of the five scans. The derivative smoothing window for all plots was set to 5°C.

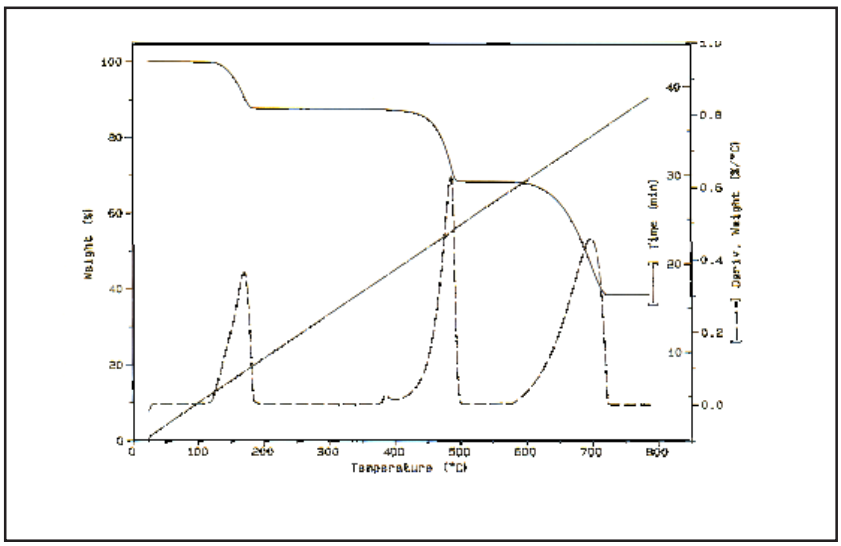


Figure 1

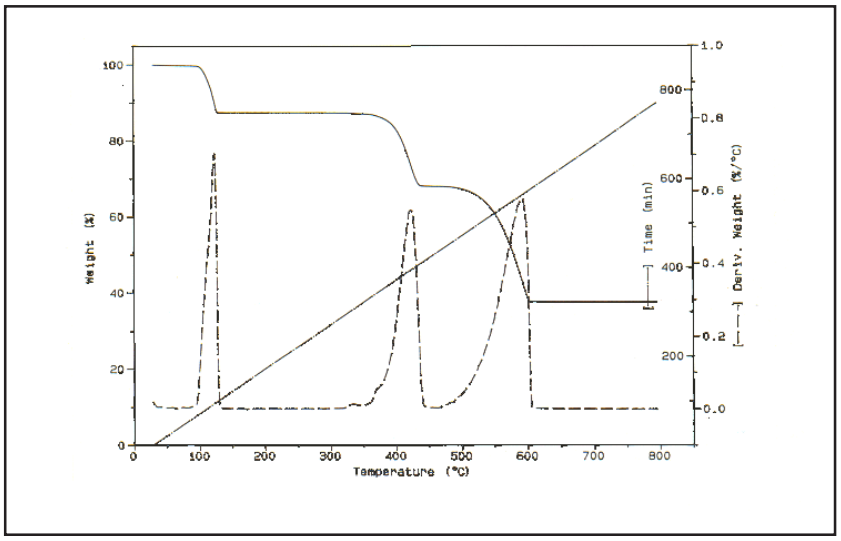


Figure 2

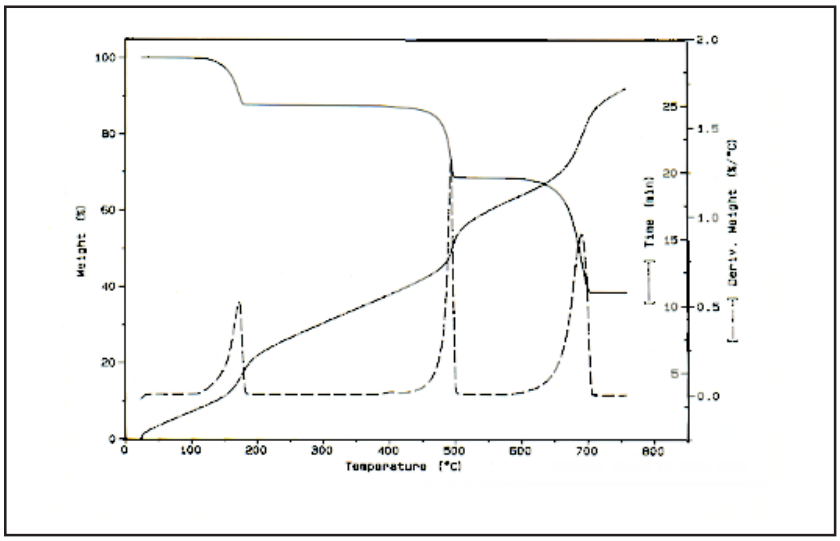


Figure 3

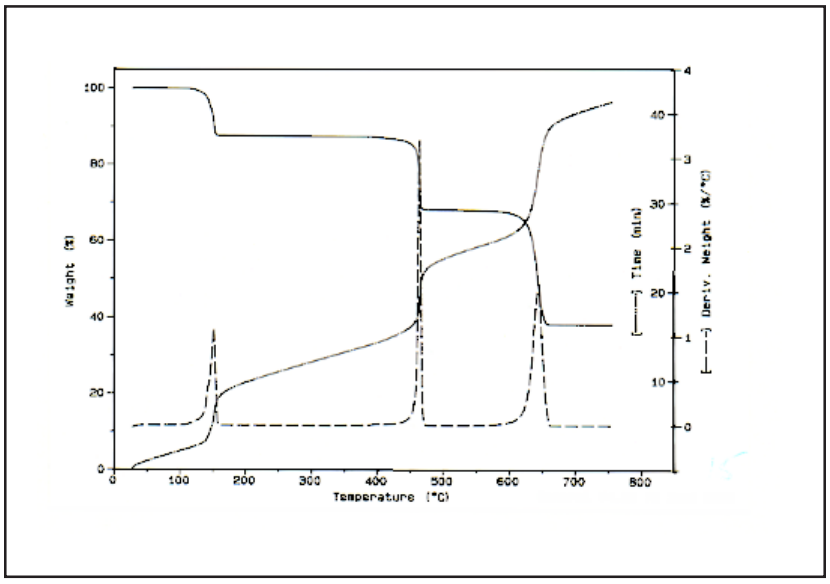


Figure 4

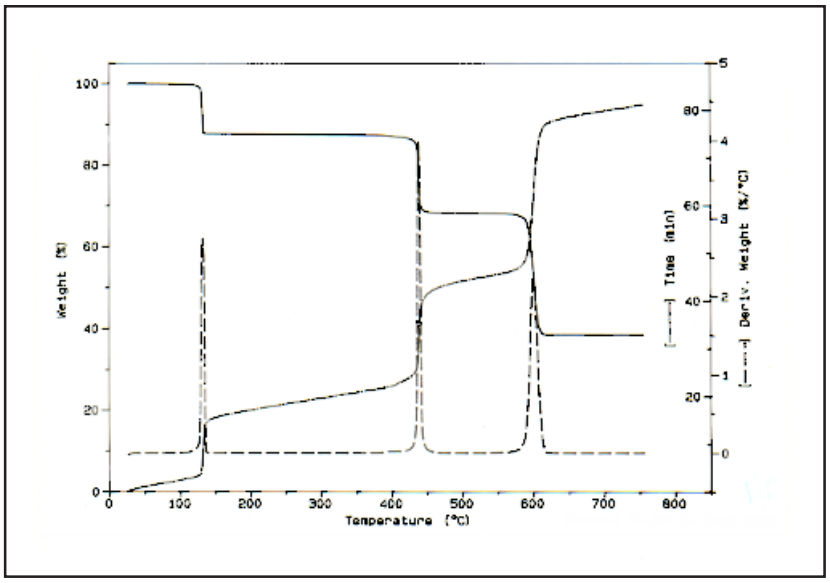
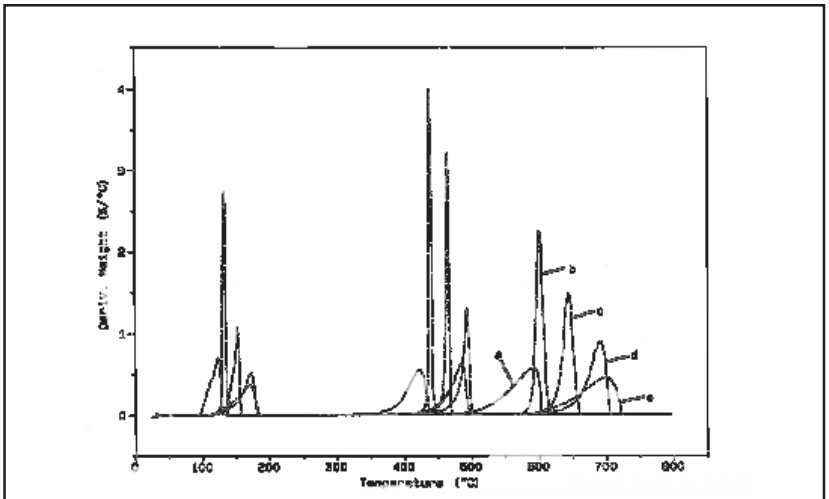


Figure 5

As can be seen in these examples, calcium oxalate has three well resolved transitions corresponding to the loss of water (1st weight loss), carbon monoxide (2nd weight loss) and carbon dioxide (3rd weight loss). Comparing the 20°C/minute and the 1°C/minute scans (Figures 1 and 2), we see some improvement in resolution of the water loss (1st transition), but little improvement in the other two transitions.

Note that the transition temperatures in the slower scan are shifted to lower temperatures as expected. The 20°C/minute scan took 39 minutes and the 1°C/minute scan took nearly 13 hours to complete.

Comparing the results of the two constant heating rate scans to the Hi-Res™ scans in Figures 3, 4 and 5 we can see that the resolution 3.0 scan (Figure 3) gave comparable results in two thirds the time of the 20°C/minute scan. The resolution 4.0 scan (Figure 4) gives much improved resolution in about the same time as the 20°C/minute scan, and the resolution 5.0 scan gives a dramatic improvement in only twice the time.



(a) 1°C/min, Normal Ramp; (b) Res 5.0, 50°C/min; (c) Res 4.0, 50°C/min; (d) Res 3.0, 50°C/min; (e) 20°C/min, Normal Ramp

Figure 6

Figure 6 shows a plot of the weight percent derivatives from each of the calcium oxalate scans overlaid on the same scale. Note how much taller and narrower the Hi-Res peaks are compared to the conventional scans. We can also clearly see that transition temperature is reduced by increasing the resolution setting. This effect is normal because with progressively higher resolution settings, transitions are constrained to lower decomposition rates which can only be maintained at lower temperatures.

As can be seen in these simple examples, the Hi-Res ramp segment is easy to use and provides significant resolution improvement, in the same time frame as conventional constant heating rate TGA. The following section on Advanced Hi-Res™ Techniques contains valuable information about additional Hi-Res methods and adjustments which will help you obtain maximum performance from this powerful analysis tool.

Advanced Hi-Res™ Techniques

This section discusses in greater detail how to use the Hi-Res features and gives specific advice which may be helpful in setting up your own experiments. As with any new analytical tool, there is a learning period required during which the user becomes familiar with the options and adjustments and gains knowledge about what can and cannot be expected from the analysis.

What Can Be Resolved and What Cannot?

"Will Hi-Res TGA improve the resolution of my transitions?" This is one of the first questions asked by most people when they are introduced to Hi-Res TGA. It would be wonderful, if the answer were always an unqualified "yes". Unfortunately, there are some applications where resolution enhancement will be minimal. Therefore, some criteria for selecting likely candidates for resolution improvement is needed. Outlined below are some guidelines which can be employed whenever a new material is considered, or when a sample is tried and no resolution improvement is obtained. (It is worth noting that substantial productivity gains are still possible, even if transition resolution is not improved.)

