Evolved Gas Analysis with Heart Cutting Technique Using a Pyroprobe with GC/MS

Author:

Karen Sam

Application Note
Polymers

Abstract
This application note presents evolved gas analysis of thermal paper, including using heart cutting technique to transfer selected group of compounds to separate sample pathway.

Introduction
Similar to the concept of thermogravimetry (TGA), Evolved Gas Analysis (EGA) is a method that uses precise temperature increments to first thermally extract and then decompose materials. The difference between TGA and EGA is that mass spectral data is produced in EGA relative to temperature instead of mass loss as in TGA, so more chemical information is gained.

However, in EGA studies on complex sample matrices, one challenge is that the target analytes may possess low concentration and overlap with many high concentration compounds that may even saturate the detector. Traditional heart cutting is a two-dimensional gas chromatography technique that serves as an effective tool to provide selectivity to resolve this issue. Here, we use the same approach to remove material, which may overwhelm the material of interest, from an EGA run.

Experimental Setup
Thermal paper, coated with a material formulated to change color when exposed to heat, is widely used at cash registers. A piece of thermal paper sample underwent EGA at 100°C per minute from 100°C to 800°C. This temperature ramping rate was 5 times faster than TGA method. A short piece of fused silica was used to connect the GC inlet to the detector. Approximately 100 μg of paper was added to a Drop-In-Sample Chamber (DISC) tube, and analyzed with a 6150 Pyroprobe coupled to a GC/MS system. The GC oven was kept at 300°C to allow evolved compounds travel immediately to the detector without chromatographic separation. The heart cutting technique was performed by combining two methods, where the beginning of the 2nd method transferred selected compounds to the vent instead of to the GC. Additionally, multi-step pyrolysis GC analysis was followed, using thermal information gained from EGA analysis to yield better resolution.

Experimental Parameters
EGA with Heart Cutting
Pyroprobe Method 1:
Use GC Ready Enabled
Issue GC Start Enabled

Initial:	100°C
Final:	350°C
Ramp:	100°C per minute
Interface:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

Pyroprobe Method 2:
Use GC Ready Disabled
Issue GC Start Disabled

Heart cutting:	450°C 60 seconds
Initial:	450°C
Final:	800°C
Ramp:	100°C per minute

GC-MS
Column: fused silica (1m x 0.10mm))
Carrier: Helium 1.25mL/min, 75:1 split
Oven: Isothermal 300°C
Ion Source: 230°C
Mass Range: 35-600amu

Multi-step Pyrolysis

Pyroprobe

DISC Chamber: 300°C 30s
400°C 30s
550°C 30s

Interface: 300°C

Transfer Line: 300°C

Valve Oven: 300°C

GC/MS

Column: 5% phenyl (30m x 0.25mm)

Carrier: Helium 1.25mL/min
75:1 split

Injector: 300°C

Oven: 40°C for 2 minutes
10°C/min to 320°C

Ion Source: 230°C

Mass Range: 35-600amu

Results and Discussion

EGA of the thermal paper is shown in Figure 1. Three decomposition peaks were observed. The region around 300°C contained m/z 59 and some m/z 213. The library search result matched amines. At 430°C, m/z 43 represented furans from the paper degradation. The third region contains m/z 104, and a library search yielded polystyrene blends.

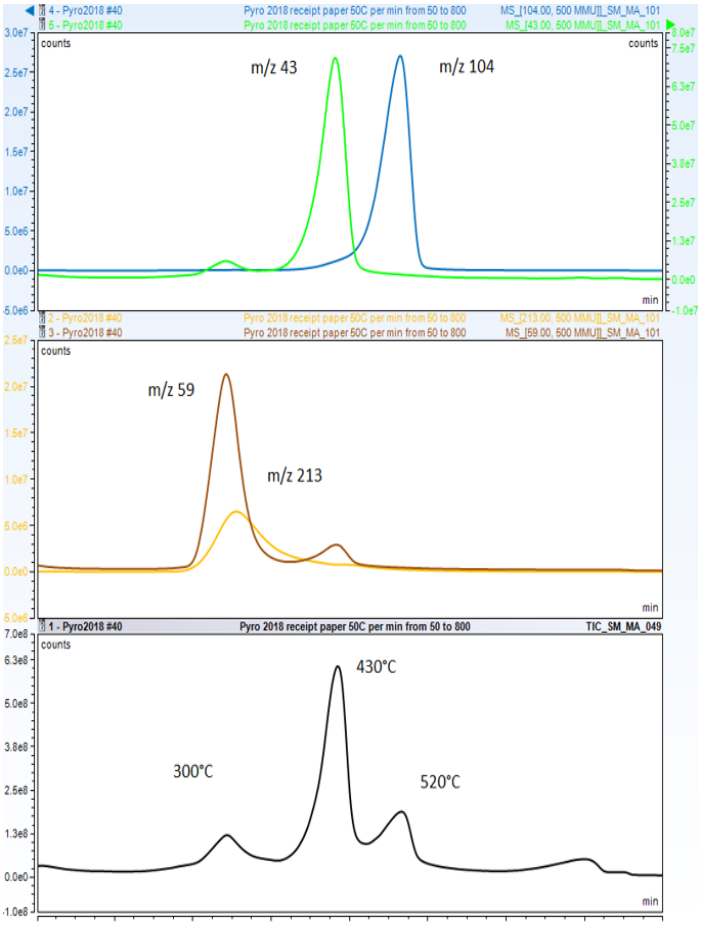

Figure 1. EGA of thermal paper: ions with m/z 43 and 104 (top), ions with m/z 59 and 213 (center), Total Ion (bottom).

