EGA for Polymer Identification Using the Pyroprobe

Application Note

Polymer, Evolved Gas Analysis, Automation, GC/MS

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Abstract

This application note demonstrates a quick and simple way to identify polymers and their constituents, using a CDS 6000 Series Pyroprobe connected directly to the mass spectrometer (MS) through a short piece of fused silica.

Introduction

Analytical pyrolysis coupled with GC/MS has long been used for the study and identification of polymeric materials, since they are frequently insoluble, non-volatile and consequently difficult to analyze. By rapid heating of the polymer, characteristic fragments are made which may be analyzed by the GC. This provides information about specific products formed during pyrolysis and the range of products (the pyrolysate) can identify the polymer. It is, however, possible to obtain a significant amount of information even without chromatographic separation of the pyrolysis products by connecting the pyrolyzer directly the detector.

By replacing the analytical column of the GC/MS with a short piece of deactivated fused silica, it is possible to process a sample thermally with nearly immediate transfer of the resulting compounds to the MS. The split inlet function can be used to limit the amount of sample entering the MS, and approximately one meter of 0.10mm fused silica provides enough restriction to permit the MS to maintain adequate vacuum. The Pyroprobe 6000 series filament is programmable in degrees per millisecond, second or minute, providing an extremely wide range of heating profiles. Pyroprobe can be programmed at heating rates the same as those used in TGA (Thermal Gravimeteric Analysis). When connected as described above, mass spectral data is produced relative to temperature instead of mass loss as in traditional TGA. Figure 1 for example compares the evolved gas analyses of several different polymers containing Bisphenol A.

CDS 6200 with Autosampler

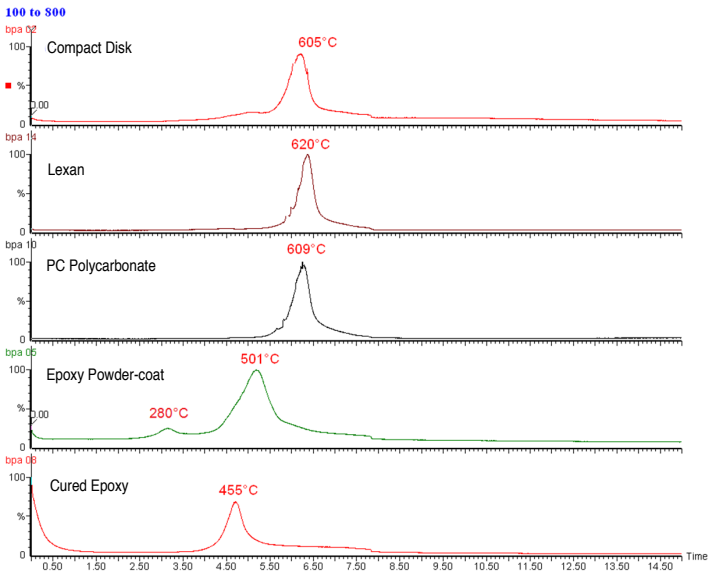

Figure 1: Evolved gas analyses of several samples containing Bisphenol A

They clearly have different thermal stabilities as indicated by the temperatures of maximum production. The epoxy powder-coat, however, also reveals an early peak which represents the evolution of semi-volatiles such as additives prior to the pyrolysis of the polymer. Examining the mass spectra at various times in the analysis can identify the types of compounds being volatilized at a certain time and the corresponding temperature. Figure 2 shows several different polymers heated to 250°C for three minutes, then ramped to 800° at 100°/minute. The initial heating at 250° vaporizes additives, such as plasticizers, allowing them to be identified before the polymer is thermally decomposed.