Unresolvable Transitions

The Hi-Res techniques provide useful tools to improve transition resolution of many sample materials, but some materials will show little or no resolution improvement. This is because these materials have transitions which cannot be separated by time and temperature alone. The transitions are usually overlapped such that the components of interest decompose at or very near the same temperature and at approximately the same rate of reaction. For these materials it may be necessary to employ other techniques separately or in conjunction with TGA, such as vacuum, switching purge gases, semi-pressurized sample containment, or evolved gas analysis.

There are some general rules-of-thumb which will help you decide if the material you are working with will be a successful candidate for resolution improvement. First, do the components of the sample material decompose at sufficiently different temperatures? This can often be determined by running a slow heating rate survey scan of the material at 1°C/minute and comparing the result to a 20°C/minute scan of the same material. Generally, the temperatures of transition will be lower in the slower scan, but if there is no observable improvement in separation of the components, then it is likely that Hi-Res™ TGA will not produce a significant separation of the components either.

Always consider purge gas to be a factor when running survey scans or heating rate trials. Generally, nitrogen and air are the most common choices for purge. In some cases, transitions which appear to be one large weight loss in which nitrogen will separate in air due to reaction with oxygen in the purge stream. Switching from air to nitrogen may help to eliminate oxidation which tends to counteract a simultaneous weight loss. A few materials are reactive with nitrogen and are better run in argon. Also, consider the purity and moisture content of the purge gas. Adding or removing moisture may change the rate or nature of the reactions taking place. When the nature of the sample is relatively unknown, it is wise to repeat scans using both air and nitrogen to see if any transitions appear or disappear, or shift in temperature or weight loss.

Another test is to determine if the components of the sample material have significantly different rates of decomposition. If so, it may be possible to improve resolution using stepwise isothermal heating, or using the constant reaction rate Hi-Res mode (negative resolution settings). To find out, run a conventional constant heating rate ramp up to the transition temperature and then hold isothermally. After the decomposition is complete, plot the derivative of weight percent versus time and look at the shape of the curve. If both components of the transition are decomposing at about the same rate, then the curve will be a continuous exponential decay. However, if the curve appears to be a rather rapid exponential decay, followed by a very gradual and somewhat constant rate of weight change, then the components have different reaction rates and improvement in separation is probably achievable.

A third technique, which may help to improve resolution, is to control the atmospheric pressure surrounding the sample while in the furnace. This can be done by placing the sample in a semi-sealed container such as a hermetic DSC pan with a very small pin hole (0.1 mm diameter or less) or in a sample cup with a lid. When the sample starts to react, the evolved gas will build a slight vapor pressure inside the sample container. This pressure may reduce or stop one or more of the overlapped reactions and, thereby, allow completion at a higher temperature. To make this test, simply try running the sample using a Hi-Res ramp with and without the sample containment to see if a difference in separation can be observed. Generally, the temperature of reaction will shift to a higher temperature, even if no improvement in separation occurs. The pressure containment technique is particularly helpful when using constant reaction rate Hi-Res mode (negative resolution settings).

Selecting a Hi-Res™ Technique

The Hi-Res TGA option consists of not one, but several techniques, which all have the common characteristic of controlling the thermal experiment based on changes in the sample weight. Both absolute weight change and the rate of weight change can be utilized. These capabilities add a whole new dimension to TGA experiments.

Some general guidelines have already been presented in the previous sections on how to set some of the parameters involved in using Hi-Res TGA. In the next section we consider more closely why one technique may give better results than another, and present additional guidelines for selecting techniques and setting parameters.

Dynamic Rate Hi-Res Ramp

In dynamic rate Hi-Res mode, one or more Hi-Res ramp segments are used with positive resolution settings. In this mode, the furnace heating rate is varied between a fixed minimum and the maximum specified in the ramp segment, but is never reduced to zero (isothermal). A mathematical function is used to relate the rate of weight change (%/minute) to the sample heating rate (°C/minute). Dependant variables to this function are resolution setting, sensitivity setting and maximum heating rate. Independent variables are both short and long-term rates of weight-change (%/minute), time and temperature. The result is the ability to directly compute the appropriate heating rate for the current weight change conditions.

Because the dynamic rate Hi-Res mode reduces heating rate smoothly and only when necessary, it is the fastest and most reliable of the various techniques. This mode gives good results with most temperature separable transitions. It is preferred for fast survey scans of unknown materials over wide temperature ranges. If no other criteria exists to select a Hi-Res technique, then dynamic rate is the preferred choice.

Constant Reaction Rate Hi-Res™ Ramp

In constant reaction rate Hi-Res mode, one or more Hi-Res ramp segments are used with negative resolution settings. In this mode the heater control system varies the temperature of the furnace as required to maintain a constant preselected rate of weight change (%/minute). Whenever the rate of weight change exceeds the percent/minute threshold, the heating rate of the furnace is reduced, even to the point of cooling if necessary. When percent/minute falls below the threshold the heating rate is increased up to the maximum specified for the ramp segment. Transition resolution is improved because sample heating is reduced or reversed during transitions allowing them to complete at the selected reaction rate before moving on to the next transition. Figure 10 shows a good example of a material (sodium bicarbonate) which was analyzed using a constant reaction rate ramp at 10°C/minute with resolution setting -4.0.

When used with semi-pressurized sample containment, constant reaction rate mode becomes even more powerful. The vapor pressure which builds up inside the sample container limits the rate of reaction of the sample. This allows the reaction to complete at a nearly constant rate and temperature. The reaction progresses more uniformly throughout the sample because vapor pressure gradients in and around the sample material are substantially reduced. The onset of higher temperature reactions is effectively suppressed until the completion of lower temperature reactions.

Constant reaction rate mode is preferred for any sample where it is important to limit or control the rate of reaction. These may include pyrotechnics, self-heating reactions, auto-catalyzing reactions and gas diffusion reactions. Constant reaction rate mode is also a good choice when it is important to accurately determine the transition temperature at a given reaction rate.

Another area where constant reaction rate heating can be helpful, is when the sample material exhibits a relatively large and somewhat constant background weight change, onto which is superimposed a relatively small transition. If the decomposition rate threshold is chosen to be close to the background percent/minute at the maximum heating rate, then the heating rate will only be changed significantly when the smaller transition occurs.

Derivative of weight change curves that are plotted versus temperature may appear cyclic and have negative peaks as well as positive ones. This effect is caused by the automatic application of cooling whenever the rate of weight change (%/minute) exceeds the specified set point. In many cases the appearance of the derivative curve can be improved by increasing the derivative smoothing window in the data analysis program.
Constant reaction rate mode works best at lower heating rates (1 to 10°C/minute), where significant reaction rate and transition temperature overshoot can be avoided. Usually several scans of the same material are required to determine the best reaction rate threshold to use. If the sample material is very reactive, or it is important not to overshoot the selected reaction rate, then even lower maximum heating rates may be required.

This is particularly true for very small reaction rates (less than 0.1 %/minute)

Since the heater control system concentrates on a very narrow band of reaction rates, transitions with slightly different reaction rates in the same scan are often given very different treatment. For example, a transition which falls short of the %/minute threshold may be passed at a fairly high heating rate, with results similar to conventional constant heating rate TGA.

Whereas, a transition which just crosses the %/minute threshold may cause a significant reduction in heating rate or even reversal of the heating process. The two transitions, although similar in nature, may appear quite different on a plot of weight change versus sample temperature. This effect can be observed in the weight loss curve of Figure 10. Note that the surface water loss at 85°C and the bicarbonate transition at 100°C are treated quite differently. This effect is most noticeable at low sensitivity settings. The effect can be reduced or eliminated by using multiple ramp segments in the method, each tailored to the needs of specific transitions. Increasing sensitivity setting may also be helpful. (See the section entitled "Adjusting Sensitivity Setting in Constant Reaction Rate Mode").

Weight Gain Experiments

It is important to note that, while most TGA work involves decomposition analysis, some applications involve weight gain such as in oxidation studies. The Hi-Res™ heating control techniques apply equally well to weight gains as to weight losses. In this case, the absolute value of the weight change signal is used for control. Weight gains of up to 200% can be accommodated. The rates of weight gain (%/minute) and their relationship to heating rate, resolution setting and sensitivity setting are exactly the same as for weight loss. No special parameters or controls are needed for Hi-Res weight gain analysis. Combinations of weight gain and weight loss in the same TGA scan are handled automatically. It is important to recognize, however, that when weight gain and weight loss transitions overlap, the resultant weight change is additive and may not be separable.

Signature Analysis

For many materials it will not be possible to separate overlapped transitions sufficiently to allow quantitative analysis of weight change. However, this does not mean that no useful information can be gained from the TGA scan of the material. It is frequently the case, particularly in quality control work, that an exact determination of sample composition is not needed. Instead, the requirement is only to identify which material of a group of known standards the unknown sample most closely resembles. Another usage is to identify lot-to-lot variation from an acceptable standard. In both of these cases the location, size, and shape of the derivative of weight change peaks of the TGA scan, or the weight curve itself, is used to create a unique pattern or "signature" of the sample material. Signature scans of standards and the unknown material are then compared to make the identification or "accept/don't accept" decision.

Since the various components of a sample, when run separately, usually decompose or evolve at unique and reproducible rates and temperatures, it is often felt that it should be possible to determine exactly what is in an unknown mixture by comparison to a library of known TGA scans of the individual components. Unfortunately, this usually does not work because the various components of a mixture typically interact with one another, so that the resultant scan is unlike either material run separately. The interactions can be chemical or physical. Some examples are evolved gases from one decomposition which slow or accelerate the decomposition or evolution of another component (*e.g.*, CO_2 from oxidizing carbon). Molecular attractions prevent a more volatile component from evolving when expected, and at the same time hasten the evolution of another less volatile component (*e.g.*, chain linkage in polymer blends). The physical matrix of the mixture may retard the evolution of a more volatile component, which then evolves at a higher than normal temperature and at a slower than normal rate (*e.g.*, oil evaporating from rubber). Or the components may react chemically at elevated temperatures and produce new compounds which decompose at different temperatures than the individual components.

Sample Quantity and Orientation

As with conventional constant heating rate TGA, sample quantity and orientation in the sample holder can be important during Hi-Res® experiments. This is particularly true if the sample is not homogeneous (*e.g.*, a laminated sheet or coated surface). With these types of samples it is wise to try scans with different surfaces exposed. Be aware that chopping or grinding the material may produce an entirely different result since physical or chemical properties may be altered.

Exposed Surface Area

Exposed surface area is often important. When samples melt they usually spread out over the bottom surface of the sample container. This will expose more or less surface area, depending on whether the original configuration was a single block (area typically increases) or a powder (area typically decreases). Usually with open sample pans it is best to try to maximize exposed surface area at all times so that evolved gases escape quickly and reactions proceed uniformly. This suggests the use of small powdered or thin samples which are uniformly distributed in the sample vessel. When semi-pressurized sample vessels are used the issue of exposed surface area is far less important.

Generally, sample sizes in the range of 5 to 15 milligrams are recommended. If the material is self heating or auto-catalytic, then smaller sample quantities may help with heating control. (This is particularly important for constant reaction rate Hi-Res mode.) On the other hand, larger sample quantities (50 to 100 mg) are recommended for reactions in which a very small weight change (less than 1 percent) is being measured. For maximum weight resolution it is advisable to keep sample weight below the TGA weight range change at 100 mg.

A problem with very large samples, which decompose rapidly and almost completely, is that the furnace purge may not be able to remove all of the evolved components and some contamination of the furnace wall and cooling jacket may result. This may affect the remainder of the experiment or future scans.

Bubble Formation

Whenever medium to large sample quantities are being run, use caution in thermocouple placement. Some materials, particularly polymers, will form a "skin" on the outer surface of the sample as it is heated which inhibits mass transport of the more volatile components.

These samples form bubbles which can rise up and touch the end of the thermocouple, ruining the experiment and possibly contaminating the thermocouple. Just as the largest chewing gum bubbles are produced by blowing slow prolonged breaths, the largest gas bubbles form in samples which are gradually heated. For this reason bubble formation is more of a concern for Hi-Res™ than conventional TGA.

