APPLICATION NOTE

Thermogravimetric Analysis – GC Mass Spectrometry

Author

Greg Johnson

PerkinElmer, Inc.
Shelton, CT 06484 USA

Qualitative Analysis of Evolved Gases in Thermogravimetry by Gas Chromatography/ Mass Spectrometry

Introduction

Thermogravimetric analysis (TGA) measures the change in the weight of a sample as a function of temperature. A limitation of TGA is that it cannot identify what material is lost at a specific temperature. The analysis of gases evolved during a TGA experiment by gas chromatography mass spectrometry (GC/MS) provides laboratories with a way to identify the compound or groups of compounds evolved during a specific weight-loss event in a TGA analysis.

This application note discusses the utility of TG-GC/MS with an example application – the identification of specific organic acids evolved during TGA analysis of switchgrass.

PerkinElmer®
For the Better

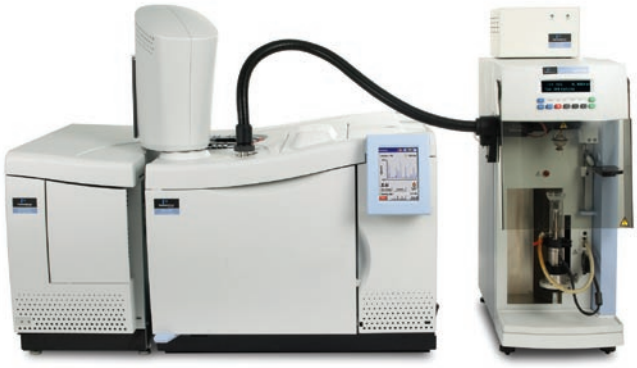

Figure 1. Clarus 600 GC/MS interfaced to the Pyris 1 TGA.

Switchgrass (Panicum Irgatum) is a perennial warm-season grass native to the northern states of the USA; it is easily grown in difficult soils. Switchgrass is potentially useful in the production of biofuels, specifically cellulosic ethanol and bio-oil.

The instrumentation used in this study was a PerkinElmer® Pyris™ 1 TGA interfaced to the PerkinElmer Clarus® 600 GC/MS with the S-Swafer™ micro-channel flow splitting device (S4 configuration). The preferred mode of operation of the TGA maintains the atmosphere around the sample at ambient atmospheric pressure. The sample is collected from the TGA by allowing the high vacuum of the MS to create a pressure drop across the GC column, causing a flow of gas from the TGA through the transfer line and the analytical column to the MS. During the analysis, there are times when the TGA inlet will be surrounded by air, rather than an inert atmosphere. This would cause air to flow into the GC/MS; this is undesirable as it will cause oxidation to a number of different areas of the system. The S-Swafer device (shown in Figure 2) is used to switch between backflushing of the TGA transfer line during non-sampling time and sampling of the TGA environment during analysis.

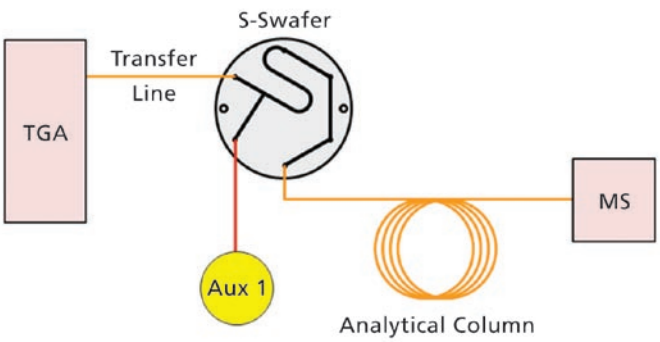

Figure 2. Schematic showing the pneumatic interfacing of the TG-GC/MS using the S-Swafer.

Figure 3 describes in greater detail the pneumatic supply to the S-Swafer device and assists in explaining why this approach is so well suited to interfacing the Pyris 1 TGA to the Clarus 600 GC/MS.

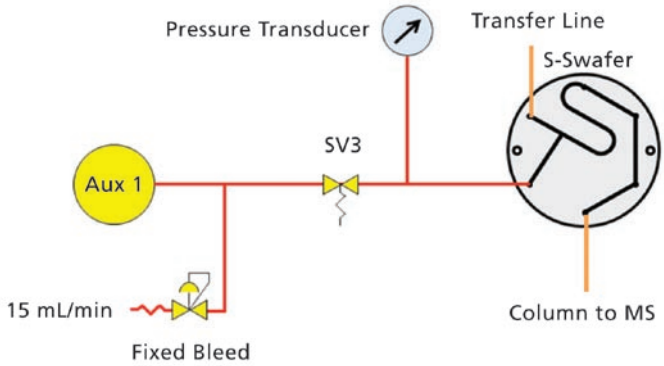

Figure 3. Schematic showing carrier-gas supply to the S-Swafer device.

