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HIGH RESOLUTION THERMOGRAVIMETRY

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A new thermogravimetric instrument is introduced, Hi-Res™ TGA 2950. The Hi-Res™ TGA gives a significant improvement to TG results. The instrument control parameters are varied as a function of the sample's rate of weight change. This novel feature improves resolution and reduces analysis time. The maximum heating rate and resolution index are user selectable.

Data presented demonstrate improved resolution for survey TG thermal curves and very high resolution for difficult to resolve complex materials. Results are demonstrated for many types of samples including: homopolymers, polymer blends, inorganic reference materials, and complex organic mixtures.

Hi-Res trademark and patent applied for by TA Instruments, Inc.

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Introduction

Resolution, the ability to separate closely occurring events, is an important criterion for most analytical instrument techniques since it effects the ability to obtain accurate, quantitative results. Thermal Analysis techniques are no exception to this basic rule. A good example is thermogravimetric analysis (TG) which measures weight changes with temperature, providing information about material compositional analysis and thermal stability. Resolution of successive TG weight losses is important for obtaining accurate, reproducible weight change values, as well as accurate component identification in the evolved decomposition gases by FTIR (Fourier transform infrared) or mass spectroscopy.

In thermal analysis, the variables affecting resolution for a specific hardware design are typically sample size, heating/cooling rate, and purge gas composition. Generally, smaller sample sizes, slower heating/cooling rates, and high thermal conductivity purge gases (e.g. helium) result in im-

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proved resolution. Varying (slowing) heating rate has proven to be a particularly effective method for enhancing resolution in TG experiments. The literature contains several references [1–3] which clearly illustrate that adjusting (slowing) the heating rate during weight changes improves resolution. J. Rouquerol in 1964 [1] used vacuum TG and based heating rate control on sensing pressure increases associated with the evolved decomposition gases. Paulik & Paulik [2] adjusted TG heating rate as necessary to achieve a constant rate of reaction (weight change). Sorenson [3] in 1978 used stepwise isothermal control to enhance TG resolution. All three of these approaches resulted in better resolution, but with substantial increases in experimental time.

TA Instruments has recently introduced another approach which delivers superior TG resolution without the time trade-off present in the earlier literature approaches. In fact, this approach (patent pending*) often provides better results in less time than conventional constant heating rate TG. This new approach is included as part of a high resolution TG (Hi–Res™ TGA) accessory for the TA Instruments TGA 2950. Thermogravimetric Analyzer which enables the operator to choose among several different heating rate approaches to obtain the best compromise of resolution and productivity for a specific situation.

Principles of operation

The Hi–Res™ TGA capability consists of four different variable heating rate algorithms (approaches) which can be used either alone or in combination to obtain the optimum results on a specific material. The basis for each of the algorithms is described below:

Dynamic rate

This is the TA Instruments patent-pending approach. It differs from the other approaches in that the heating rate of the sample material is dynamically and continuously varied in response to changes in the sample's rate of

* High resolution thermal analysis (includes high resolution thermogravimetric analysis) and 'Hi-Res™ TGA' are concepts for which TA Instruments, Inc. has filed patent and trademark applications respectively.

decomposition so as to maximize weight change resolution. This approach allows very high heating rates to be used in regions where no weight changes are occurring while avoiding transition temperature overshoot.

Because the dynamic rate approach 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

In the constant reaction rate approach the heater control system varies the temperature of the furnace as required to maintain a constant preselected rate of weight change (%/min). 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

