# Evolved Gas Analysis and Multi-Step Pyrolysis: Two Powerful Tools for Polymer Analysis

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## Application Note
General, Polymer and Rubber

## Abstract
This application note demonstrates EGA and Multi-Step Pyrolysis of two different vinyl polymers.

## Introduction
The plastics and rubber industry play a significant role in bringing us to the modern age, which emphasizes the balance between life convenience and environmental sustainability. From the very beginning of this industry, four different categories of additives were incorporated into the products as stabilizers, plasticizers, lubricants and flame retardants. The function of these additives were to either enhance the physical performance of the finished products or to assist the manufacturing process.

A vast number of chemical species are being used as polymer additives nowadays. The molecular weight of common additives varies from 200 to 1000 Da with a wide range of boiling points. These additives placed a major challenge in the quality control process. As a matter of fact, a single step pyrolysis GC/MS analysis often produces cluttered chromatograms without adequate separation within residual solvents, pyrolysis fragments, contaminants, and additives. Evolved Gas Analysis (EGA) in conjunction with multi-step pyrolysis can address this challenge very effectively. EGA provides thermal information which can be used to select appropriate multi-step thermal extraction temperatures. Each thermally sliced chromatogram will further provide sample separation to yield well-resolved chemical information.

## Experimental Setup
Two vinyl samples, a clear transparent sheet and a small green toy, underwent EGA at 50°C per minute from 50°C to 800°C. This temperature ramp up rate is 2.5 times faster than the traditional thermal gravimetric analysis (TGA). A short fused silica column was used in the EGA run. Approximately 100$\mu$g of vinyl polymer was added to the Drop-In-Sample Chamber (DISC) tube, and analyzed with a CDS 6150 Pyroprobe, which was connected to a GC/MS system.


Pyroprobe for EGA

| | |
|---|---|
| Initial: | 50°C |
| Final: | 800°C |
| Ramp Rate: | 50°C per minute |
| DISC Interface: | 300°C |
| Transfer Line: | 300°C |
| Valve Oven: | 300°C |

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 |

## Results

Figure 1 displays EGAs from the two vinyls, including Total Ion Chromatograms, and Extracted Ion Chromatograms. Both vinyls have several regions of thermal degradation. The clear vinyl as 3 defined regions, while the green toy shows less delineation.

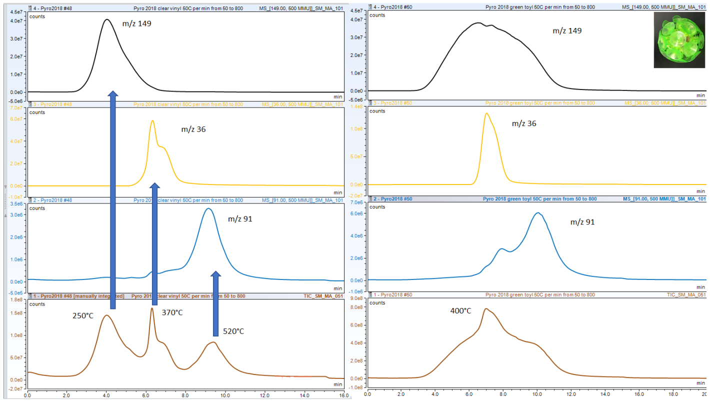


Figure 1. EGA plots of clear vinyl (left) and green vinyl (right), TICs (bottom), and EICs (top and middle).

The EGA data shows three peak regions at 250°C, 350°C, and 500°C. The first peak region is contributed by semi-volatiles (m/z=149) from phthalate plasticizers desorbed from the clear vinyl. The second and third regions are from polymer decomposition. The second region has an abundance of m/z=36 with a top match for HCl. This represents the first step of polyvinyl chloride pyrolysis to remove the chlorine side group. The last region has multiple masses associated. The aromatics at m/z=91, 106, and 115 represent the pyrolysis of the remaining polymer chain.

After obtaining the EGA information, 250°C, 350°C, and 500°C were chosen to separate semi-volatiles and polymeric components for GC-MS analysis. For the thermal slice at 250°C, dioctyl phthalate (Figure 2) was identified in the clear vinyl, and terephthalate (Figure 3) was spotted in the green vinyl. In the RoHS 2.0, the Ortho substituted phthalates are regulated but the terephthalates are not. At 400°C in both vinyls, additives dioctyl phthalate and terephthalate are still extracting as the vinyl breaks down releasing HCl. At 500°C, the remaining portion of the vinyls were stabilized to aromatics.

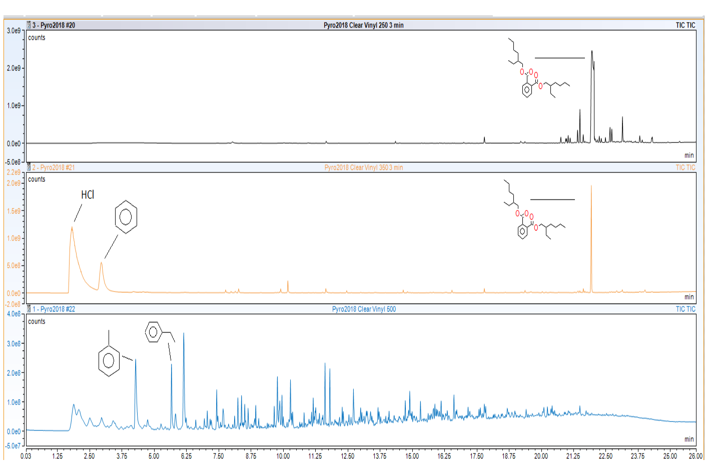


Figure 2. Clear Vinyl at 250°C (top), 350°C(middle) and 500°C (bottom).

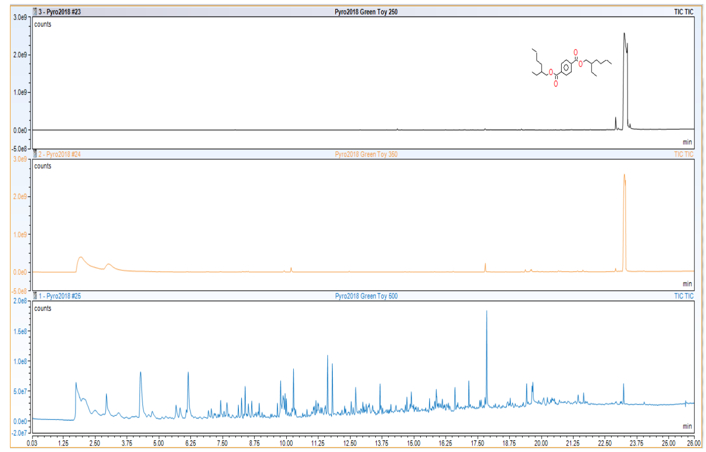

Figure 3. Green Vinyl at 250°C (top), 350°C(middle) and 500°C (bottom).

## Conclusion

Evolved Gas Analysis (EGA) in conjunction with multi-step pyrolysis can be used to effectively chose multi-step pyrolysis parameters, simplifying chromatography results of complex polymeric matrices.