Determining Volatiles in Polyethylene Terephthalate Using the Q5000 IR Thermogravimetric Analyzer

Keywords: Q5000 IR, TGA, Infrared Furnace, Volatiles, Polyethylene Terephthalate, PET, Baseline flatness, Sensitivity TA326

ABSTRACT

This publication highlights the use of features inherent in the design of the TA Instruments Q5000 IR Thermogravimetric Analyzer to solve issues of detectability of low-level volatile components in a sample matrix.

INTRODUCTION

The presence of unexpected volatiles is often a problem in the production and use of resin systems. When a plastic formulation contains even small amounts of water, solvent or monomer, it may produce bubbles or other imperfections during processing. While the determination of volatiles content can be carried out using a thermogravimetric analyzer (TGA), there is always a concern over the level of detectability in the analysis. Normally, the uncertainty of a TGA determination is a few tenths of a percent. This practical limitation comes from a number of error sources: from sample inhomogeneity, to adsorption or desorption of moisture during sample preparation, and to uncertainty in the TGA baseline. For many laboratories, especially in the pharmaceutical industry, detecting volatiles to a few tenths of a percent is just not good enough.

SOURCES OF ERROR

In their development of a TGA system, the engineers at TA Instruments focused on understanding the various sources of error that affect sensitivity in order to find ways to improve performance. One of the best ways to see the manifestation of these errors is to observe a blank baseline run at high sensitivity, such as shown in Figure 1. This data run on a competitive TGA shows a typical baseline, namely, an initial apparent weight gain caused by convection effects due to hot gases rising from the furnace walls that cause a downdraft in the middle of the furnace where the sample pan is situated. Since this so-called "convective effect" or "initial offset" tends to vary with heating rate and starting temperature, it is difficult to remove by subtraction. At higher temperatures a typical TGA baseline shows an apparent weight gain due to buoyancy. As temperature increases, the gas surrounding the sample pan becomes less dense, so the pan experiences less buoyant lift (per Archimedes' principle). Other instrumental problems that result in drift in the baseline include temperature rise in the balance chamber, and build-up or dissipation of static charge on the hang down wires.

The apparent weight changes observed during a heating analysis when there is no sample present - only an empty pan - would also be observed if a sample were present (in addition to the weight losses associated with the sample specimen). Hence, any apparent weight changes observed in the blank baseline would result in an error in the thermal curve unless the baseline errors are extremely reproducible and the baseline data (run under identical conditions) is subtracted from the sample data. Since few thermal analysts run and subtract identically run baselines, it is realistic to consider that displacement in the blank baseline represents error in the TGA analysis. To address that problem engineers at TA Instruments designed the Q5000 to reduce the blank baseline effects by roughly an order of magnitude - with a resulting improvement in sensitivity and accuracy.

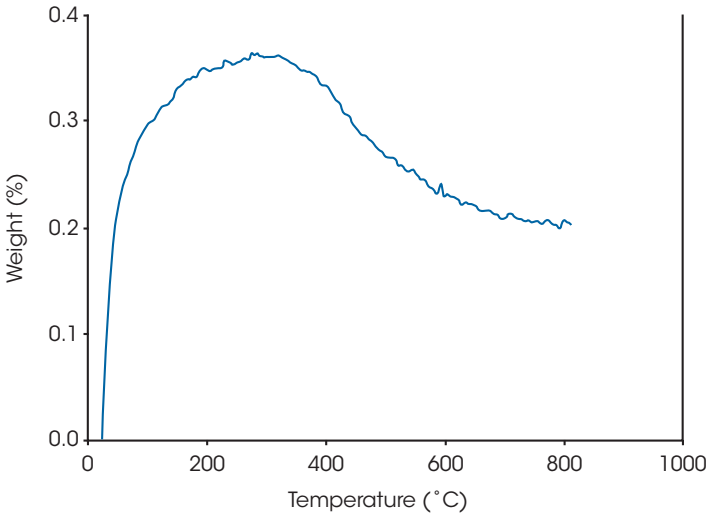

Figure 1. A typical TGA Blank baseline displayed at high sensitivity (e.g., 1 mg sample)

Q5000 TGA IMPROVEMENTS

The Q5000 IR Thermogravimetric Analyzer (Figure 2) was completely redesigned to provide numerous improvements in both performance and user convenience, and some of these changes directly impact TGA sensitivity.

