APPLICATION BRIEF

Thermogravimetric Analysis – GC Mass Spectrometry

The Analysis of PVC with Different Phthalate Content by TG-MS and TG-GC/MS

Introduction

The combination of thermogravimetric analyzers (TGA) with mass spectrometers (MS) to analyze the gases evolved during a TGA analysis is a fairly well-known technique. In cases of complex samples, TG-MS often results in data in which it is nearly impossible to differentiate gases that evolve simultaneously.

Combining TGA with gas chromatography mass spectrometry (GC/MS) allows for a more-complete characterization of the material under analysis and precisely determines the products from the TGA. This application will demonstrate the relative advantages of TG-MS and TG-GC/MS – a summary of the strengths of each technique is presented in Table 1 (Page 2).

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Table 1. **Relative Advantages of TG-MS and TG-GC/MS.**	
TG-MS	**TG-GC/MS**
Real-time analysis	Sequential analysis
No resolution capabilities	Resolves overlapping events
Limits to library effectiveness	Resolution improves GC libraries effectiveness
Oxygen sensitive	Oxygen sensitive
	Can use alternate/multiple detectors
Simple	More complicated

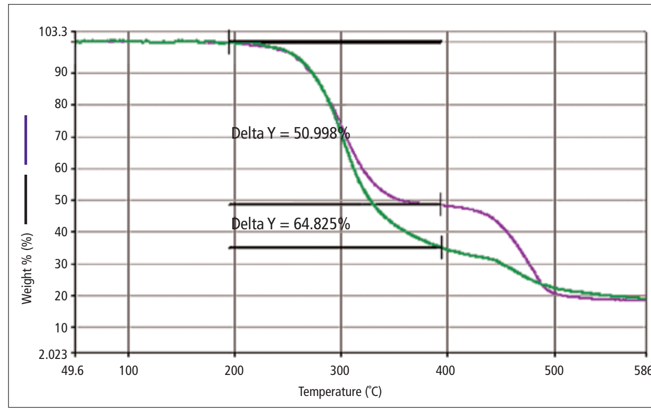

Figure 1. TGA percent-weight-loss curve generated from the analysis of two PVC samples: one with DINP (purple), a regulated phthalate, and a weight loss (delta y) of 50.998%; and a second with a mixture of non-regulated phthalates (green) and a weight loss (delta y) of 64.825%.

Experimental

This analysis was performed on a PerkinElmer® Pyris™ 1 TGA using alumina pans and the standard furnace. The instrument was calibrated with nickel and iron and all samples were run under helium purge. Heating rates varied from 5 to 40 °C/min, depending on the sample under test. The furnace was burned off between runs in air. Samples were approximately 10-15 mg. Data analysis was performed using Pyris 9.0 Software.

During the TG-GC/MS analysis, the PerkinElmer Clarus® 680 C GC/MS was used. In the TG-MS work, a 0.1 mm I.D. deactivated fused-silica transfer line was connected directly to the MS. The transfer line was heated to 210 °C. In the TG-GC/MS work, a 0.32 mm I.D. deactivated fused-silica transfer line was plumbed into the GC injector port where it was connected to the Elite™-1ms capillary GC column. In both cases, data analysis was performed using TurboMass™ GC/MS Software.

Results

In this example, polyvinylchloride (PVC) formulated with two different types of phthalates – disiononyl phthalate (DINP) which is regulated and another formulation of non-regulated phthalates are analyzed to determine if a difference can be seen and correlated to the phthalate type.

Figure 1 is the thermogram from the analysis of the two different PVC samples. The purple line in the thermogram with a weight loss of 50.99% in the first event corresponds to the PVC sample with DINP. The green line with the weight loss of 64.82% corresponds to the PVC with the non-regulated mixture of phthalates.

The weight-loss curve from TGA shows a clear difference between the two materials. This may be a result of either different additives or the amount of additive needed to achieve specific physical properties in the PVC sheeting.

The evolved gas from each sample was analyzed by both MS and GC/MS to determine if either technique would confirm the presence or absence of regulated vs. non-regulated phthalates. Figure 2 demonstrates the MS data obtained from the analysis of each sample.

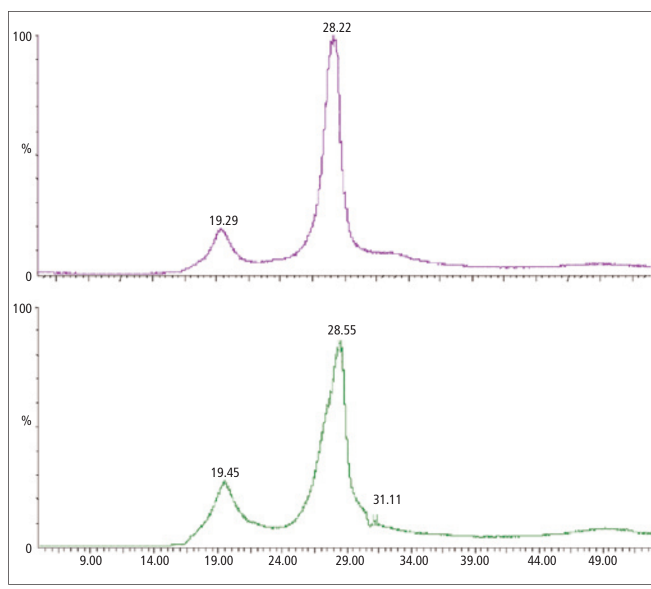

Figure 2. The MS analysis of the evolved gas generated during the TGA analysis of PVC materials with DINP (purple - top) and a mixture of non-regulated phthalates (green - bottom).