The S-Swafer configuration is optimal because it will ensure a very rapid adjustment of carrier gas to the Swafer device, allowing for a rapid switch between backflush of the transfer line and sampling from the TGA. The samples of evolved gas are collected by setting a simple parameter in the GC method; multiple samples can be collected during a TGA analysis. Additionally, backflush of the transfer line will isolate the GC/MS and enable purge gas at the TGA to be switched from an inert gas (during analysis) to an air supply for cleaning of the TGA pan prior to the next sample.

Oven subambient cooling will be extremely useful in this application, allowing protracted sampling periods to be refocused into a narrow band of analytes on the column.

Experimental

The deactivated fused-silica transfer line used here was 1.6 m x 0.32 mm i.d. A few centimeters of the deactivated fused silica protrudes into the sample weighing area of the TGA. Approximately 30 cm of fused silica passes through the injector into the oven environment and is connected to the S-Swafer using specialized SilTite™ nuts and ferrules to ensure a leak-free connection that will not shrink and leak during normal or even extended thermal cycling of the main oven.

In all cases, a 30 m x 0.32 mm analytical column was employed as this allows a carrier flow of approximately 1 mL/min with the fixed 1.00 atmosphere pressure drop from ambient at the TGA to vacuum at the MS. Data was acquired using an Elite™ WAX stationary phase.

A small quantity of dried and ground switchgrass was placed on the TGA pan and weighed using Pyris software. A rapid TGA analysis based on heating the sample from 30 ˚C to 1000 ˚C at 100 ˚C/min in a nitrogen atmosphere was performed to determine which regions of the weight-loss curve were to be further studied using the TG-GC/MS technique.

The primary reason for using such rapid heating, which reduces the resolution of the weight-loss curve produced by the TGA, is to transfer the evolved gas quickly into the GC column. A quick transfer will improve GC peak shape, sensitivity and resolution.

After the sample was loaded onto the TGA and the furnace raised, the analysis was started immediately. The first step in the TGA heating program maintained the low initial furnace temperature for 5 to 10 min. During this time, the furnace environment is being purged with helium (or nitrogen/argon), and the carrier-gas pressure of 7.0 psig maintained at Aux 1 (Figures 2 and 3) ensures that no sample can enter the analytical column. After this initial hold period, the TGA furnace begins to heat the sample, and simultaneously, the GC/MS run is started using an external start command.

Based on previous TGA runs on the same sample, timed events within the GC method switch off the carrier gas supplied by the Aux 1 PPC module and then close the solenoid valve (SV3) shown in Figure 2 (Page 2). This begins the sampling and this procedure is reversed to bring the sampling period to an end. After the sampling is complete, both the GC oven-temperature program and MS data acquisition begins. The TGA can now be programmed to switch purge gases to clean the system using oxidation at elevated temperature, prior to the next analysis.

A typical TGA weight-loss curve for the switchgrass is shown in Figure 4 and reveals a typical weight % loss curve for the sample of switchgrass that was tested. In addition, superimposed on the weight-loss curve is the derivative of this curve which greatly assists the analyst in setting up the GC

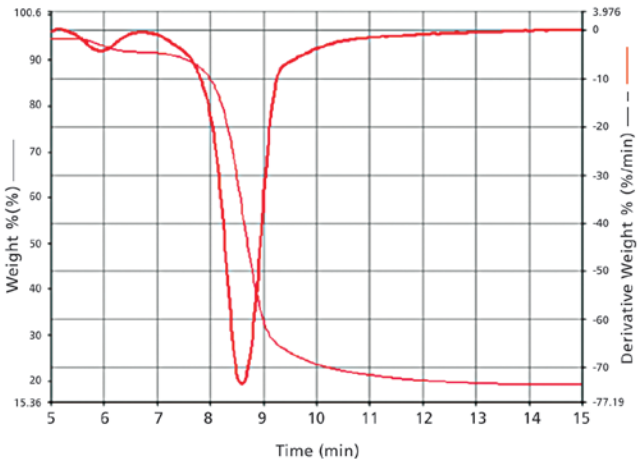

Figure 4. Typical result for the TGA analysis of switchgrass.

timed events that will be used to sample the evolved gases onto the GC/MS column. Note that the TGA is held isothermal for the first 5.0 min at which point heating begins. Simultaneously, the GC/MS analysis is started.