Another effect of bubble formation is a sudden small unexpected change in weight and accompanying spike in the percent/minute curve as the bubble bursts. An excellent example of bubble noise can be seen in the scan of ethylene-vinyl acetate in Figures 7 and 8. In Figure 7 the effect of bubble formation and bursting can be seen as a sudden drop in weight at about 400°C during the second weight loss. This appears in the derivative curve as a peak shoulder. In Figure 8 we can clearly see the formation and bursting of several large bubbles in the percent/minute curve between 65 and 85 minutes into the run. Again, these effects tend to be more noticeable in Hi-Res TGA because larger bubbles form due to the slow heating process. The best solution to bubble noise is to decrease resolution setting and/or increase maximum heating rate. Reducing sample size may also help.

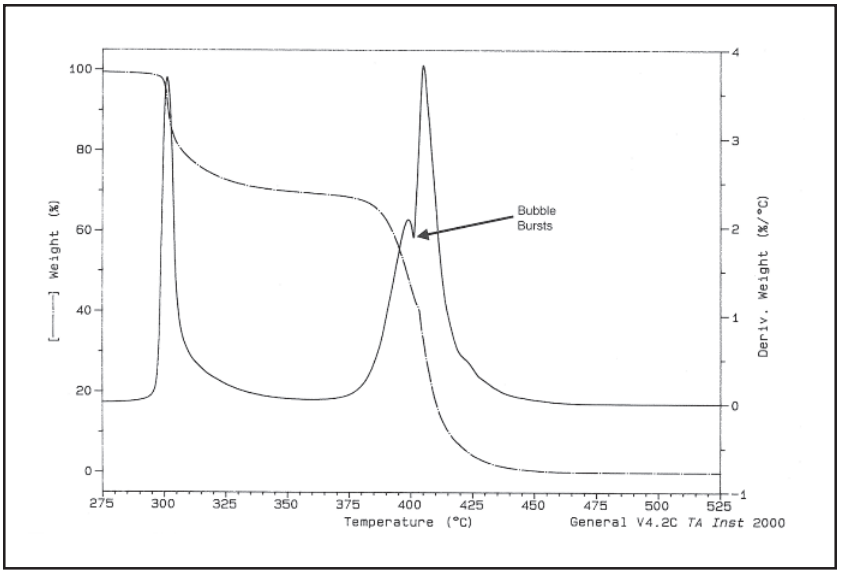


Figure 7

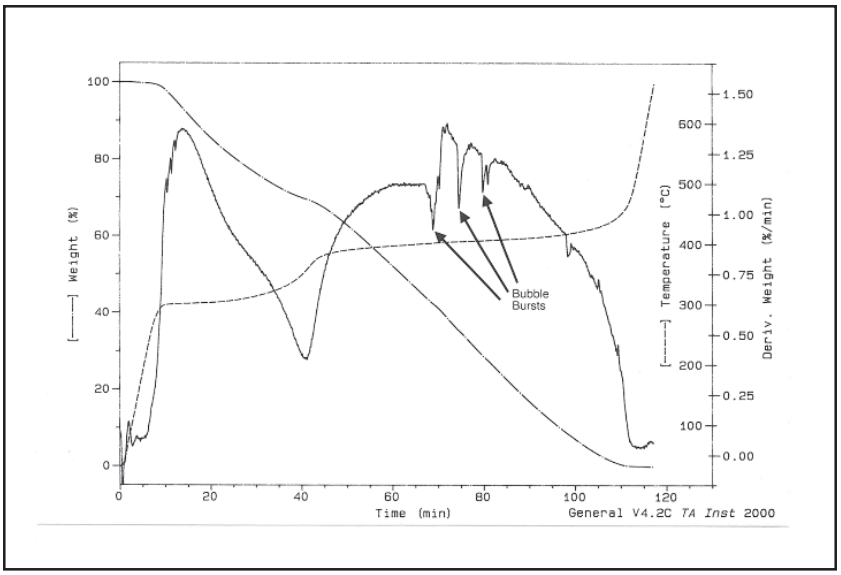


Figure 8

Thermocouple Placement

Generally, the thermocouple should be placed 2 to 5 mm above the bottom of the sample container (1 to 4 mm above the edge). Placement 1 mm above the edge is recommended for most applications. Longer distances will not degrade heater control and are sometimes helpful in reducing any adverse effects of sample self-heating or bubble formation.

Data Analysis Effects

Hi-Res™ TGA, due to its technique of changing heating rates dynamically, causes very significant non-linearity of data points across transition regions when plotted versus temperature. This is not a problem when making plots, but when automatic limit selection is used during data analysis report generation the analysis program can sometimes become confused about where to place the limits. This situation can be identified by curve tick marks and tangent lines which are poorly placed on the weight curve or may even be plotted off of the curve.

The difficulty is caused by the fixed size of the transition onset and endset windows (the first and last 12.5% of the analysis region). The data analysis program assumes that data points are uniformly distributed throughout this region. If the number of data points in the baseline portion of a window is very small compared to the number of points in the sloped portion of the window (the usual case with Hi-Res scans) then the tangent lines will be excessively weighted toward this cluster of points and may be nearly vertical or even fall off the curve entirely.

Improved results can be obtained by moving the transition start and stop limits farther away from the transition so that the onset and endset windows remain completely on the baseline portion of the curve. If this fails to help, the transition tick marks can be placed manually on the curve.

Derivative Plots

Another data analysis problem caused by unequally spaced temperature data points is unusually shaped or flattened derivative plots versus temperature. This is due to the assumption that data points are equally distributed over a moving window (the smoothing window) used to compute the derivative. If the derivative smoothing window is too wide, derivative peaks will flattened and apparent resolution will be reduced. If the window is too narrow, derivative peaks will be needle sharp and noisy.

The default smoothing window is 0.2 minutes for derivatives with respect to time (%/min and %/min/min) and 10°C for derivatives with respect to temperature (°C/min and °C/min/min). For typical Hi-Res™ TGA scans, the quality of derivative plots with respect to temperature can be improved by decreasing the temperature window to 5°C. If extremely sharp results are desired, try a smaller window. Less than 1°C is not recommended. The smoothing window for time does not normally need adjustment. If the time derivative seems particularly noisy, try increasing the window to 1 minute.

In conventional constant heating rate TGA, the plot of percent/minute and the plot of percent/°C are essentially identical because there is a direct linear relationship between time and temperature. Percent/minute is conventionally chosen for transition peak analysis and plotting. With Hi-Res TGA there is no linear relationship between time and temperature because the heating rate is constantly changing. When plotting the derivative of weight change versus temperature for a Hi-Res TGA scan, you should use percent/°C. A plot of percent/minute versus temperature can still be useful for locating minor transitions and determining the rate of reactions.

Adjusting Heating Rate

Heating rate has long been used to control transition resolution. The typical thermal analyst makes most runs at 20°C/minute and drops down to 5 or 1°C/minute for hard-to-resolve transitions, or just to see if there is anything else interesting going on that might have been missed in the faster scan. 1°C/minute scans are generally not routine due to the enormous amount of time required to run them.

With Hi-Res™ TGA the heating rate is varied automatically to give the benefit of slow heating rates during transitions and fast rates during baseline. However, it is still necessary to specify a maximum heating rate. This is because in Hi-Res TGA, just as in constant heating rate TGA, the maximum heating rate affects the results of the experiment and, as such, is an important adjustment to consider.

Heating rate adjustment is particularly critical if the transitions of an overlapped group are very closely spaced in temperature. At 50°C/minute the normal temperature lags in the TGA furnace can be enough to overshoot the first transition, which may reduce separation from the other transitions in the group. This will be most noticeable when the percent/minute baseline preceding a rapid transition is relatively constant and several orders of magnitude below the peak rate of the transition. Running at 20°C/minute instead of 50°C/minute is recommended for most routine work using positive resolution settings particularly if only one scan can be made of each unknown material. Less than 10°C/minute is usually not required.

For negative resolution settings the selection of heating rates is usually quite different because reaction rate overshoot must be minimized. Generally, 1, 2, 5 and 10°C/minute are the most useful rates to use with negative resolution settings. Try 5°C/minute to start.

An important difference between the dynamic rate (positive resolution setting) and constant reaction rate (negative resolution setting) Hi-Res mode, is that the maximum heating rate selected is only an upper limit in negative mode, but it is a gain factor in positive mode. In other words, in negative mode the maximum heating rate is irrelevant to heating control, except when the reaction rate drops to such a low level that heating rates higher than this maximum limit are required to maintain the selected percent/minute.

In negative mode, as long as the maximum heating rate is high enough to allow completion of the transition at the selected percent/minute set point, and not so high as to cause percent/minute overshoot, transitions will appear largely the same from one heating rate to the next. A word of caution, however: *always keep in mind that the background (baseline) rate of weight change will be accelerated at higher maximum heating rates.* This will move the background percent/minute closer to the control point you have selected with the resolution setting. If noise is present in the background percent/minute, it may fool the control algorithm into thinking a transition is starting and result in a premature reduction in heating rate to avoid predicted set point overshoot. In extreme cases, heating rate cycling can occur, particularly at high sensitivity settings. (See Figure 13.) To cure this problem reduce maximum heating rate and/or sensitivity setting.

Adjusting Resolution Setting

The purpose of the resolution parameter is to select the range of percent/minute values over which the heater control system will vary heating rate in response to changes in the rate of weight change. In dynamic rate mode (positive resolution settings) the range of percent/minute values selected by each resolution setting is fairly wide (about two orders of magnitude). This width is adjustable using the sensitivity parameter.

In constant reaction rate mode (negative resolution settings) the resolution setting specifies the percent/minute value that will be used as the control set point for furnace heating. In this case the system will adjust heating rate as required to maintain this constant rate of weight change. Table 1 (on the next page) shows the negative resolution settings and their associated percent/minute values.

Table 1
Negative Resolution Settings and Associate Values

Res	%/min	Res	%/min	Res	%min	Res	%/min
-0.1	28.2	-2.1	2.82	-4.1	0.282	-6.1	0.0282
-0.2	25.1	-2.2	2.51	-4.2	0.251	-6.2	0.0251
-0.3	22.4	-2.3	2.24	-4.3	0.224	-6.3	0.0224
-0.4	20.0	-2.4	2.00	-4.4	0.200	-6.4	0.0200
-0.5	17.8	-2.5	1.78	-4.5	0.178	-6.5	0.0178
-0.6	15.8	-2.6	1.58	-4.6	0.158	-6.6	0.0158
-0.7	14.1	-2.7	1.41	-4.7	0.141	-6.7	0.0141
-0.8	12.6	-2.8	1.26	-4.8	0.126	-6.8	0.0126
-0.9	11.2	-2.9	1.12	-4.9	0.112	-6.9	0.0112
-1.0	10.0	-3.0	1.00	-5.0	0.100	-7.0	0.0100
-1.1	8.91	-3.1	0.891	-5.1	0.089	-7.1	0.0089
-1.2	7.94	-3.2	0.794	-5.2	0.079	-7.2	0.0079
-1.3	7.08	-3.3	0.708	-5.3	0.071	-7.3	0.0071
-1.4	6.31	-3.4	0.631	-5.4	0.063	-7.4	0.0063
-1.5	5.62	-3.5	0.562	-5.5	0.056	-7.5	0.0056
-1.6	5.01	-3.6	0.501	-5.6	0.050	-7.6	0.0050
-1.7	4.47	-3.7	0.447	-5.7	0.045	-7.7	0.0045
-1.8	3.98	-3.8	0.398	-5.8	0.040	-7.8	0.0040
-1.9	3.55	-3.9	0.355	-5.9	0.036	-7.9	0.0036
-2.0	3.16	-4.0	0.316	-6.0	0.032	-8.0	0.0032

The process of initially picking, and then adjusting resolution setting, is not exacting or calculated. It is based largely on experience and some general guidelines. This is because no single resolution setting will give dramatically different results from all the others. The change from one number to another is rather gradual. Another reason you might wish to experiment with more than one setting is that some materials react differently from others to increasing or decreasing the resolution setting. This is due to the time as well as the temperature-dependant nature of transitions, and to the interaction between the rate of weight change (%/minute) and heating rate (°C/minute). As percent/minute increases heating rate is reduced by the control algorithm, but the reduction in heating rate usually causes an accompanying reduction in percent/minute, and vise versa. Therefore, attempting to directly compute optimal resolution settings from percent/minute information gathered from previous runs becomes a very questionable and usually frustrating experience.