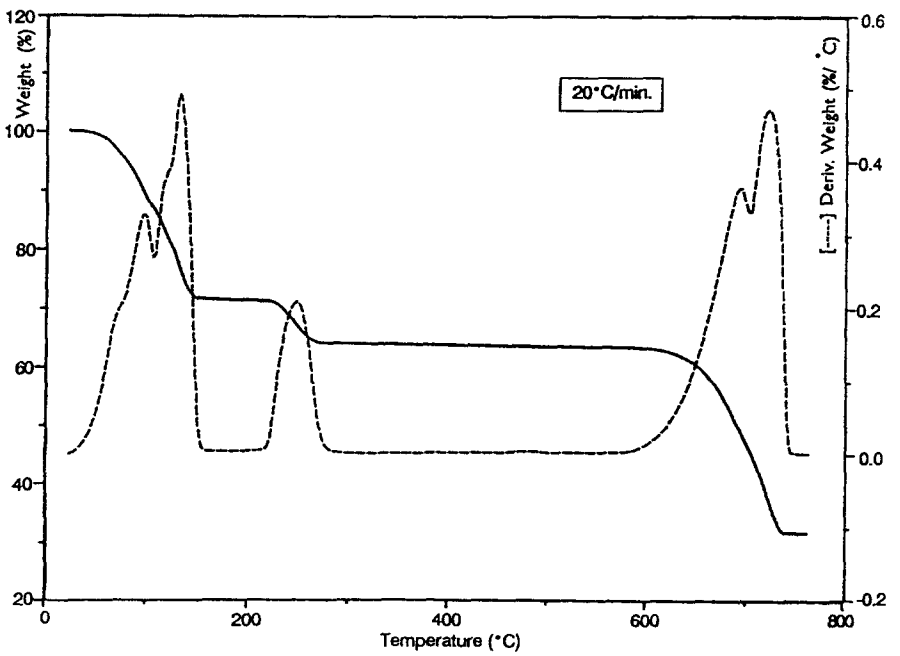

Fig. 1 Copper sulfate pentahydrate-conventional TG

reduced or reversed during transitions allowing them to complete at the selected reaction rate before moving on to the next transition.

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-catalysing 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.

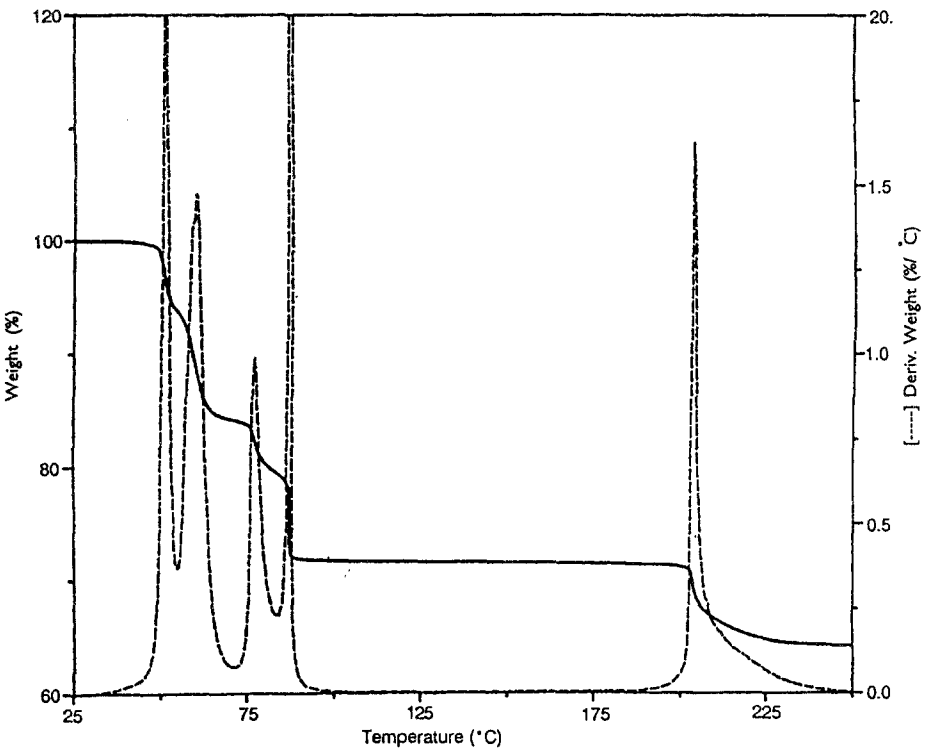

Fig. 2 Copper sulfate pentahydrate–Hi–Res™ TGA (Dynamic rate)

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 superimposed a relatively small transition. If the decomposition rate threshold is chosen to be close to the background rate at the maximum heating rate, then the heating rate will only be changed significantly when the smaller transition occurs.

Stepwise isothermal

The stepwise isothermal approach consists of heating at a constant rate until a weight change begins as determined by an operator chosen rate or amount of weight loss and then holding isothermally until the weight change is complete. This sequence of heating and isothermal holding is repeated for each weight change encountered.

