Pyrolysis Gas Chromatography—Time-of-Flight Mass Spectrometry

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1. Introduction

Pyrolysis is the breaking apart of chemical bonds by thermal energy, with the production of smaller, more volatile components. Analytical pyrolysis, with a coil or ribbon probe, is used to introduce certain sample types to a gas chromatograph, which can only handle compounds in the semivolatile range. These sample types include solids and high molecular-weight compounds. Pyrolysis is also used to minimize sample preparation, or when analysis of a whole sample is desired. Applications for pyrolysis include forensics, paints, ink, art materials, polymers, adhesives, surfactants, and even microorganisms.

One of the benefits of pyrolysis is that sample preparation is usually minimal, consisting of trimming and weighing solid samples into a quartz tube or boat. Or, liquid samples can be delivered onto a probe ribbon using a microliter syringe. In both cases, the sample capacity is in the microgram or low milligram range. When sample preparation is minimized, the full advantage of a fast instrumental method can be realized, such as Gas Chromatography—Time-of-Flight Mass Spectrometry (GC-TOFMS). With TOFMS, up to hundreds of spectra/second can be acquired, making it the ideal detector for fast GC. This note illustrates examples of pyrolysis combined with fast GC-TOFMS using a LECO Pegasus GC-TOFMS.

2. Pyrolysis GC-TOFMS

Pyrolysis was conducted with a CDS Analytical Pyroprobe 2000 mounted on the split/splitless injector of the GC. The coil probe was used with pyrolysis temperatures ranging from 800 to 1000°C. The inlet was maintained in split mode. The GC column was a J&W Scientific 10 m x 0.18 mm x 0.18 µm DB-5. Initial GC oven temperature was always 40°C. Fast GC oven programming varied depending on the application shown from 20 to 75°C/minute.

A LECO Pegasus GC-TOFMS acquired electron ionization spectral data at various rates up to 30 spectra/second depending upon the application. The stored mass range varied from 45u up to a maximum of 850u. The source temperature was always 220°C.

3. Results

Figure 1 is a pyrogram for polyethylene using a GC oven program of 20°C/minute and a constant flow of helium carrier at 1.6 ml/minute. A polyethylene pyrogram consists of triplets of dienes, alkenes, and alkanes, which sequentially increase in carbon (C) numbers (Figure 2). Under the GC conditions here, the peak widths are approximately 2 seconds, and 12 spectra/second is an adequate acquisition rate.

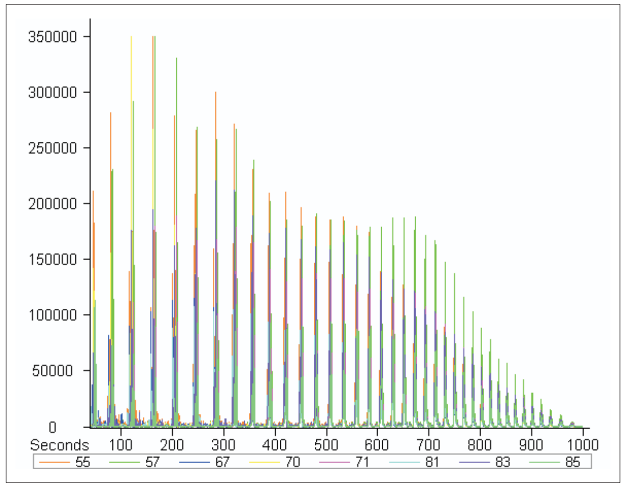

Figure 1. GC-TOFMS pyrogram of polyethylene. Extracted ions are plotted for diene, alkene, and alkane chemical classes. The C45 group elutes in less than 17 minutes.