Let us then consider what guidelines and rules-of-thumb we can use to help make the selection process easier. As stated earlier in the section on Hi-Res® ramps, if you do not know what resolution setting to start with, try resolution +3.0 and 50°C/minute heating rate. This will give a rapid scan with moderate application of the Hi-Res™ heating technique. Results should be at least as good as a 20°C/minute conventional scan of the same material, and will usually be better. If time permits, it is often helpful to have a constant heating rate 20°C/minute scan of the material available for comparison.

Useful Resolution Settings

After some experience with Hi-Res TGA, you will find that the most useful resolution settings fall within the range +3.0 to +5.0 for the positive numbers and -3.0 to -5.0 for the negative numbers, and that adjustment by +/- 0.5 is usually adequate. This is similar to the situation with heating rates. You can adjust heating rate to any value from 0.01 to 200.0°C/minute in steps of 0.01°C but most people use 1, 5, 10, 20 and 50°C/minute exclusively because a finer adjustment does not produce significantly different results. With this guideline alone we have reduced the number of resolution settings to deal with from 80 to only 5 for each Hi-Res mode while covering the majority of materials of interest.

The next step is how to proceed after the first Hi-Res run is complete. If the first run was made at resolution setting 3.0, try the second one at 4.0. Generally, increasing resolution setting by a whole number will increase the time to complete the TGA scan by a factor of 2 to 5 times. Therefore, you must consider whether you can afford the added run time as well as the extra setup time. This balance between increased run time and adequate resolution is usually the determining factor on what resolution setting to live with.

The benefit to having more range and "resolution" to the resolution setting than seems to be necessary, is that on a rare occasion a material requires a very fine adjustment or an extreme treatment. Don't forget that the maximum heating rate is a factor in determining resolution as well as the resolution setting.

Lower resolution settings allow materials which already have well-separated transitions to be analyzed at super high heating rates such as 200°C/minute with excellent resolution in a fraction of the time required at a constant rate of 20°C/minute. Resolution settings above 5.0 are useful when exact decomposition temperatures are needed ,or when the decompositions are explosive in nature, or when overlapped transitions are extremely close but highly temperature selective.

The effect of adjusting the resolution setting in dynamic rate mode while holding other experimental factors constant can be seen in Figure 13.

Temperature Calibration

TGA temperature calibration is useful if accurate transition temperatures are required. The major causes of temperature inaccuracy in a TGA are thermal gradients between the sample thermocouple and the sample being studied. The magnitude of these gradients is proportional to heating rate. The Hi-Res® TGA techniques inherently reduce thermal gradients by slowing down the heating rate during transitions.

Another way to reduce the effect of thermal gradients is to temperature calibrate the TGA. The general procedure for temperature calibration is found in the online help and documentation. Temperature calibration involves analyzing a magnetic standard to determine its curie temperature. The curie temperature corresponds to the extrapolated endpoint on the "S" shaped thermal curve.

However, when the calibration is intended for use with Hi-Res™ TGA experiments (*i.e.*, dynamic rate, constant reaction rate or stepwise isothermal), then a slow heating rate conventional ramp of 5°C/minute or less should be used for calibration. A faster ramp rate is only used when calibrating for constant heating rate experiments. The reason for this is that the Hi-Res heating control system reduces the heating rate during transitions.

Hi-Res™ Transition Temperatures

The TGA provides precise weight measurements coupled with relative temperature information. The resolution setting of a Hi-Res® ramp controls the reaction rate of sample transitions. It is reaction rate, more than anything else, which will determine the apparent transition temperature of a decomposition reaction.

The shift in measured transition temperature caused by changing resolution setting can easily be an order of magnitude larger than the thermal gradients you are trying to correct with calibration. This effect can be clearly observed in the mixture of bicarbonates example (Figure 13). In light of this fact, it is acceptable in many cases to simply not use temperature calibration when employing the Hi-Res TGA techniques for decomposition analysis.

Hi-Res™ Sensitivity Segment

The Hi-Res sensitivity segment sets an additional parameter associated with Hi-Res ramp segments which can be used to adjust the response of the Hi-Res temperature control algorithm. This is sometimes necessary because of the wide variation in decomposition mechanisms of typical sample materials. This segment has the following format:

Hi-Res sensitivity <sens_setting>

where:

<sens_setting> is the Hi-Res sensitivity setting (1.0 to 8.0)

example:

Hi-Res sensitivity 2.0

Hi-Res sensitivity segments execute immediately when encountered in a method and simply set the sensitivity setting to the new value provided. The last value set is used for all subsequent Hi-Res ramps until a new value is set. If no Hi-Res sensitivity segment has been encountered in the method before the execution of a Hi-Res ramp segment, then the default sensitivity (1.0) is used.

The sensitivity setting is a unitless number, ranging from 1.0 (lowest sensitivity) to 8.0 (highest sensitivity). The setting is used by both the dynamic rate (positive resolution setting) and the constant reaction rate (negative resolution setting) modes of the Hi-Res ramp segment. There is no limit to how many times the setting can be changed during a method. Increasing sensitivity setting tends to increase experiment time.

Understanding Sensitivity Setting

The TGA Hi-Res™ control algorithms have been pretuned to respond correctly to most transition situations with the default sensitivity setting of 1.0. This means that in most cases it will not be necessary to adjust sensitivity setting at all. The key is knowing when and how to make the adjustment.

It is easy to confuse resolution setting and sensitivity setting since both values can affect the resolution of the TGA scan. However, there is a simple way to think of the difference between the two parameters.

Resolution setting controls the temperature at which the transition will occur (*i.e.*, how far from the theoretical isothermal decomposition temperature) by selecting the reaction rate (%/minute) at which heating rate is reduced. The closer the reaction is to the isothermal decomposition temperature the lower the reaction rate and the longer the reaction will take. You will find that you can use the resolution setting to literally move the measurement of transitions on the temperature axis. (See Figure 13.)

Sensitivity setting controls the response of the Hi-Res system to changes in the rate of reaction (%/minute). Larger sensitivity settings cause the system to be more reactive or "sensitive" to small changes in the rate of the reaction. Lower sensitivity settings dampen this response. Generally, it is best to adjust resolution setting first with sensitivity set to a low value, and then after a good result is obtained, try increasing sensitivity to see if any resolution improvement can be obtained.

Use caution when adjusting sensitivity since over adjustment can cause oscillation or anomalies in the weight versus temperature curve.

Adjusting Sensitivity in Dynamic Rate Mode

In dynamic rate Hi-Res™ mode (positive resolution settings), the sensitivity setting is used to further increase the resolution of some transitions once an appropriate resolution setting has been determined. This is accomplished by narrowing the range of percent/minute values over which the heating rate is proportionally varied. Higher sensitivity settings result in progressively narrower percent/minute ranges and generally increased resolution.

In this mode the resolution setting selects the general neighborhood of percent/minute values that will drive changes in furnace heating rate. For example, resolution setting 3.0 selects the neighborhood of approximately 1.0 to 20.0%/minute for most of the variation in heating rate. Whereas, setting 4.5 selects 0.1 to 2.0%/minute. Sensitivity setting controls the relative width of this range. Setting 1.0 allows use of the full range. Setting 2.0 reduces the range to about one half the full range. Setting 3.0 to about a third and so on up to 8.0. In general, higher sensitivity settings bring the furnace to the transition temperature more quickly but then tend to remain at that temperature longer. In other words, higher sensitivity settings bring the control closer to stepwise isothermal heating. (See "Stepwise Isothermal Heating" in the section on using Abort Segments for more information.)

The recommended procedure for adjusting sensitivity setting for dynamic rate mode is to start with a sensitivity setting of 1.0 and adjust resolution setting to get the best separation possible in the desired time frame. Then increase sensitivity to 2.0, 4.0 and 8.0 to see if a useful improvement in resolution results.

It is possible that no improvement in resolution will result. This is usually caused by overlapped transitions which are weakly temperature-dependant and strongly time-dependant. In this case, it doesn't matter how precisely we control at a specific temperature, the individual components of the sample material are all going to decompose more or less together in the neighborhood of the decomposition temperatures we have selected via the resolution setting. About all we can do is lengthen or shorten the total time of decomposition by selecting larger or smaller resolution settings.

The effect of changing sensitivity settings in dynamic rate mode can be seen in Figure 14.

Adjusting Sensitivity in Constant Reaction Rate Mode

In constant reaction rate Hi-Res™ mode (negative resolution settings) the sensitivity setting is used to adjust the heater control system to minimize transition temperature overshoot and heating control fluctuation. Higher sensitivity settings result in decreased percent/minute overshoot and tighter control at the beginning of transitions. Lower settings have the opposite effect.

In this mode sensitivity setting is used to adjust the response of the heater control system to changes in the rate of weight change (%/minute). For materials that react gradually, low sensitivity settings are generally preferred because they help dampen noise and greatly reduce the possibility of control cycling. However, when it is very important to avoid percent/minute overshoot, or if the sample is highly reactive then higher settings will be required. The problem with too high a sensitivity setting is that control cycling or heating rate "ringing" may occur (see Figure 11).

The recommended procedure to adjust sensitivity setting for constant reaction rate mode is to start with a sensitivity setting of 1.0 and observe the transition for percent/minute overshoot and control cycling. If overshoot is acceptable, no further adjustment is needed. If overshoot is excessive, increase sensitivity setting by 1.0 and recheck overshoot and cycling. Continue increasing sensitivity until the results are acceptable or until control cycling becomes excessive.

If no satisfactory sensitivity setting can be found, the problem may be too low a resolution setting or too high a heating rate. Try a higher resolution setting (larger negative number) to reduce the percent/minute set point and rerun the experiment. Set points in the range of 0.1 to 1.0%/minute (resolution settings -5.0 to -3.0) generally give the best results.

If the percent/minute overshoot is primarily associated with the first transition of a group of overlapped transitions, the problem may be too high a maximum heating rate. Try reducing the heating rate of the Hi-Res ramp segment by one half and rerunning the experiment. Heating rates in the range of 1.0 to 5.0°C/minute generally give the best results.

When heating rates higher than 5.0°C/minute are used, proper adjustment of sensitivity setting becomes critical to maintaining smooth heating control. The default sensitivity of 1.0 is usually too low at these higher heating rates and typically results in significant transition temperature overshoot and heating control "ringing" as shown in Figure 9. At high heating rates a setting of 3.0 or 4.0 will give better results for most materials. The improvement can be seen in Figure 10. If sensitivity setting is adjusted too high, then continuous control cycling may result as shown in Figure 11. With some experimentation, an optimal setting can usually be found. When very high heating rates are used (greater than 10/°C/minute) it may be impossible to completely eliminate control ringing. However this should not affect the quantitative measurement of weight loss for the transition.