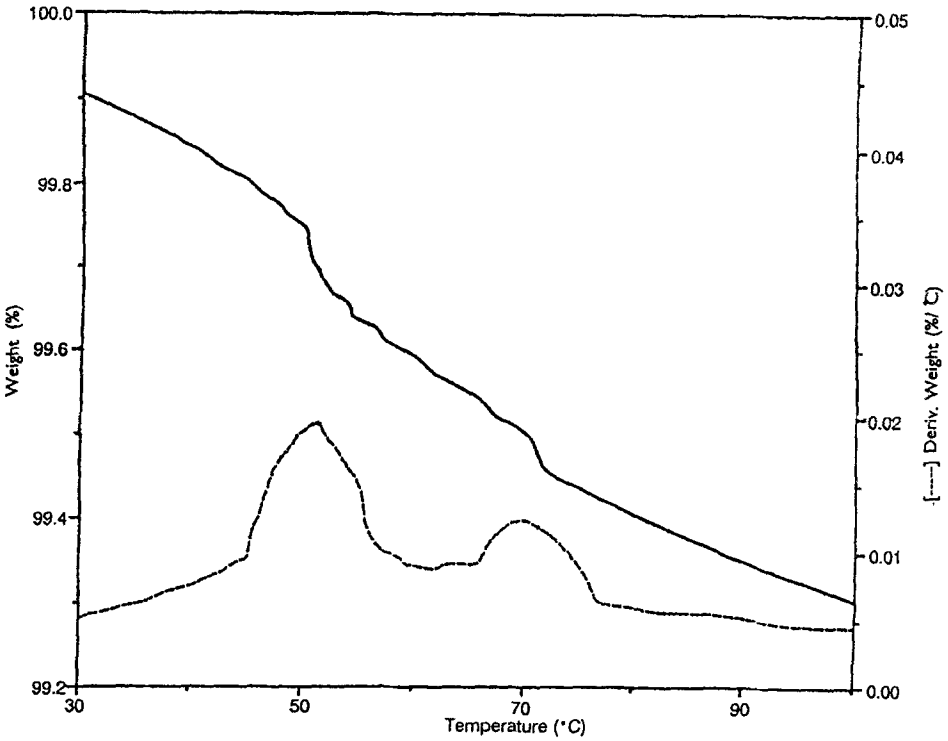

Fig. 3 Cement–Hi–Res™ TGA (Constant reaction rate)

Constant heating rate

This is the Conventional TG approach a constant heating rate is used throughout the experiment. Using slower heating rates 1–2 deg·min^{-1} or less, is often required to obtain any resolution enhancement from this approach.

Applications

A series of applications which illustrate the power of Hi-Res™ TGA is included in this section. The example applications shown are not meant to be all inclusive, but are chosen to illustrate the type of results possible.

Inorganics

Inorganics are convenient materials for assessing TG resolution because they are readily available and often degrade with well-defined stoichiometric weight losses. Cupric sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) is a typical example. Figure 1 shows the conventional TG results for cupric sulphate at 20 $deg \cdot min^{-1}$. The solid line indicates a series of weight losses beginning at about 70 °C. These weight losses between 70 °C and 250 °C represent the loss of five waters of hydration. Although conventional TG provides a well-defined weight loss of the last hydration water, the initial water weight losses are difficult to resolve even using the derivative curve (broken line) and