Figure 2. Q5000 TGA IR

Balance System: The balance was designed for superior baseline flatness and thus better detectability of small weight losses. The overall performance improvements result from gains in meter movement support, frame rigidity, interior balance housing temperature control, isolation from both the furnace and the environment, plus electrical grounding. For example, the balance chamber is maintained at a constant temperature within one hundredth of a degree even at elevated furnace temperatures. This greatly reduces long-term drift, even at high temperature isotherms, where heat rising from the furnace increases the balance temperature in most TGAs.

Infrared furnace heating system: The Q5000 IR uses a unique configuration (see Figure 3) to heat the sample without generating temperature gradients in the sample chamber that cause convective offset. The heater is a distributed infrared source outside the furnace chamber that radiantly heats a low-mass thermal diffuser that is part of the furnace internal structure. This minimizes temperature gradients, therefore reducing weight errors due to convection. This performance, when combined with the improved balance performance, results in a baseline that is within a few micrograms of zero even under fast heating rate conditions. The uniform heating of the sample chamber also leads to more precise and repeatable temperature control, and to better temperature output accuracy.

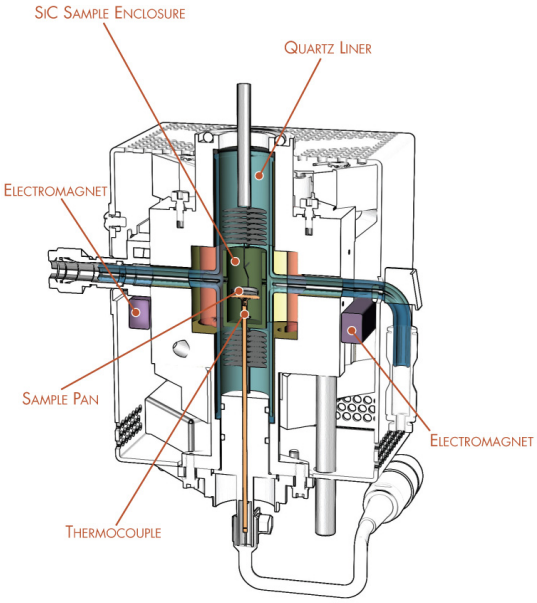

Figure 3. Q5000 TGA Furnace

Another virtue of this heating system is that equilibration is rapid - less than a minute even when using heating rates up to 500 °C/min. This low mass system also allows faster cool-down as well.

A further advantage of this system is that the high performance is achieved without resorting to a diminutive sample pan size.

Run-time capsule opening: For low-level volatile analysis it is often necessary to maintain samples in a sealed environment until just before they are loaded into the furnace for analysis. Otherwise samples waiting in an autosampler queue may lose volatiles (or conversely, pick up moisture from the air) leading to an erroneous analysis. The problem with some run-time pan-piercing systems is that the hole produced is small, and the variability of the effusion area is large, which can lead to inconsistent results. Another potential problem of earlier systems is that the piercing point may become contaminated by contact with a sample, and thus lead to contamination of other samples. These problems have been overcome on the Q5000 IR by deflecting inward the top of the specially designed, sealed pan without the deflector entering the sample capsule. The opening mechanism is similar in function to that of a "pop-top" aluminum beverage can but occurs in the inverse direction. The resultant opening is now large enough that small differences in lid deflection produce relatively small differences in the area available for volatilization.

EXPERIMENTAL DETAILS

Post-consumer polyethylene terephthalate bottle material was selected for detection of volatiles because the content of volatiles is small, but not immeasurable. Sample specimens were cut from the lip or collar sections of beverage bottles. Having already been processed at high temperature in the formation of the bottle preform, these samples would be expected to have a low volatile content except for moisture pick-up from the environment.

In a series of performance tests to demonstrate measurement sensitivity, the Q5000 IR was operated in a typical laboratory environment. Sample pans used were standard 10mm diameter platinum reusable open-top pans, while sample masses varied from 2.4 to 8.5 milligrams. (Use of small specimen sizes serves to demonstrate the high sensitivity performance, since the pans could have accommodated more than 10 times the sample size.) The heating rate used was 10 °C/min, slow enough to allow time for diffusion of volatiles from the interior of the sample specimen to the edge. The purge conditions were the standard default conditions for this analyzer, namely 10 mL/min through the balance chamber and 25 mL/min through the furnace chamber.