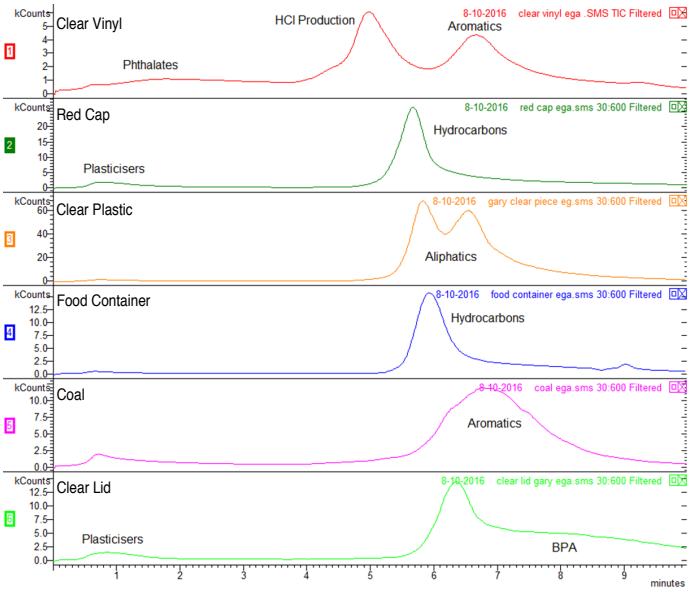

Figure 2: EGA of different materials indicating characteristic products formed

Because there is no chromatographic separation, all the analytical products are transferred directly to the mass spectrometer. At any point in time a spectrum could be a composite of multiple compounds entering the mass spec at that time. Averaging the spectra for the run provides a single spectrum containing information on all the products formed throughout the entire analysis. Creating these averaged spectra for a range of known polymers produces a library of spectra that can be used to identify unknown polymers. Figure 3 shows the EGA run for an unknown clear plastic.

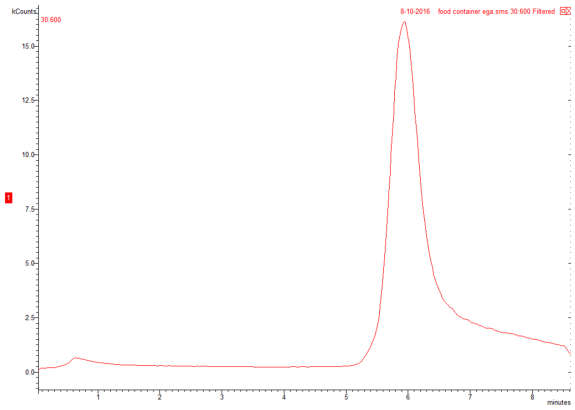

Figure 3: EGA analysis of an unknown clear plastic

Averaging the full run and using the CDS Polymer Library of averaged spectra identifies the unknown material as PET, as shown in Figure 4.

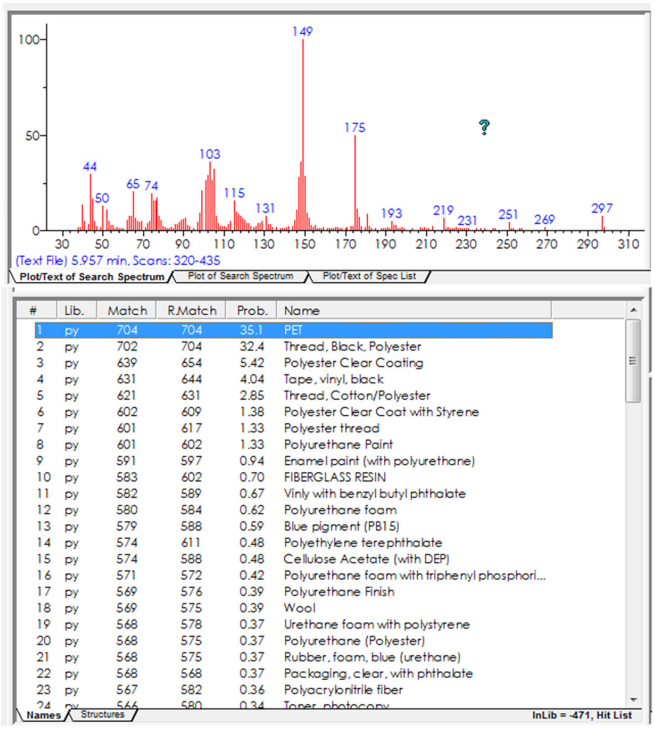

Figure 4. Library search identifying the unknown material in Figure 3 as Polyethylene Terephthalate (PET).

Further examples are shown for several common polymers including a polyurethane foam and a vinyl toy containing phthalate plasticizers (Figure 5)

Experimental Parameters

The sample was pyrolyzed in a quartz tube, using a CDS Pyroprobe 6200 Autosampler.