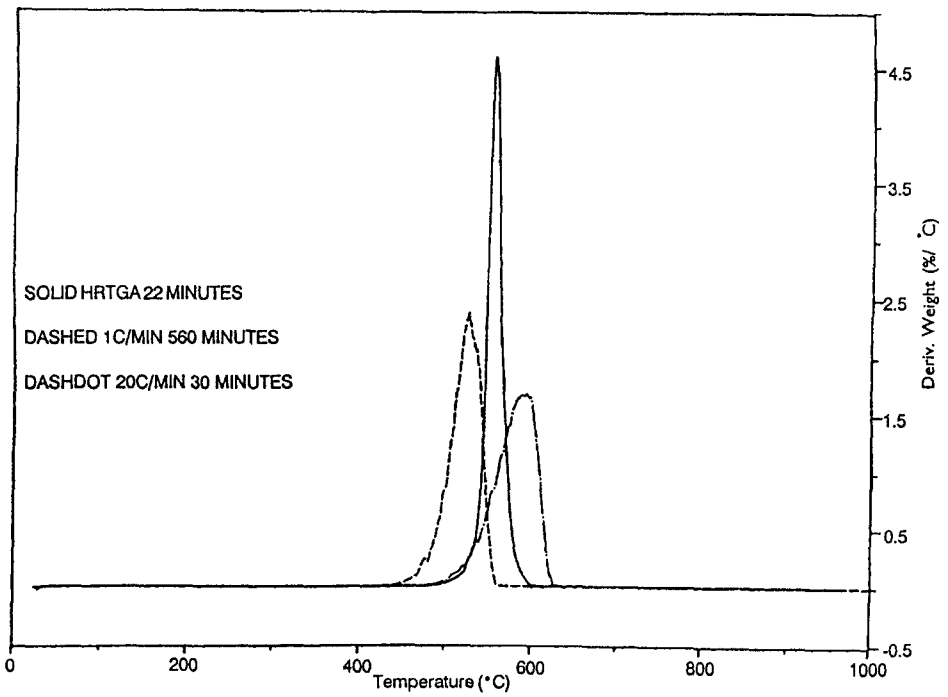

Fig. 4 Polytetrafluorethylene (PTFE) decomposition comparison of derivative curves

hence, are difficult to quantify. The Hi-Res™ TGA results (Fig. 2), however, shows sharp well-resolved peaks which provide easy quantitation of all five water losses. Figure 3 shows the results of another Hi-Res™ TGA experiment where the area of interest is waters of hydration. In this case, however, the weight losses associated with water evolution are so small and gradual that they cannot be detected by conventional TG Hi-Res™ TGA, in effect, provides enhanced sensitivity.

Homo polymers

Figure 4 illustrates the comparative derivative curves for polytetrafluoroethylene (PTFE) using conventional and dynamic rate Hi-Res™ TGA. PTFE is representative of pure homopolymers which typically decompose by simple, single step processes. Hence, resolution of overlapping weight loss peaks is not an issue. However, the results illustrate that the resolution as indicated by the derivative peak sharpness (wt.% per °C) is improved in Hi-Res™ TGA even over conventional TG at 1 deg·min^{-1}.

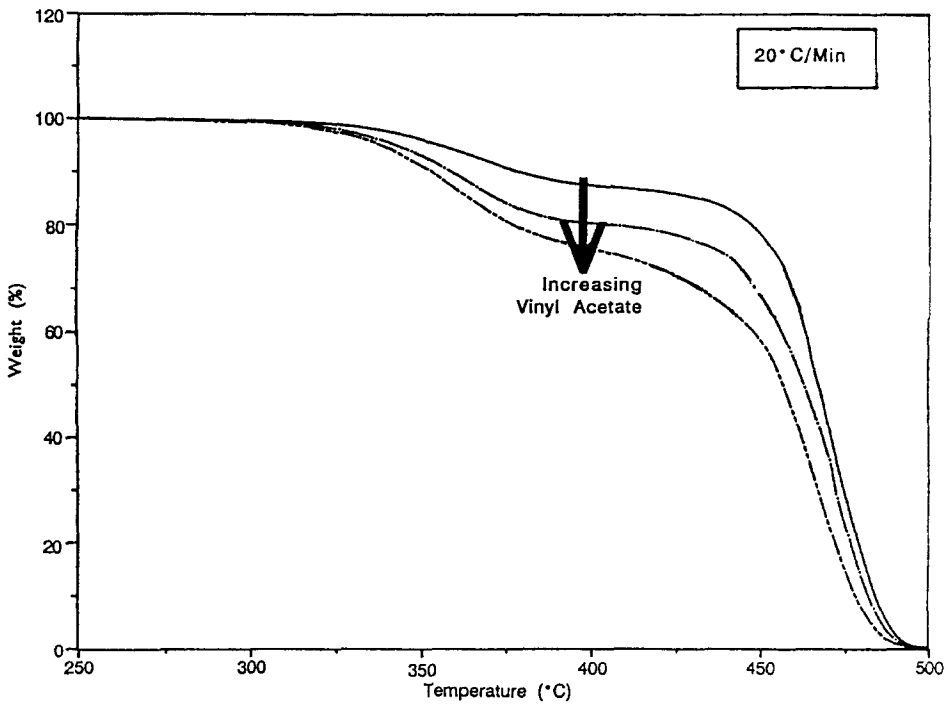

Fig. 5 Ethylene vinylacetate–conventional TG

Furthermore, the Hi-Res™ TGA results are achieved in less time than conventional TG results at 20 deg·min^{-1}. This is a perfect example of Hi-Res™ TGA's value as a survey technique.