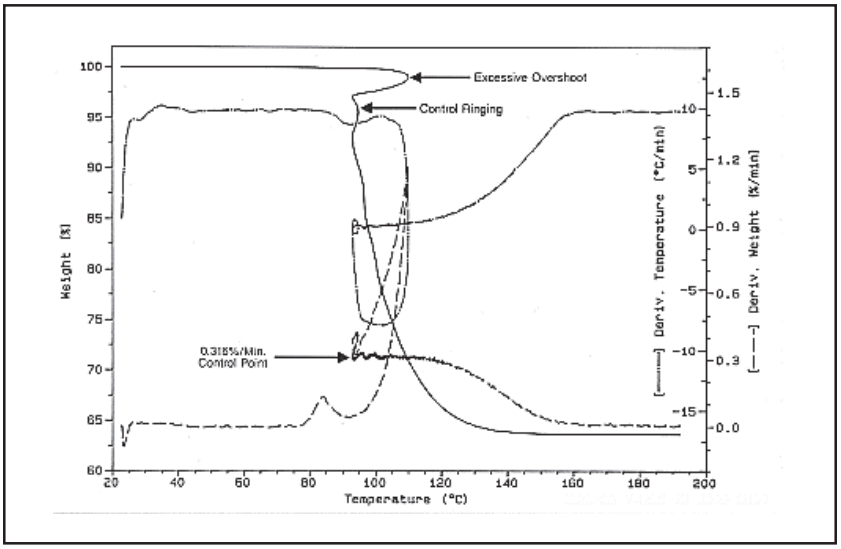


Figure 9
Sensitivity Setting Too Low

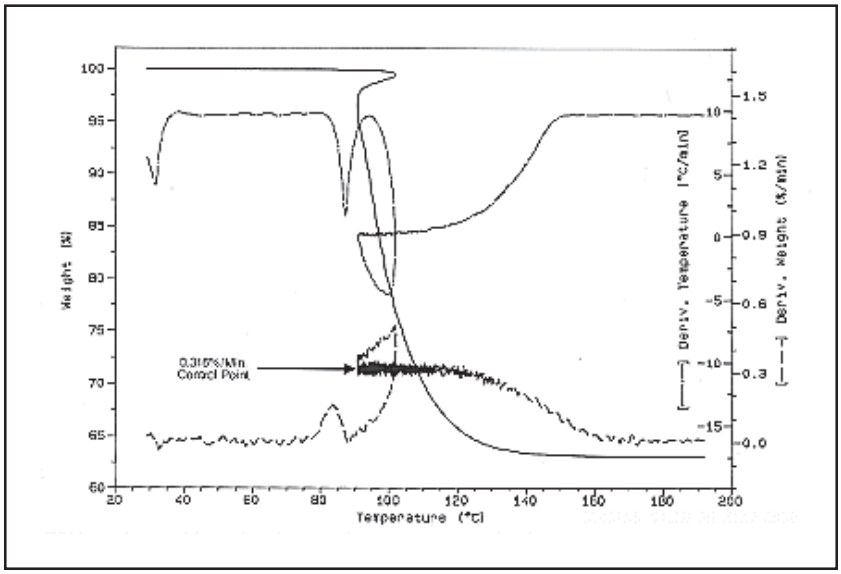


Figure 10
Correct Sensitivity Adjustment

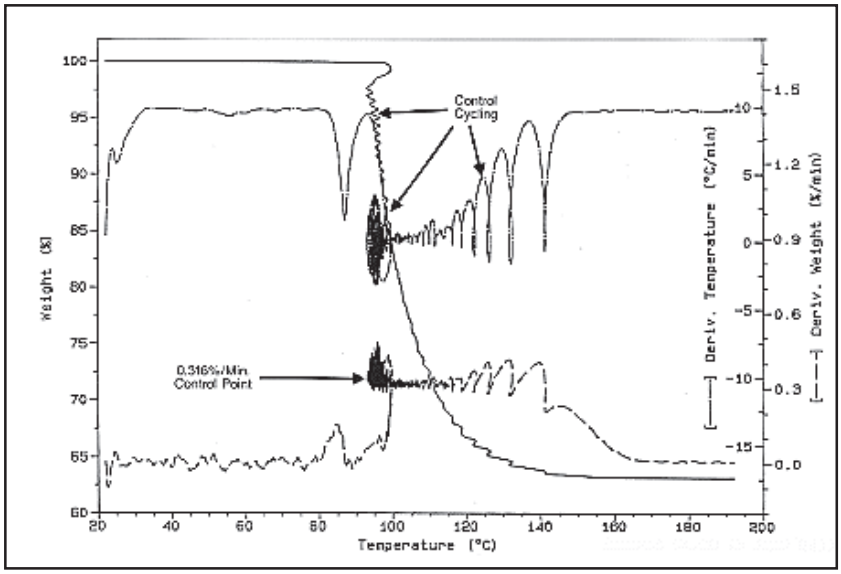


Figure 11
Sensitivity Setting Too High

Abort Segment

The abort segment provides a mechanism to skip over or terminate other method segments when specific weight change conditions are met. This segment has the following format:

Abort next seg if <signal> <condition> <value>

where:
<signal> is the real-time measurement used to decide whether to abort or not (weight % or weight %/minute)
<condition> is the limit condition for aborting ("<" or ">")
<value> is the abort limit which is compared with the real-time signal

example:

Abort next seg if % < 20.0

Abort segments execute immediately when encountered in a method and simply establish conditions for testing the next segment. The specified limit, designated by the **<signal>**, **<condition>** and **<value>** parameters, is tested before and during the execution of the next method segment. If the limit is reached at the beginning of a segment, that segment is skipped and method execution continues with the next segment. If the segment following the abort segment is equilibrate, initial temperature, ramp, Hi-Res ramp, isothermal or step, and the limit has not been reached yet, the limit will be tested at the rate of 2 times per second until the segment terminates normally or the limit is reached. If the limit is reached during the execution of a segment, the remaining portion of the segment is skipped. Method execution then continues with the next segment in the method.

The conditions for determining whether limits have been reached for each type of limit are as follows:

% - If the condition operator is "<" and the sample weight percent is less than or equal to the limit percent, or if the condition operator is ">" and the weight percent is greater than or equal to the limit percent, then the limit is reached. Values greater than 100% are permitted to accommodate weight gains.

%/min -If the condition operator is "<" and the derivative of sample weight percent is less than or equal to the limit percent/minute, or if the condition operator is ">" and the derivative of weight percent is greater than or equal to the limit percent/minute, then the limit is reached. Negative values indicate weight gain and positive values indicate weight loss.

Abort segments are very versatile because they can be used in front of any method segment (including other abort segments) to dynamically change the execution of a method. For example, an abort segment can be used to control the switching of a purge gas or activation of an event relay based on the rate of reaction or the amount of weight loss. An abort segment in front of a repeat segment provides a mechanism to terminate a loop prematurely. Abort segments can be used to customize a method for a particular material by allowing different ramp and/or isothermal segments to be used for each tran-sition region without regard to specific temperature limits. Abort segments can be used to control data storage so that file size is minimized by turning off storage or increasing sampling interval during baseline sections of a scan.

Abort segments provide a convenient mechanism for shortening experiments after the data of interest has been collected. For example, if a heating ramp is used to analyze a material which has two weight losses and the only data of interest is the percent weight loss during the first transition, then an abort segment can be used to terminate the ramp after the beginning of the second weight loss by specifying a "%" limit condition. This is particularly useful for Hi-Res ramps because the reduced heating rate during a weight loss causes the majority of the transition to occur during a very narrow temperature range, making termination by final temperature difficult to predict.

Stepwise Isothermal Heating

Another useful TGA technique which can be implemented with abort segments is transition- controlled *stepwise isothermal heating*. This process consists of heating a sample via a ramp segment until a certain rate of weight change is detected, and then switching to an isothermal segment to hold constant temperature until the transition has completed. Then the sample heating is continued until the next transition is detected, whereupon, isothermal holding is again initiated, and so on until the final temperature is reached.

The stepwise heating technique can be easily implemented by placing a ramp segment followed by an isothermal segment into a "repeat to final temperature" loop, and preceding the ramp and isothermal segments with abort segments. The abort segment preceding the ramp is setup to terminate the ramp when the "%/minute" is greater than a specified limit. The abort segment preceding the isothermal segment terminates the holding period when the "%/minute" is less than a second limit. An example of this type of method is shown below.

1: Abort next seg if %/min > 0.5
2: Ramp 10 ˚C/min to 700 ˚C
3: Abort next seg if %/min < 0.05
4: Isothermal for 500 minutes
5: Repeat segment 1 til 700 ˚C

The "%/min" limit for the isothermal segment is selected to be equal to the baseline rate of weight change encountered during the onset of the transition of interest via a normal constant heating rate scan of this material. (Be sure to use the same ramp rate as that selected for stepwise heating.) The "%/min" limit for the ramp segment is selected to be about an order of magnitude greater than that selected for the isothermal segment (but not more than the maximum rate of weight change encountered during the transition of interest). The ramp final temperature and the repeat final temperature are set to the final experiment temperature. The isothermal time is set to an arbitrary time, which is sufficiently large such that the segment will not terminate until the percent/minute limit has been reached.

Stepwise heating often improves transition resolution because transitions are time dependent as well as temperature dependent. Stepwise heating gives transitions more time to complete, thereby, reducing overlap with neighboring transitions.

To get the maximum benefit from stepwise heating it will be necessary to run several TGA scans to properly "tune" the reaction rate thresholds used to start and stop heating. Relatively slow heating rates are generally required to prevent transition overshoot. A rough rule-of-thumb is to use a heating rate which is about one tenth the transition temperature difference between the transitions being resolved. For example, if the transitions are separated by 10˚C then use 1˚C/min as the heating rate prior to, between and following the transitions. If precise reaction temperatures are important, then slow heating rates should always be used prior to encountering transitions of interest even though they may be well separated in temperature, and the "%/min" limit for the ramp segment should be set closer to the limit for the isothermal segment. To avoid excessively long experiments, higher heating rate ramps or equilibrate segments can be used to skip over baseline portions of the scan.

A disadvantage to stepwise heating is that most experiments take much longer in total time to complete than by a conventional constant heating rate scan. Another disadvantage of stepwise heating is that the decision to leave isothermal mode and continue heating is somewhat arbitrary and may lead to incorrect assumptions about the number and size of transitions.

This is particularly true for materials which have transitions that are overlapped even at very slow heating rates (such as the sodium/potassium bicarbonate mixture in the Examples section). As a general rule, stepwise isothermal heating cannot be used to reliably separate transitions which cannot be separated by conventional TGA at very slow heating rates.

Another problem to watch out for with stepwise heating is the creation of anomalies in the weight loss versus temperature curve. These appear as small unexpected secondary weight losses following a larger transition. These anomalies can be caused by two factors.

The first cause is using too high a heating rate in the ramp which follows the transition. Any small amount of sample material which did not finish decomposing during the transition will now quickly decompose due to the rapid elevation of the furnace temperature. This will cause the decomposition rate (%/minute) to rise substantially. If the rising decomposition rate crosses the abort threshold for the ramp segment then a second isothermal period will be introduced which will appear on the weight loss versus temperature plot as a small unexplained transition. Generally it is best to use the same heating rate on both sides of a transition. This rate can then be accelerated if desired after the furnace temperature is some distance from the transition.

The second cause of anomalies is leaving the isothermal holding period prematurely during a transition because the percent/minute threshold for aborting the isothermal segment was set too high. This situation leaves a significant amount of undecomposed sample material which now accelerates its rate of decomposition. As in the case of too high a ramp rate, the increasing temperature causes the remaining sample to quickly decompose which raises the rate of weight loss (%/minute) to a high level and either triggers another isothermal hold period or shows up as a backside shoulder on the weight loss curve.

An example of using stepwise isothermal heating is shown in the following "Hi-Res™ TGA Examples" section.