Pyroprobe

Initial: 250°C for 3 minutes
Ramp: 100°C/minute
Final: 800°C

Interface

Rest: 300°C
Initial: 300°C
Ramp:
Final: 300°C for 8 minutes
Valve oven: 300°C
Transfer line: 315°C

GC/MS

Column: 1 m x 0.1 mm uncoated
Carrier: Helium
Split: 100:1
Oven program:
275°C isothermal for 10 minutes

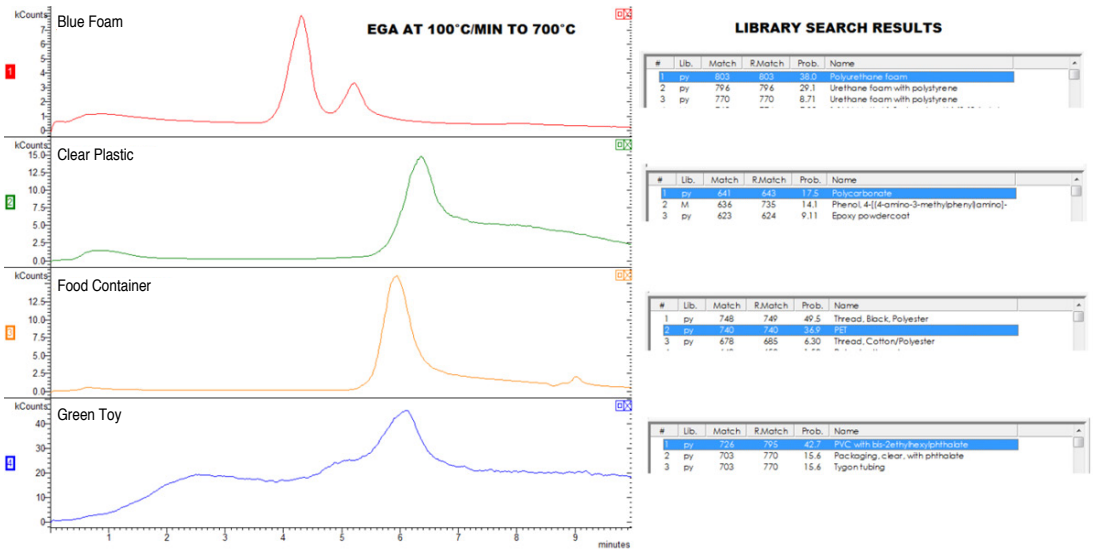

Figure 5. Identification of unknown polymers using EGA and the CDS Polymer Library.

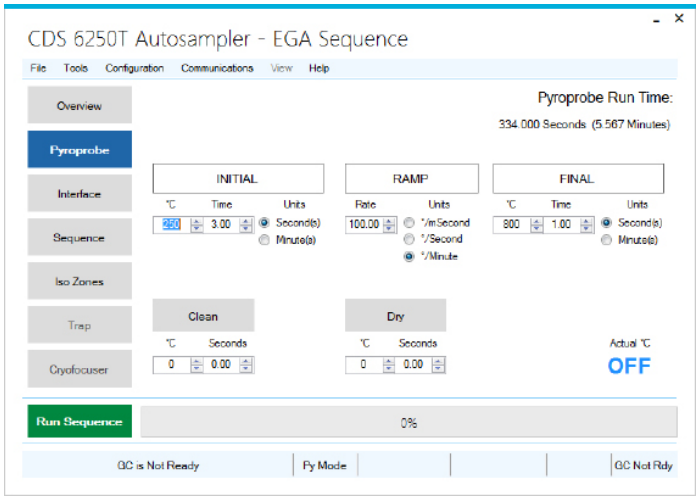

Figure 6. 6200 Pyroprobe parameters

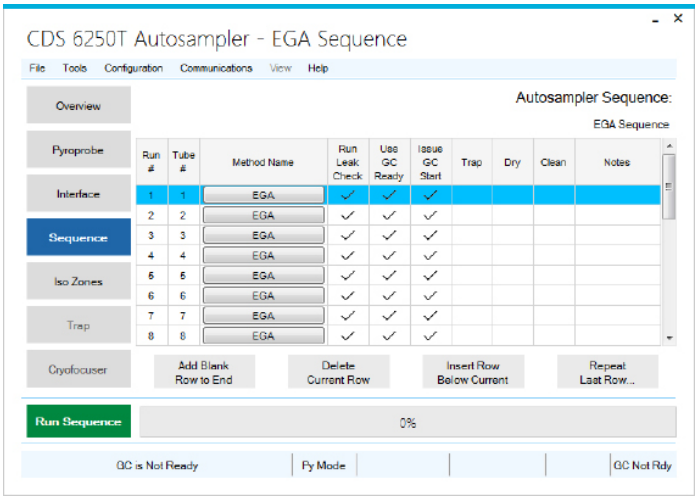

Figure 7. The autosampler Sequence Table supports dynamic sample loading during the run