Polymer blends

Polymer blends represent a large class of valuable materials which are difficult to evaluate by conventional TG and which, therefore, represent a large opportunity for Hi-Res™ TGA. Ethylene vinyl acetate (EVA) is a common copolymer which illustrates the ability of TG to determine the relative percentages of the polymer present based on the degradation profile. In nitrogen, EVA degrades in a two step process, where the first weight loss corresponds to acetic acid. Using a weight ratio, which accounts for the vinyl acetate/acetic acid stoichiometry, it is possible to determine the % vinyl acetate present in the copolymer [4]. Figure 5 shows the weight loss curves for several different EVA formulations by conventional TG. Although it is clearly evident that the formulations are different, there is some opportunity

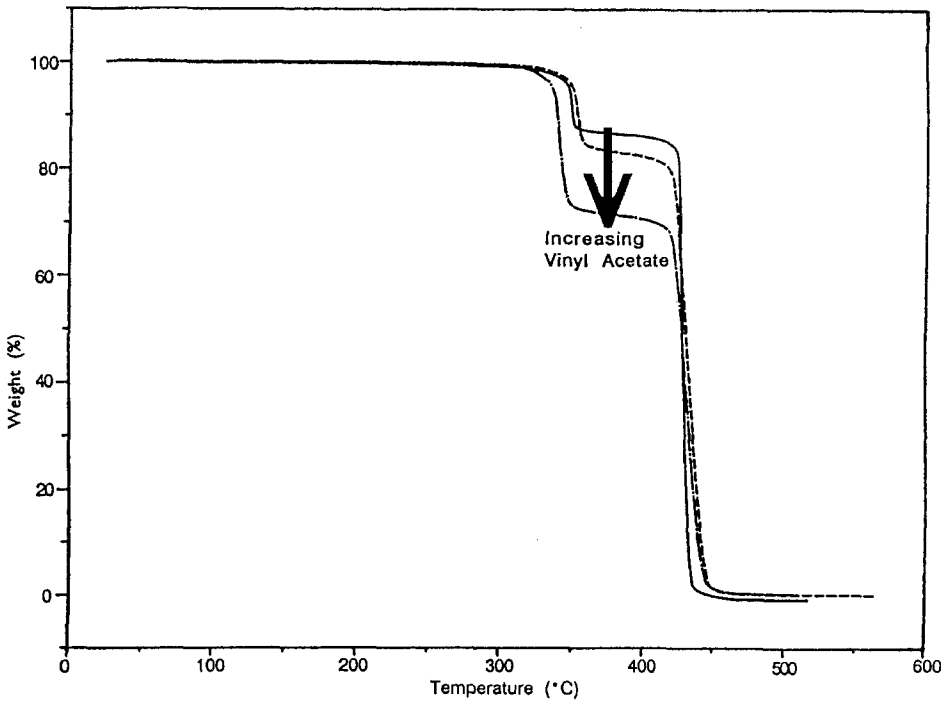

Fig. 6 Ethylene vinylacetate-Hi-Res™ TGA (Dynamic rate)

for operator subjectivity when choosing the initial weight loss completion and hence, the amount of vinyl acetate present. Figure 6, on the other hand, illustrates the results of EVA materials using Hi-Res™ TGA. With Hi-Res™ TGA, it is easy to determine when the first weight loss is complete.