RESULTS AND DISCUSSION

The results of three representative runs of PET at sample weights of 2.4, 5.5 and 8.6 mg can be seen in Figure 4. The Y-scale is expanded to show the first 0.5% weight loss full scale. The observed weight loss from these and other data range from 0.22% to 0.24%, demonstrating the ability of the Q5000 IR to easily detect low-level components.

Figure 5 shows one of these data sets with the weight change calculation performed. It is conventional to take volatile weight loss from the highest point of the weight loss curve so that any baseline offset occurring before the loss of volatiles will not be included in the weight loss data. From Figure 1 it is evident that this procedure would not work very

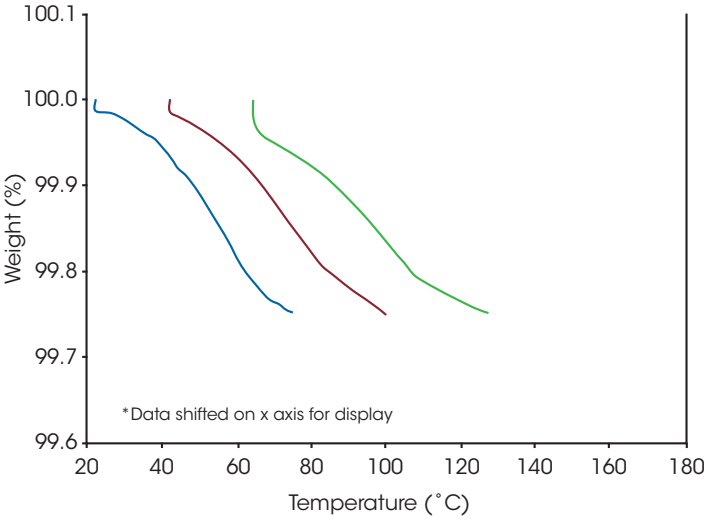

Figure 4. Volatiles in PET

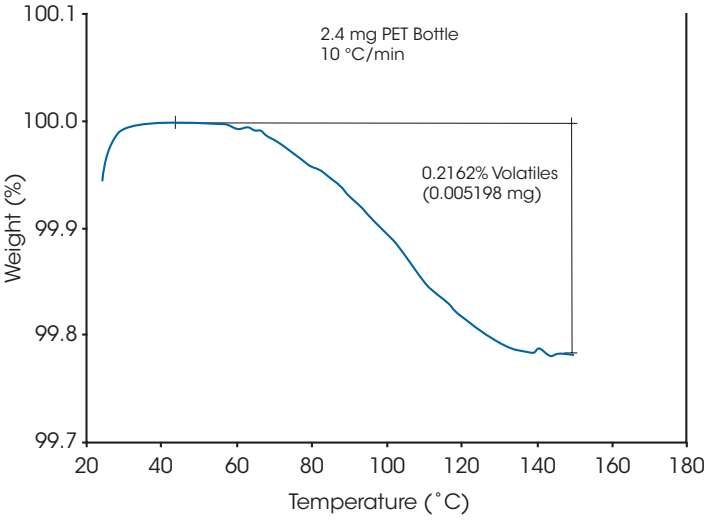

Figure 5. Volatiles Calculation of PET

well for some TGAs since the baseline offset is still increasing rapidly above 100 °C. However, as shown in Figure 5, the small baseline offset on the Q5000 IR reaches a plateau in roughly two minutes by 42 °C after starting the scan at 25 °C. Hence, error from convective rise, which can reach several tens of micrograms on some TGAs, was found to be less than two micrograms over the measured weight loss region. It is thus possible to measure the PET volatiles loss of 0.21% to within two micrograms, or 0.02% of the 8.6mg sample weight. This indicates that high sensitivity volatiles analysis such as this can be carried out with a modest sample size of a few milligrams and still obtain sensitivity better than 0.1% without subtracting a baseline.

CONCLUSION

The analysis of the volatile content of PET gives an indication of the improved gravimetric sensitivity of the Q5000 IR TGA. This improvement is based on significant, new technology in the balance and furnace systems. This technology leads to improved temperature control and remarkably flat TGA baselines that will benefit not only sensitivity, but also the precision and accuracy of most TGA methods.

ACKNOWLEDGMENTS

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