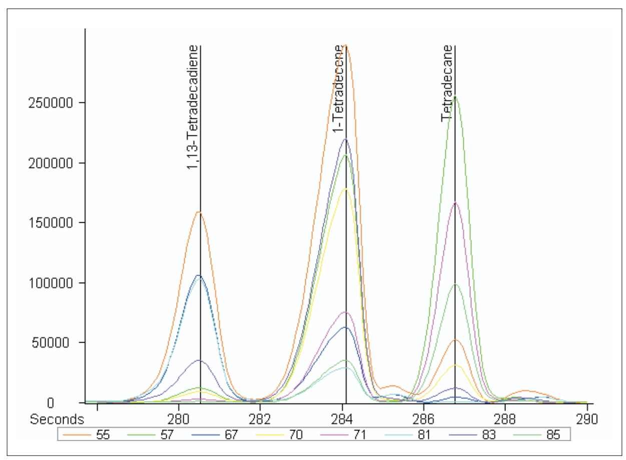

Figure 2. Zoom chromatogram of triplet diene, alkene, and alkane from pyrolysis of polyethylene. Extracted ions representing the various chemical classes are plotted. Peak widths are approximately 2 seconds, and the acquisition rate is 12 spectra/second.

With faster oven programming (75°C/minute) and a higher carrier flow (5 ml/minute), the polyethylene pyrogram can be compressed to less than 6 minutes, with no real loss in information (Figure 3). The peak widths have now been reduced to less than 1 second (Figure 4), so 30 spectra/second were collected to fully define the peaks.

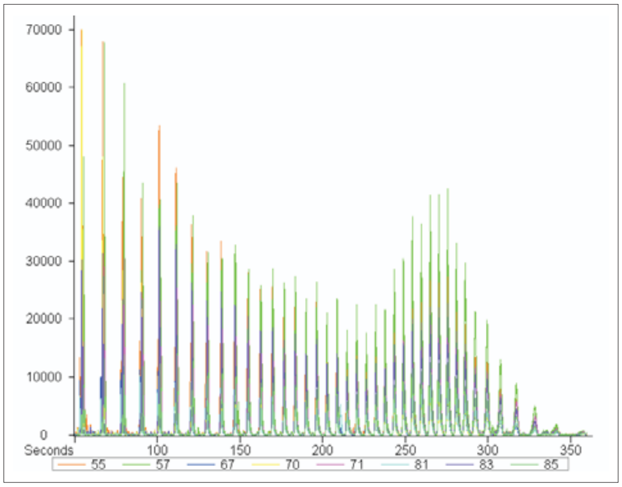

Figure 3. Ultra-fast GC-TOFMS pyrogram of polyethylene. Extracted ions are plotted for diene, alkene, and alkane chemical classes. The C48 group elutes in less than 6 minutes.

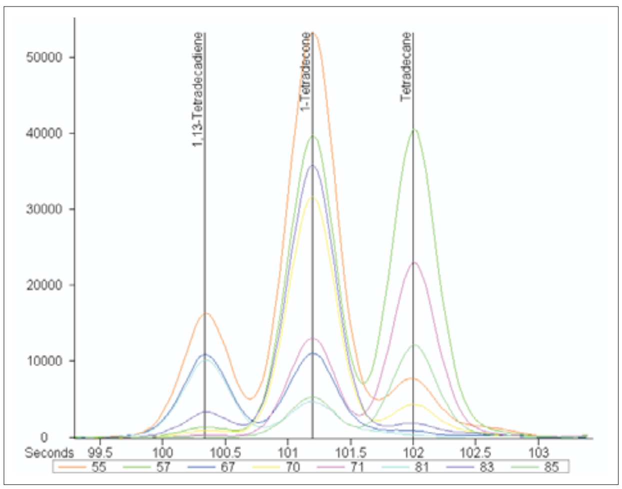

Figure 4. Zoom chromatogram of triplet diene, alkene, and alkane from pyrolysis of polyethylene. Extracted ions representing the various chemical classes are plotted. Peak widths are less than 1 second, and the acquisition rate is 30 spectra/sec.

Another benefit of using TOFMS for pyrolysis GC is that powerful Peak Find and Deconvolution algorithms can be employed to automate handling of complex pyrograms. Figure 5 shows the total ion chromatogram (TIC) for a piece of a plastic cell phone that has been pyrolyzed. Many plastics contain brominated flame-retardants, compounds that are of environmental concern, but how can they be located in such a complex data set? The acquisition speed and spectral reproducibility of TOFMS combine to enable the location of smaller peaks in the presence of matrix created from the pyrolysis of plastic (Figure 6), followed by their spectral deconvolution from the matrix. Subsequent library searching of the deconvoluted spectra is used to identify the found peaks (Figure 7). For this application, pyrolysis did not necessarily reduce all compounds to smaller, more volatile components. Instead, the brominated compounds may have been released from the plastic matrix by the thermal energy of pyrolysis.