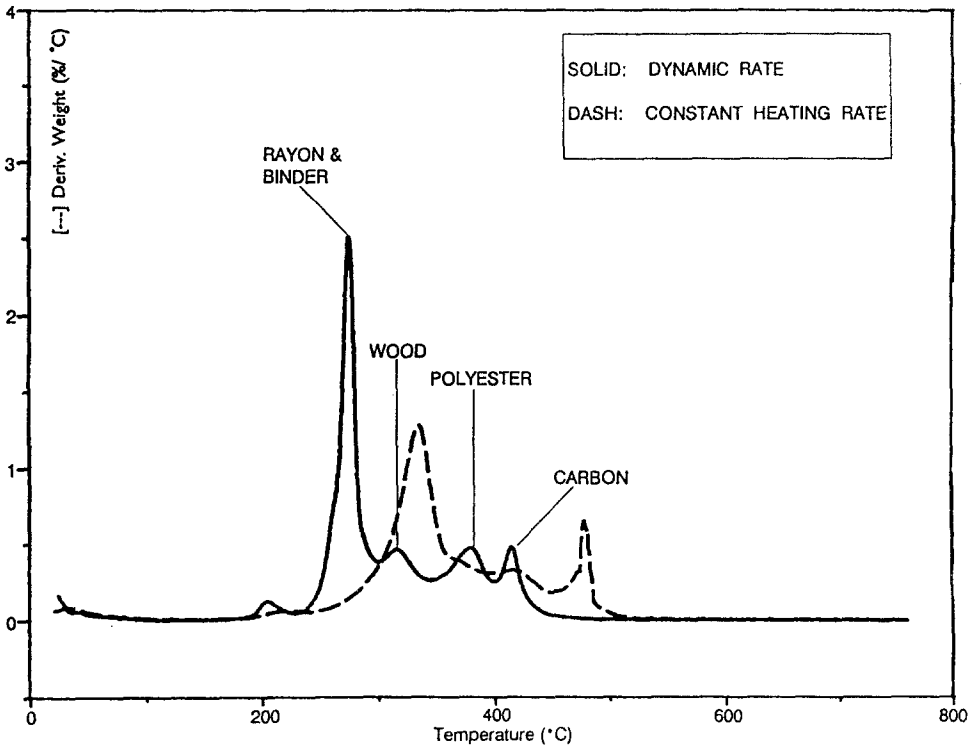

Fig. 7 Textile blend–dynamic rate and constant heating rate TG

Polymer fibres are frequently blended together or with natural fibres to make fabrics, thread, or yarn which has characteristics not found in the individual fibres. In this case, a blend of Rayon™, polyester, wood-pulp and binder was analysed using dynamic rate Hi-Res™ TGA and constant heating rate TGA. As seen in Figure 7, the resolution of the weight losses is improved with the Hi-Res™ method. The carbon is the char remaining after the decomposition of the component fibres.