Hi-Res™ TGA Examples

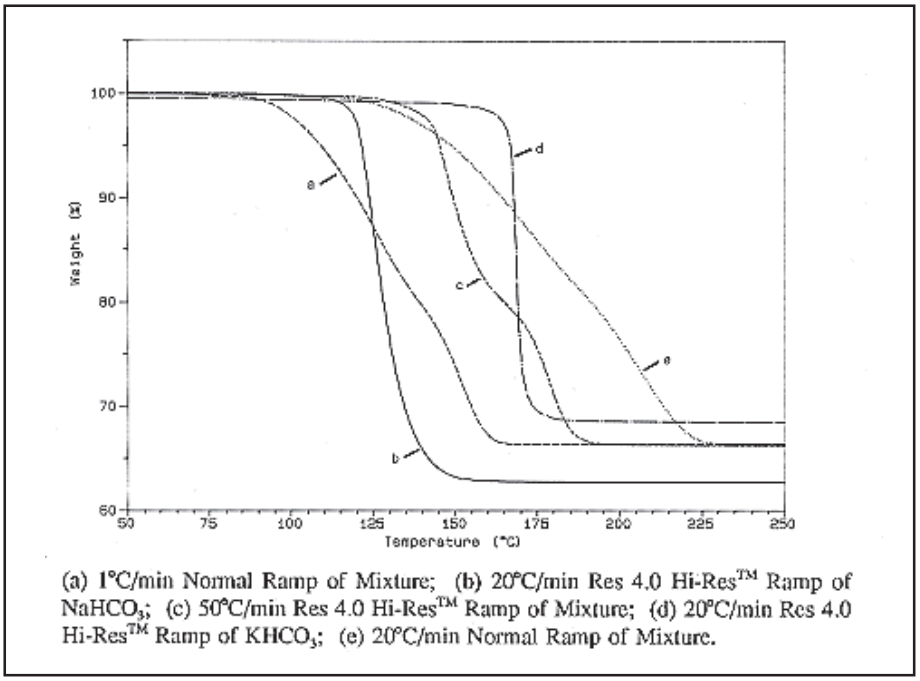
Included in this section of the manual are example TGA scans of common materials. These examples can be used to compare the results of using Hi-Res TGA heating control with the results of conventional constant heating rate TGA. Where possible the effects of using the different Hi-Res modes and parameters are shown.

Mixture of Bicarbonates

A mixture of potassium bicarbonate (potassium hydrogencarbonate) and sodium bicarbonate (sodium hydrogencarbonate) was chosen to demonstrate the effects of different Hi-Res techniques and parameter settings. The individual bicarbonates decompose to carbonates between 100°C and 200°C with the simultaneous release of CO_2 and H_2O. Potassium bicarbonate decomposes at approximately 50°C higher temperature than sodium bicarbonate. When mixed together the decompositions of the two bicarbonates are overlapped in temperature and are very difficult to resolve. You can easily make this sample yourself by thoroughly mixing equal parts (by weight) of finely powdered potassium bicarbonate ($KHCO_3$) and sodium bicarbonate ($NaHCO_3$). Inadequate mixing or large granule size will reduce weight loss reproducibility. Note that potassium bicarbonate is very hygroscopic. The mixture must not be exposed to ambient humidity for long or a significant surface water transition will become evident between 70°C and 100°C which will affect the overall weight loss percentages. When mixing and using this sample be sure to keep the sample supply containers tightly capped. Load the TGA quickly and use a dry purge gas (air, nitrogen or argon). Dry air purge at 100 mL/min was used for all example scans shown. Sample sizes varied from 20 to 40 mg. Small variations observable in weight loss reproducibility in the example scans are largely due to the non-homogeneity of the sample mixture and variations in ambient humidity from run to run.

Dynamic Rate Scans

In Figure 12 (below) we have overlaid the individual bicarbonate decompositions (curves b and d) along with the decomposition of the mixture by conventional TGA (curves a and e) and by dynamic rate Hi-Res® TGA (curve c). Reducing the heating rate of the mixture from 20°C/minute (curve e) to 1°C/minute (curve a) gave a very slight improvement in resolution. Comparing these results to the 50°C/minute Hi-Res scan we observe a significant improvement in resolution with Hi-Res TGA in about twice the time of the 20°C/minute scan, and about one tenth the time of the 1°C/minute scan. The method used for all scans was a single ramp segment.

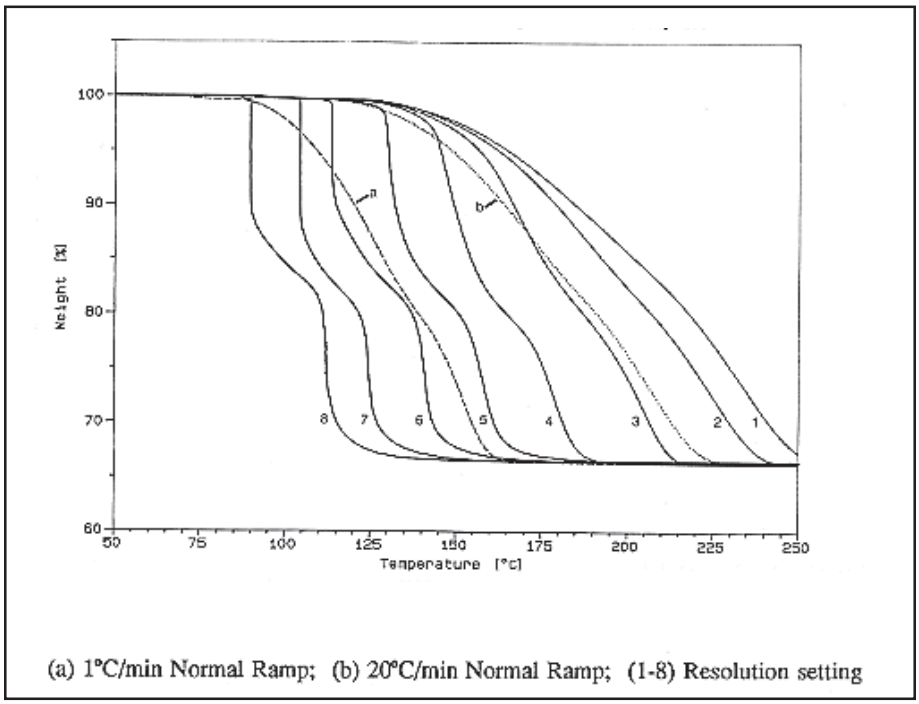


(a) 1°C/min Normal Ramp of Mixture; (b) 20°C/min Res 4.0 Hi-Res™ Ramp of $NaHCO_3$; (c) 50°C/min Res 4.0 Hi-Res™ Ramp of Mixture; (d) 20°C/min Res 4.0 Hi-Res™ Ramp of $KHCO_3$; (e) 20°C/min Normal Ramp of Mixture.

Figure 12

Varying Resolution Setting

In Figure 13 we have overlaid the conventional constant heating rate decompositions of the bicarbonate mixture (curves a and b) with dynamic rate Hi-Res scans at eight different resolution settings (curves 1 through 8). All of the Hi-Res scans were run at 50°C/minute with the default sensitivity setting of 1.0. Note that increasing resolution setting increases the resolution of each transition and simultaneously reduces the transition temperature. The initial weight losses of approximately 1% on each curve are due to the evaporation of surface water absorbed by the mixture.

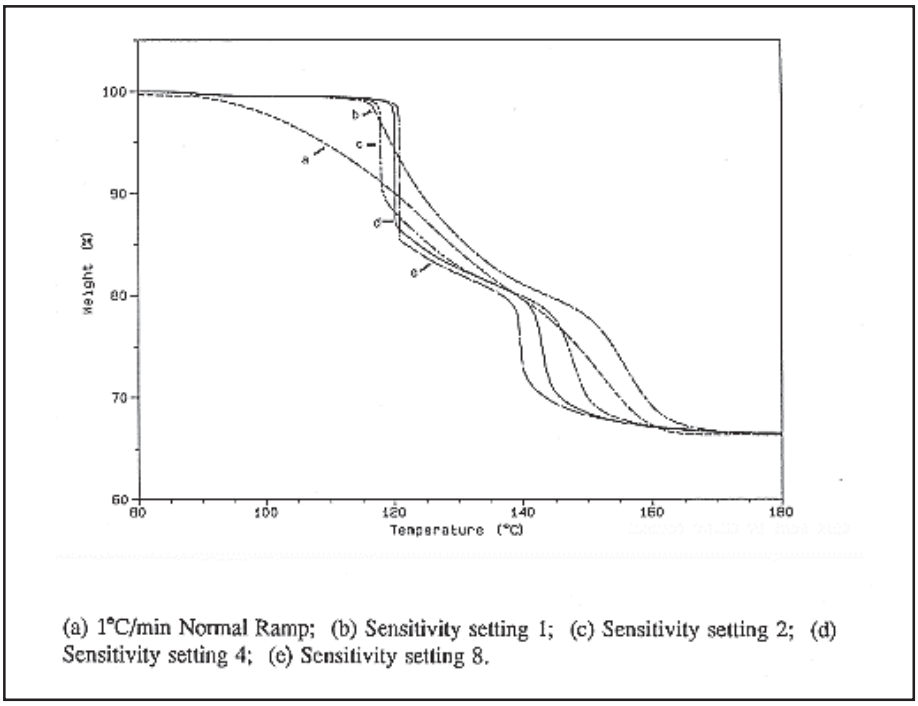


(a) 1°C/min Normal Ramp; (b) 20°C/min Normal Ramp; (1-8) Resolution setting

Figure 13

Varying Sensitivity Setting

In Figure 14 we have overlaid the 1˚C/minute conventional constant heating rate decomposition of the mixture (curve a) with a dynamic rate Hi-Res scan at four different sensitivity settings (curves b through e). All of the Hi-Res scans were run at 20˚C/minute with a resolution setting of 5.0. Note that increasing sensitivity setting increases the sharpness of each transition, but does not substantially change the transition temperature.



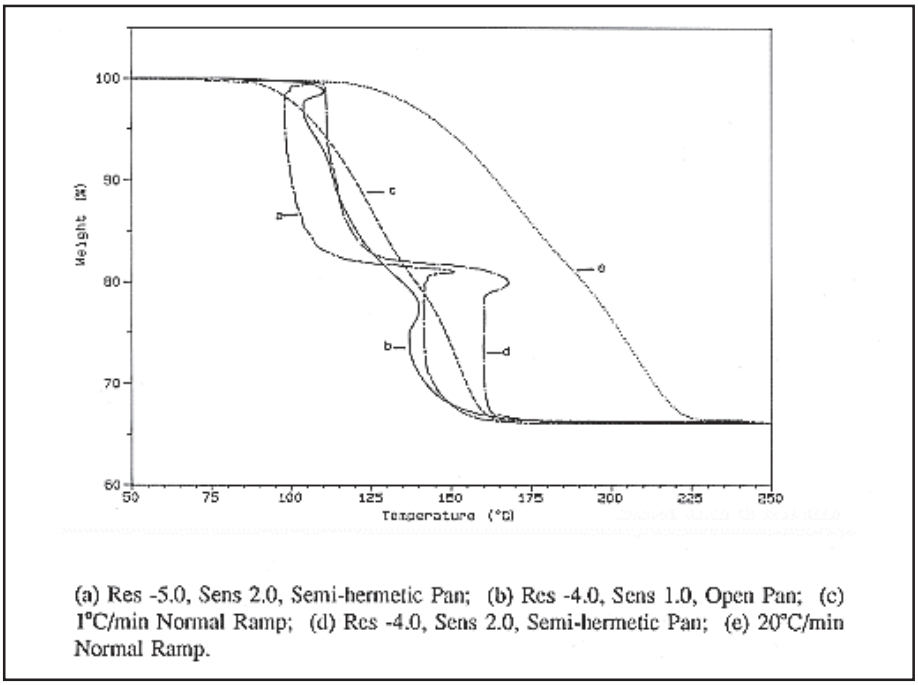
(a) 1°C/min Normal Ramp; (b) Sensitivity setting 1; (c) Sensitivity setting 2; (d) Sensitivity setting 4; (e) Sensitivity setting 8.

Figure 14

Constant Reaction Rate Scans

In Figure 15 below we have overlaid the conventional constant heating rate decompositions of the bicarbonate mixture (curves c and e) with constant reaction rate Hi-Res™ scans at different resolution and sensitivity settings. Curve b shows the Hi-Res scan run in an open sample pan at resolution setting -4.0 and sensitivity setting 1.0. For curve d (resolution -4.0) and
curve a (resolution -5.0) the sample was contained in a hermetic aluminum DSC sample pan with a 0.1mm pin hole in the top. All of the Hi-Res scans were run at 5°C/min.

Comparing curve b to curves a and d, we can see a significant improvement in resolution due to the vapor pressure build up in the semi-hermetic sample container. Because the sample pan was open in curve b, there was no opportunity for a vapor pressure/reaction rate equilibrium to occur as the sample decomposed resulting in only partial separation of the transitions. The pressure buildup in the closed container (Curves a & d) retarded the potassium bicarbonate decomposition until the sodium bicarbonate decomposition had completed. As with dynamic rate mode (Figure 13), we see that higher resolution setting (larger negative number) reduces transition temperature.