In Figure 2, it is difficult to find a difference between each material. The gas evolved in the TGA showed little difference in the MS. Each of the two major weight-loss events generated a mixture of gases generating many ion fragments simultaneously. TG-MS is very useful when the evolved gases are relatively simple; here resolution of the evolved gas is needed to identify each component.

The TGA analysis was performed again; however, a sample of the first weight loss was collected and introduced into a GC column. This will allow some resolution of evolved gases and better identification of specific components. Figure 3 demonstrates the chromatogram of the analysis of the gas evolved during the first weight loss of the TGA. It can be seen that the gas evolved is indeed very complex with a chromatogram full of different components – many unresolved.

In this case, differences can be noted in the evolved gas of each TGA. Most significant were in the peaks around 30 minutes. These peaks contained a strong response at *m/z* 149 – an ion associated with many phthalates. Further work would need to be done to determine if qualitative and/or quantitative data is provided by the analytical approach used here, but differences are much more significant when TG-GC/MS is employed over TG-MS.

Conclusions

TGA analysis allows quantification of the weight loss of a material at specific temperatures. MS increases the power of the technique by providing the ability to identify the species evolved during thermal analysis; however, if a complex gas is evolved during a single event, the MS data is difficult to interpret. The use of TG-GC/MS adds chromatographic separation of co-evolved gases, enabling identification of individual components, making data interpretation easier than TG-MS.

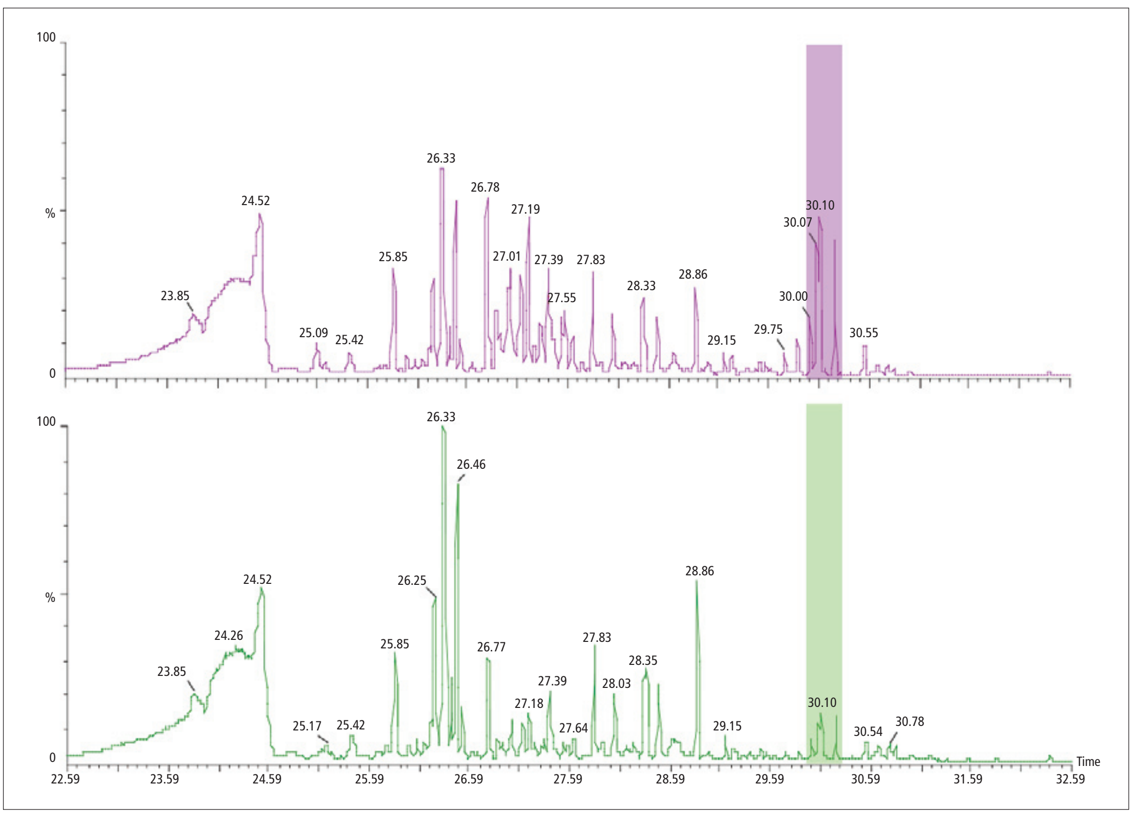

Figure 3. The GC/MS data collected during the TGA analysis of PVC with DINP (purple - top) and with a mixture of non-regulated phthalates (green - bottom). Differences are noted in peaks with tentative identification as phthalates around 30 minutes.

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