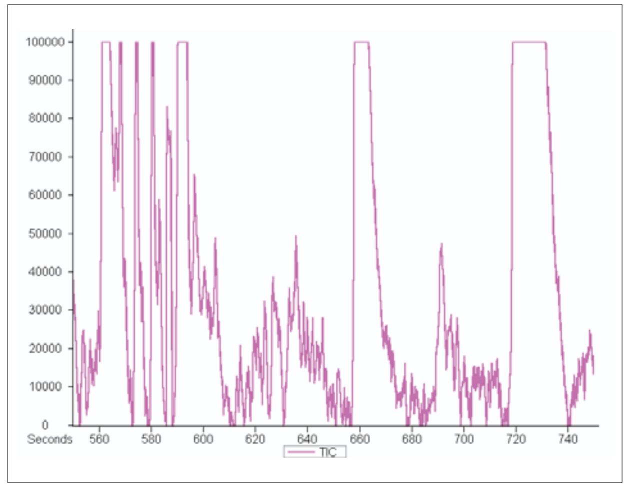

Figure 5. Total ion chromatogram from the pyrolysis of a piece of plastic cell phone.

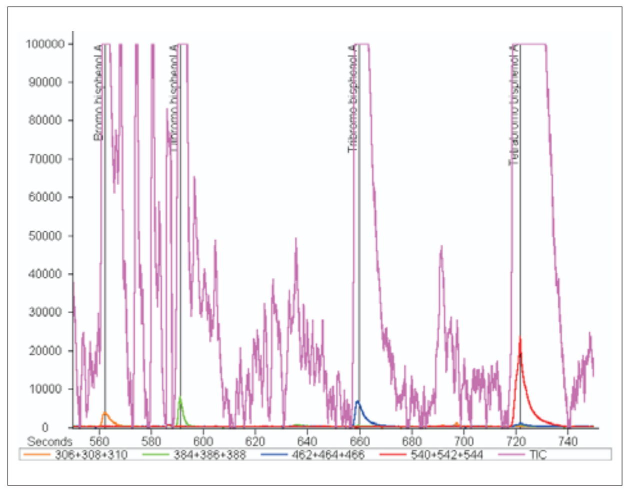

Figure 6. Extracted ion chromatograms for bromo bisphenols plotted versus the total ion chromatogram to demonstrate automatic peak find for TOFMS.

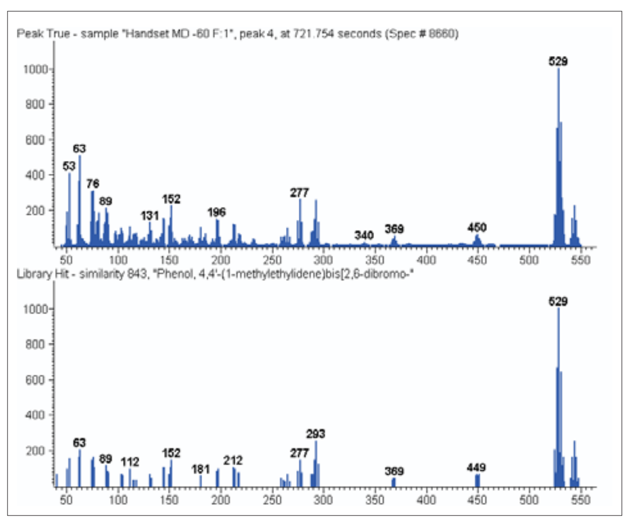

Figure 7. Deconvoluted (top) and NIST library mass spectra (bottom) for Tetrabromo Bisphenol A.

4. Conclusions

Pyrolysis GC-TOFMS is a fast way to characterize samples that would otherwise not be amenable to gas chromatography. TOFMS supplies the necessary acquisition rate to define narrow peaks, and powerful Peak Find and Deconvolution algorithms automate processing of complex pyrograms.

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