(a) Res -5.0, Sens 2.0, Semi-hermetic Pan; (b) Res -4.0, Sens 1.0, Open Pan; (c) 1°C/min Normal Ramp; (d) Res -4.0, Sens 2.0, Semi-hermetic Pan; (e) 20°C/min Normal Ramp.

Figure 15

Stepwise Isothermal Scans

In Figures 16 and 17 we see the result of stepwise isothermal scans of the bicarbonate mixture using a conventional 1˚C/minute ramp and the abort segment. The following method was used for the scan in Figure 16:

1: Abort next seg if %/min > 0.15
2: Ramp 1 ˚C/min to 300 ˚C
3: Abort next seg if %/min < 0.015
4: Isothermal for 500 minutes
5: Repeat segment 1 til 300 ˚C

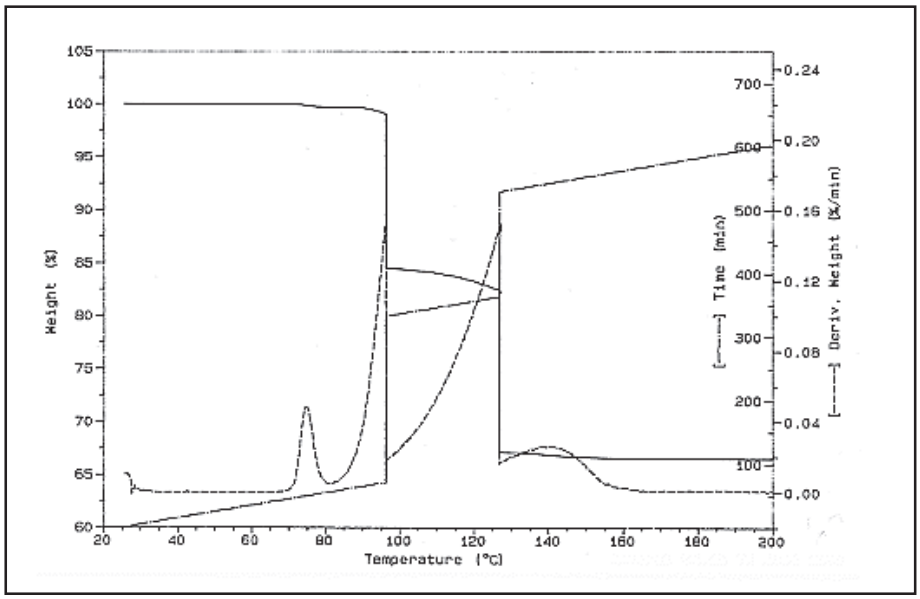


Figure 16

Although this method gives apparently excellent separation results, the quantitative value of the weight loss plateau between the two bicarbonate decompositions is in question because there is no inflection point in the plateau and the rate of weight loss immediately increases after the isothermal segment is aborted. This indicates that the two decompositions are still overlapped and that holding for a longer isothermal time period during the first transition would have resulted in a lower weight loss plateau between transitions.

In Figure 17 the same stepwise isothermal method is repeated with the %/minute limits for the abort segments set to smaller values (0.05%/minute for the ramp abort and 0.005%/minute for the isothermal abort). The following method was used for the scan in Figure 17:

1: Abort next seg if %/min > 0.05
2: Ramp 1 ˚C/min to 300 ˚C
3: Abort next seg if %/min < 0.005
4: Isothermal for 500 minutes
5: Repeat segment 1 til 300 ˚C

The scan in Figure 17 is a definite improvement over the result in Figure 16. This is because the abort limit for the isothermal segment (0.005%/minute) was chosen to be equal to the baseline %/minute immediately preceding the sodium bicarbonate transition observed in a conventional constant heating rate scan of the mixture at 1˚C/minute. The theory supporting this decision is that if the two transitions are separable then the rate of weight loss should return to baseline between the transitions. The %/minute limit for the ramp segment was then chosen to be ten times larger than that for the isothermal segment.

Although the weight loss result in Figure 17 seems more reasonable, we are suspicious that the decomposition of the potassium bicarbonate (2nd transition) has already started because the rate of weight loss immediately increases as heating is resumed at 88°C. Another problem is the torturous 1300 minute time frame of the experiment.

As can be seen by these results, caution must always be employed when interpreting results from stepwise isothermal heating experiments. It is usually wise to run confirming experiments by other TGA techniques, particularly if the sample material is of relatively unknown composition.

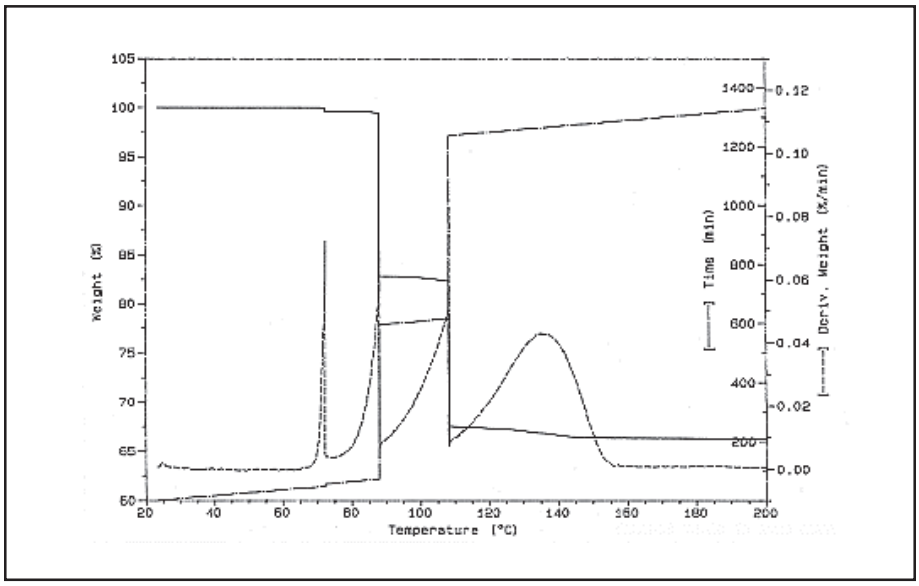
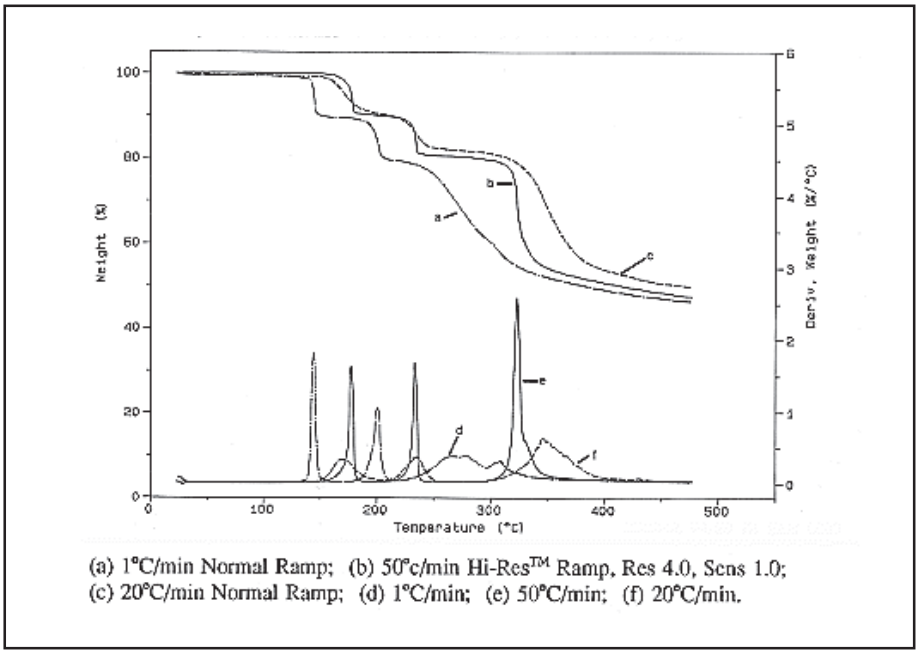


Figure 17

Monosodium Glutamate

In Figure 18 we analyzed Accent® brand monosodium glutamate (MSG), a common salt used for seasoning foods, which has three well resolved transitions below 500°C. Curves a and c show the result of conventional constant heating rate scans of MSG at 1 and 20°C/minute. Curve b shows the result of a dynamic rate Hi-Res scan at resolution setting 4.0 and sensitivity setting 1.0. As can be seen by the derivative of weight loss curves, the Hi-Res scan gives resolution comparable to the 1°C/minute scan in a fraction of the time.



(a) 1°C/min Normal Ramp; (b) 50°c/min Hi-Res™ Ramp, Res 4.0, Sens 1.0;
(c) 20°C/min Normal Ramp; (d) 1°C/min; (e) 50°C/min; (f) 20°C/min.

Figure 18

If you should decide to run this sample, be aware that MSG foams significantly at these temperatures. If a sample size greater than about 10 mg is used, the sample material may rise up in the pan and touch the sample temperature thermocouple. If MSG is heated to temperatures well above 500°C, it will leave a residue which is difficult to remove from the sample pan.

Banana Taffy

In Figures 19 and 20 we analyzed a sample of artificial banana taffy, a common confectionery product composed primarily of water and sugar, which has a number of overlapped transitions between 100˚C and 500˚C. Figure 19 shows the result of a conventional constant heating rate scan of taffy at 10˚C/minute. Figure 20 shows the result of a 50˚C/minute dynamic rate Hi-Res scan at resolution setting 4.0 and sensitivity setting 1.0.

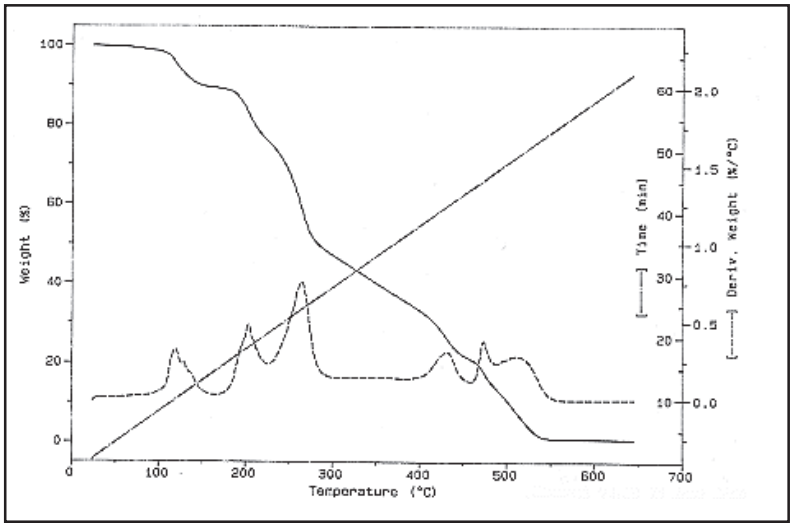


Figure 19

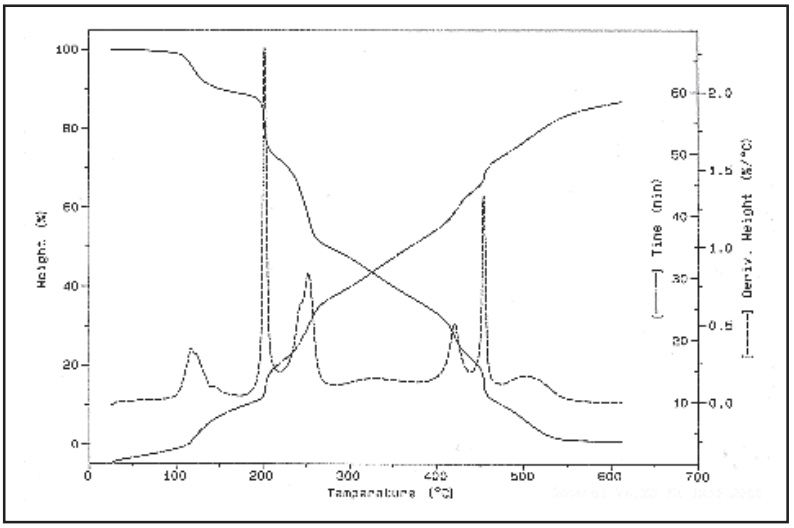


Figure 20

As can be seen by comparing the derivative of weight loss curves in Figures 19 and 20, the Hi-Res™ scan gives improved resolution in the same time as the conventional scan. This is possible because the Hi-Res TGA ramp heats the taffy sample rapidly during baseline portions of the scan and slowly during transitions, resulting in an average heating rate of about 10˚C/minute. A 200˚C/minute Hi-Res scan of this sample takes about the same time as a 20˚C/minute conventional scan while providing resolution improvement similar to that observed with the 50˚C/minute Hi-Res scan.