Based on the temperature information gained from EGA, 300°C , 400°C and 550°C were selected as the temperature setting points of multi-step pyrolysis to separate additives from the polymers and further identify the polymers shown in Figure 2.

At 300°C, bisphenol A and a long chain amide was identified. Bisphenol A is the reactant compound or color developer, and stearic acid amide is a sensitizer. At 400°C , the cellulose of the paper pyrolyzed. While at 550°C , the paper's coating pyrolyzed. The Pyrogram matched polystyrene as the coating material.

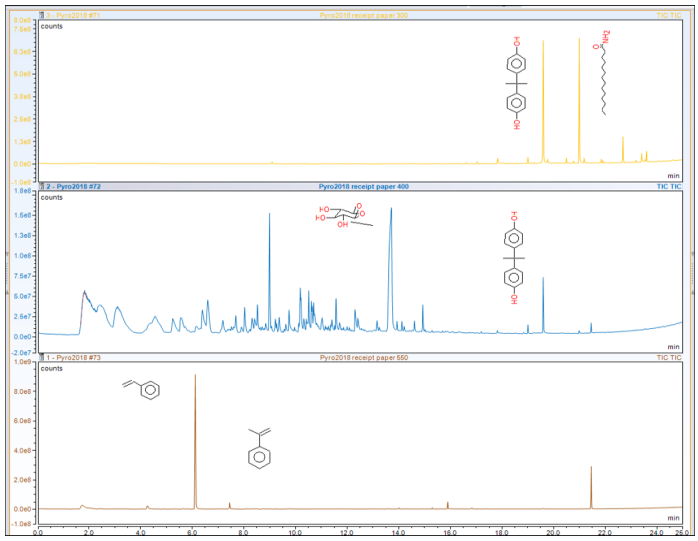

Figure 2. Thermal paper multi-step analysis at 300°C(top), 400°C(center) and 550°C(bottom)

Specific materials of interest, which may be a minor constituent of the finished product, like the additives and the polymer coating, can be more closely targeted by removing the undesired polymer, which overwhelms the EGA run. This technique was demonstrated in a second EGA run of thermal paper. The data comparison is presented in Figure 3.

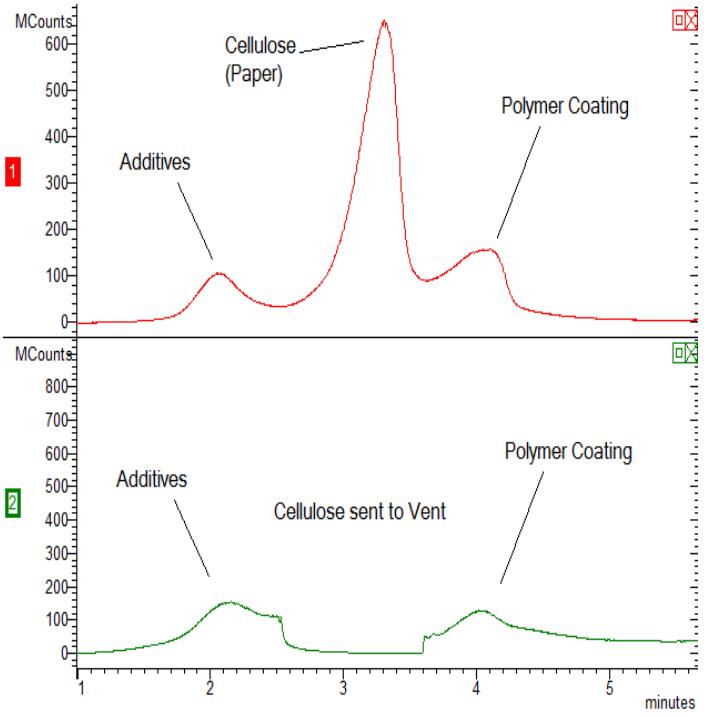

Figure 3. EGA of thermal paper at 100°C per minute (top), EGA of same sample with heart cutting to remove cellulose(bottom).

Observing from the data, pyrolysates from cellulose were blocked by the heart cutting technique, where two Pyroprobe methods were chained together for one run. The first method performed EGA from 100°C to 350°C to evaporate the semi-volatiles, after which the Pyroprobe continued to the second method with a heart cutting step to vent at 450°C for 60 seconds to remove the cellulose portion of the analysis. Then EGA resumed from 450°C to 800°C to the detector.

Conclusion

Evolved Gas Analysis (EGA) in conjunction with multi-step pyrolysis is a powerful tool to identify compounds in complex matrices. The Heart cutting went another step further to provide unique capability in selecting target of interest in detection.