Figure 5 illustrates the TG-GC/MS analysis of the switchgrass based on timed events that collect the evolved gases from the main transition shown in Figure 4. The smaller earlier transition, also seen in the same figure, was also sampled onto the GC/MS but preliminary findings indicate that this is simply evolved water. The major transition produced large numbers of oxygenated volatile organic compounds (VOCs), including some very polar species. Earlier work using a non-polar capillary column had generated extremely smeared-out early-eluting peaks. The chromatogram below was generated using a thick-film polar Elite WAX column.

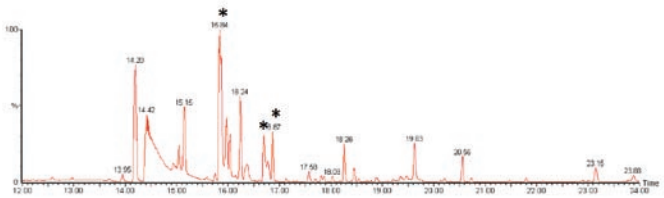

Figure 5. TG-GC/MS analysis of the switchgrass sample on a 30 m x 0.32 mm x 1 µm Elite WAX column.

The three peaks labeled with asterisks in Figure 5 are identified as a homologous series of free fatty acids (Figure 6 – Page 4), based on a library search of their MS spectra (NIST® 2008). Usually in GC, a homologous series tends to elute in carbon-number order but here, the elution order appears to be acetic, followed by formic, followed by propanonic acid. As this retention behavior is not typical and in the absence of a literature reference or a similar chromatogram in the public domain, it seemed prudent to analyze a simple retention-time standard to confirm this tentative result. Figure 7 (Page 4) shows the same analysis again but with the retention-time standard shown in parallel. This standard was a simple mixture diluted in water with a small (5 µL) aliquot of this aqueous solution deposited by syringe onto the TGA pan for analysis.

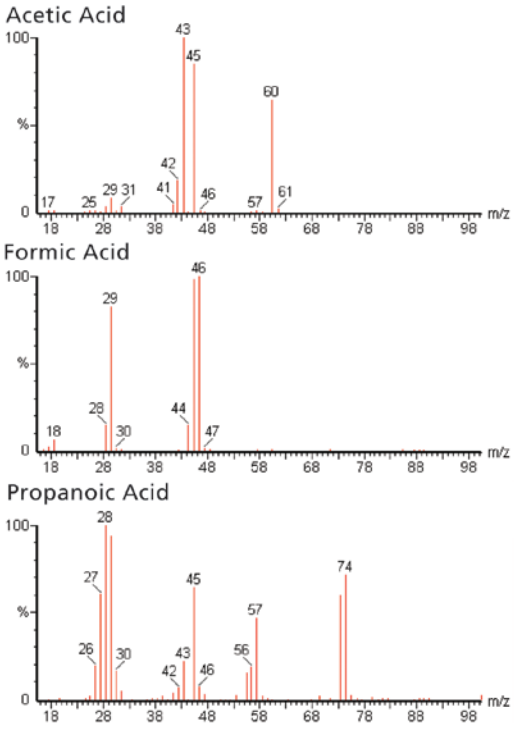

Figure 6. Mass spectra extracted from the total ion chromatogram of the switchgrass sample. The spectral data matches that of acetic, formic and propionic acid respectively available in the 2008 NIST® mass spectral library.

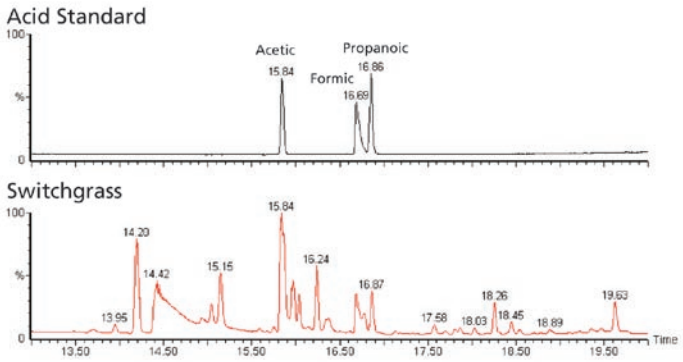

Figure 7. TG-GC/MS analysis of the switchgrass sample (bottom) on a 30 m x 0.32 mm x 1 µm Elite WAX column and the analysis of a simple retention time mix (top) under the same TGA and GC conditions.

Conclusions

In this application note, we describe the technique of TG-GC/MS through the analysis of switchgrass. TG-GC/MS is demonstrated to be a valuable technique in the separation and identification of complex mixtures of gas evolved during a TGA analysis. The S-Swafer device is demonstrated as a means to interface a TGA to GC/MS. The main benefits are its simplicity and the inertness of the entire sample path.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

009030_01