Plastic Laboratory Tubing

In Figures 21 through 25 we analyzed a sample of Tygon® R-3603 plastic tubing, a poly-vinyl chloride (PVC) based clear flexible tubing commonly used in laboratories and industry. A number of overlapped transitions are evident between 100°C and 350°C, followed by two well resolved transitions at approximately 400°C and 500°C. Of interest are the changes in resolution
of the various transitions as maximum heating rate changes in both the conventional and Hi-Res scans.

Observing the two conventional scans (Figures 21 and 22) we see that the resolution of the initial overlapped transitions is good in the 1°C/minute scan, but poor in the 20°C/minute scan. In contrast, the resolution of the two transitions at 400°C and 500°C are best in the 20°C/minute scan and reduced in the 1°C/minute scan. In both cases, however, the small backside transition at 25% to 35% weight loss is barely discernable. Comparing the conventional TGA results in Figures 21 and 22 to the 50°C/minute Hi-Res scan in Figure 23, we see that all of these transitions are better resolved in the Hi-Res TGA scan in a timely fashion.

Using Figures 23, 24, and 25 we can compare the result of changing the maximum heating rate of a dynamic rate Hi-Res scan. Maximum heating rates of 50°C/minute (Figure 23), 20°C/minute (Figure 24) and 10°C/minute (Figure 25) were used with a method consisting of a single Hi-Res ramp segment.

Sample size (approximately 10.45mg), sensitivity setting (1.0), purge gas (100 mL/minute dry air) and sample pan (open platinum) were all held constant from run to run.

As can be seen in the examples, the results are similar in each scan except that the measurement of transitions is moved to slightly lower temperatures as heating rate is reduced, and each run takes about 50% longer to complete when heating rate is reduced by 50%. Most noticeable, however, is that transition resolution is best in the fastest scan. This is because higher maximum heating rates allow the TGA furnace temperature to change more quickly between transitions which reduces transition overlap and flattens weight loss baseline. As an added benefit, experiment time is reduced compared to traditional resolution enhancement techniques. Here we can see the real beauty of dynamic rate Hi-Res™ TGA: better results in the same or less time as traditional constant heating rate TGA.

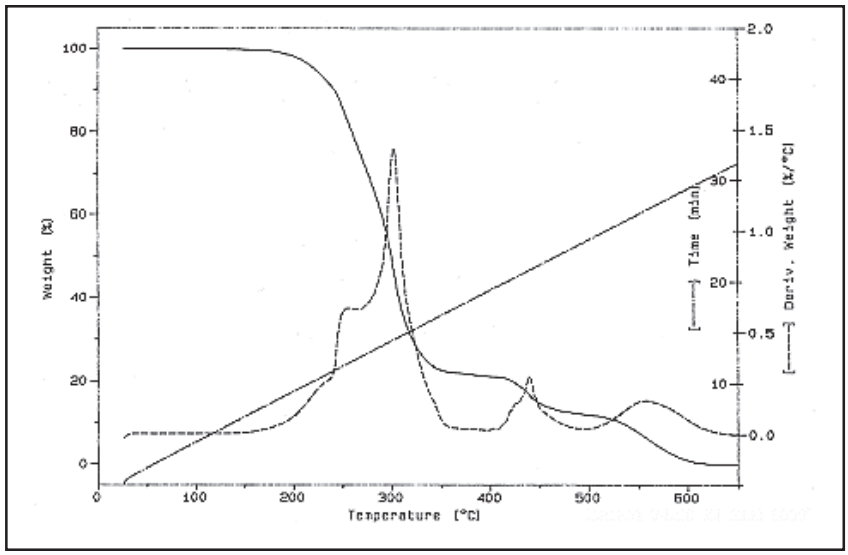


Figure 21

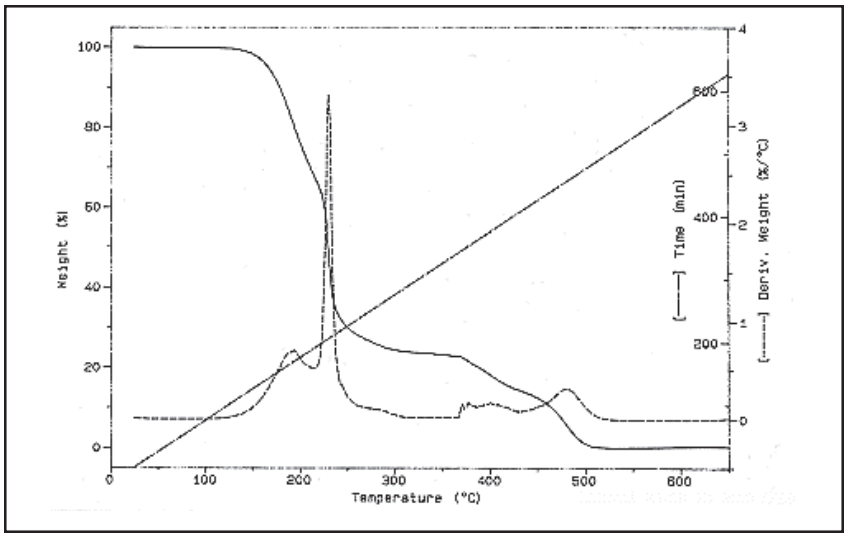


Figure 22

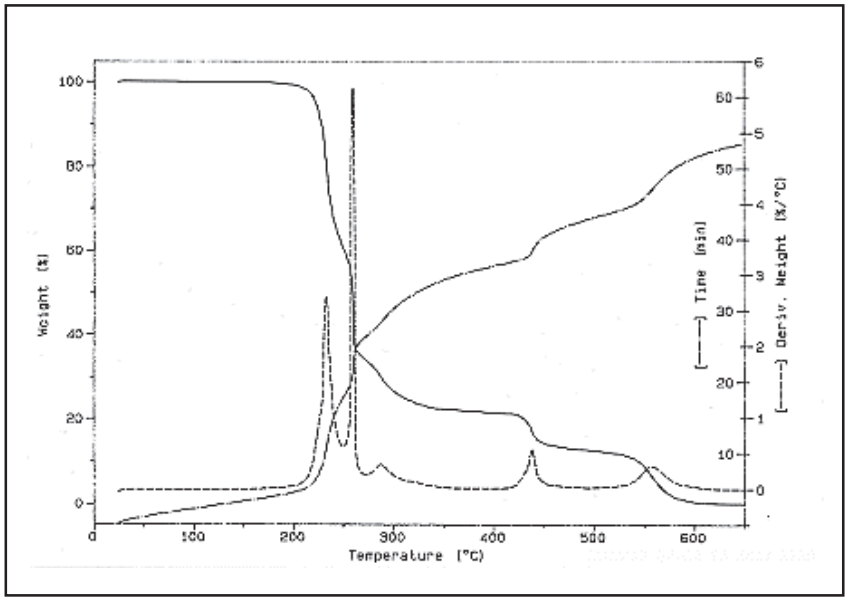


Figure 23

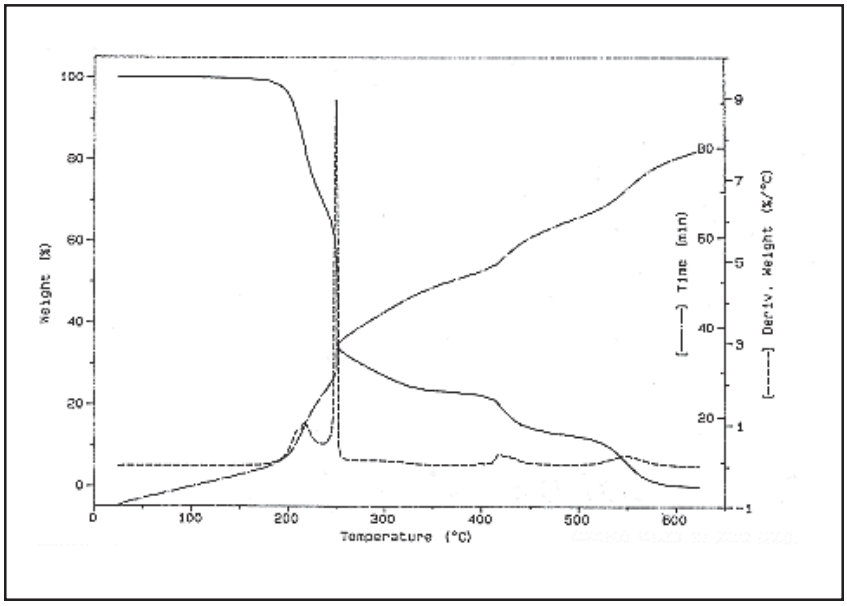


Figure 24

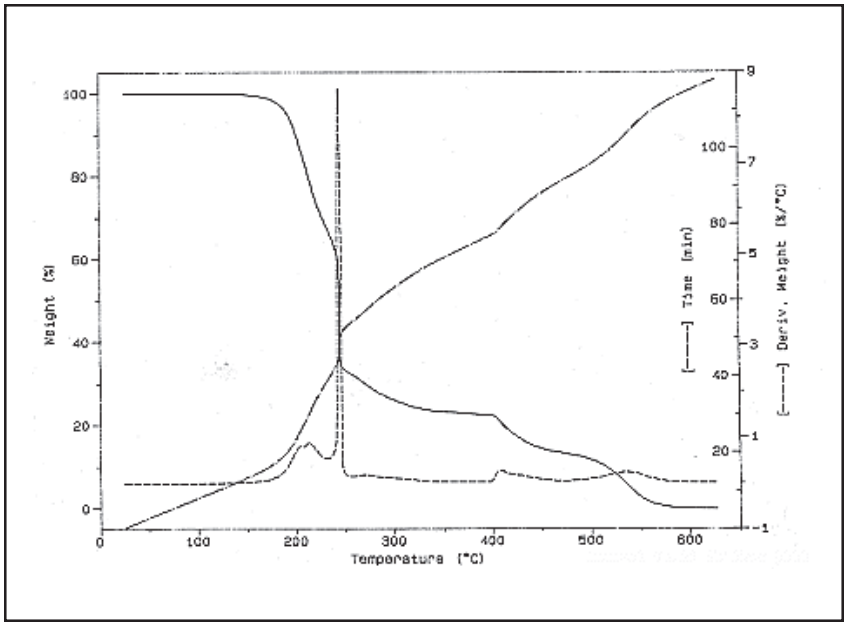


Figure 25

References

Listed below are two excellent additional references for specific materials and techniques. These have been chosen because they give a broad review of the techniques involved and address the physical and chemical processes taking place, as opposed to a specific analysis of any one sample material. Each paper contains an extensive list of additional references for specific materials and techniques.

1. Thermoananlytical Examinations Under Quasi-Isothermal - Quasi-Isobaric Conditions, F. Paulik & J. Paulik, Thermochimia Acta., 100 (1986) 23-59.

2. Controlled Transformation Rate Thermal Analysis: The Hidden Face of Thermal Analysis, J. Rouquerol, Thermochimica Acta., 144 (1989) 209-224.

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