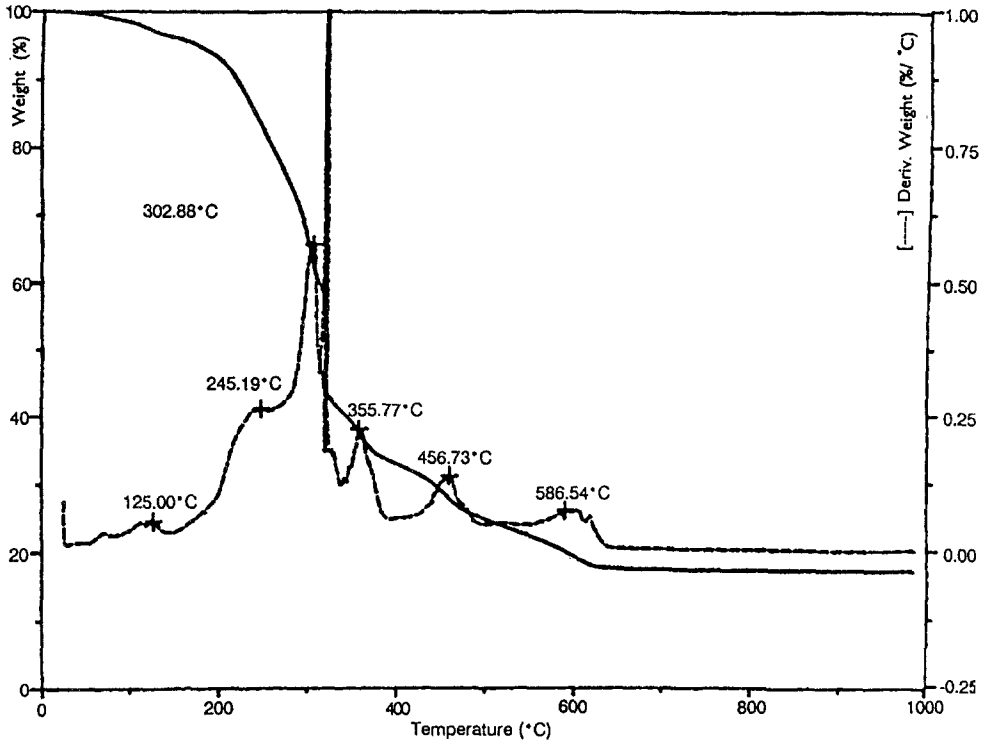

Fig. 8 Premium soap–conventional TG

Complex materials

Foods, natural products, and pharmaceuticals are materials that usually exhibit complex TG profiles. Figures 8 and 9 show comparative results for a premium hand soap using conventional and Hi-Res™ TGA. The improved resolution obtained in the latter case makes it potentially easier to identify and quantify the various weight loss components. Further resolution enhancement of specific weight loss regions can be obtained with additional adjustment of Hi-Res™ TGA experimental parameters. Even without further resolution improvement, however, these Hi-Res™ TGA results can be used as shown earlier with EVA to rapidly generate distinctive 'fingerprints' that facilitate comparison of competitive products or checking batch-to-batch in formulation.

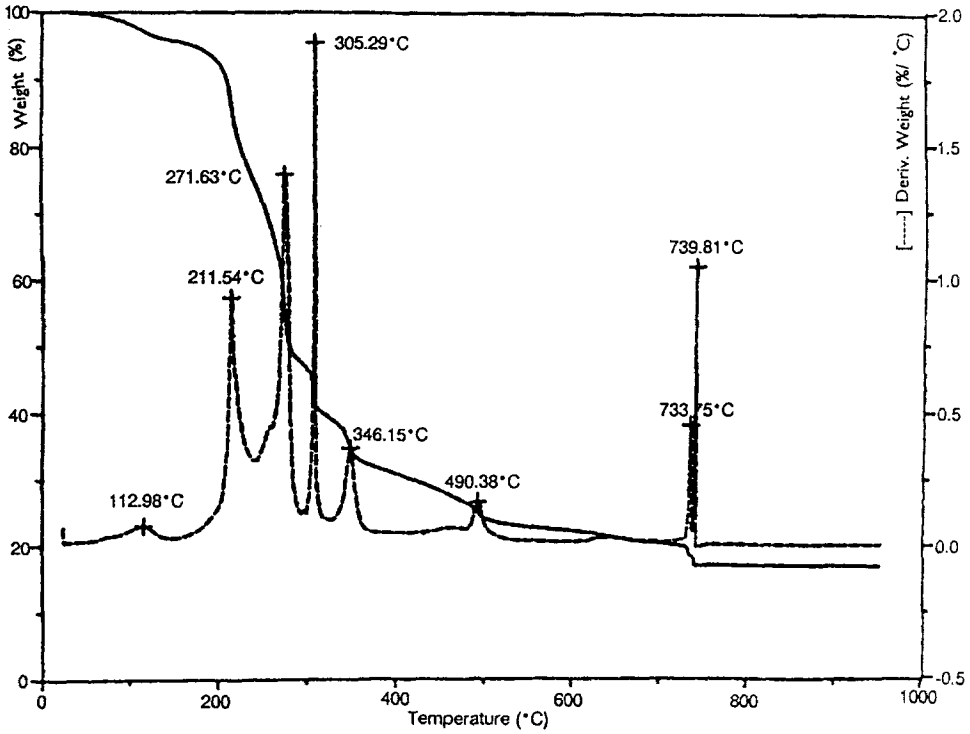

Fig. 9 Premium soap–Hi-Res™ TGA (Dynamic rate)

Conclusions

High resolution TGA is a new technique that promises to revolutionize the quality of results that can be obtained from TG experiments. Using a series of different approaches, the thermal analyst can choose the best resolution/productivity compromise for his materials.

References

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Zusammenfassung — Es wird das neue thermogravimetrische Gerät Hi-Res™TGA2950 vorgestellt. Mit Hilfe von Hi-Res™TGA2950 ergibt sich eine eindeutige Verbesserung der TG-Resultate. Die Kontrollparameter des Gerätes werden als eine Funktion der

Massenänderungsgeschwindigkeit der Probe geändert. Diese neue Eigenschaft verbessert die Auflösung und verringert die Analysenzeit. Maximale Aufheizgeschwindigkeit und Auflösungsindex können vom Anwender bestimmt werden.
Die dargelegten Daten zeigen eine verbesserte Auflösung der TG-Kurven und eine sehr hohe Auflösung für schwer aufzulösende komplexe Substanzen. Es werden Ergebnisse für zahlreiche Beispiele gegeben: Homopolymere, Polymergemische, anorganische Referenzsubstanzen und komplexe organische Gemische.
Das Warenzeichen Hi-Res und das Patent wurde von TA Instruments,Inc. beantragt.