Quantitative Analysis of Methyl Methacrylate in Ink Toner using Pyrolysis GC-MS

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Application Note
Polymer

Abstract
This application note demonstrates quantitative analysis of methyl methacrylate in a toner by a Py-GC-MS method.

Introduction
Toner is comprised of particles of carbon black and a binder resin polymer, such as a styrene-acrylic polymer. The binder resin polymer sticks to paper, and is melted into place by heat and pressure. The amount of methyl methacrylate (MMA) in the binder resin polymer has a great influence on the interaction between the toner particle surfaces[1]. Under strongly acidic conditions, MMA in the toner is coiled and toner particles are attracted to each other, while alkaline conditions causes the MMA to extend, and the particles remain dispersed. Either condition leads to poor printing quality. Therefore, the amount of MMA in the binder resin polymer needs to be quantified.

In this application note, Evolved Gas Analysis was performed on toner to determine the degradation temperature. Then, a calibration curve of sub-percent levels of MMA in toner was created, and an unknown sample was quantified.

Experiment Setup
Toner standards of 0.2%, 0.3%, 0.4%, and 0.5% MMA were obtained from a commercial manufacturer. Three milligrams of each toner standard were added to individual 2mL vials, and then 0.5mLs of 2-butanone was added to each toner, which was then sonicated for 2 hours to create stock solutions. Using the Pyroprobe Application Decision Making Tree[2] as our guide, Evolved Gas Analysis (EGA) of 5μL of the 0.5% stock solution was performed as the first screening step. Using the information from the EGA, single step pyrolysis GC-MS was performed on 1μL of the 4 stock solutions of MMA in toner to create a calibration curve.

EGA

Pyroprobe 6150	GC-MS
Initial: 100°C	Column: Fused silica (1m x 0.10mm)
Final: 800°C	Carrier: Helium 1.25mL/min 80:1 split
Ramp Rate: 100°C per min	Injector: 360°C
Interface: 300°C	Oven: 300°C
Transfer Line: 300°C	Ion Source: 230°C
Valve Oven: 300°C	Mass Range: 35-550amu

Pyrolysis

Pyroprobe 6150	GC-MS
DISC:	Column: 5% phenyl (30m x 0.25mm)
600°C 1 min	Carrier: Helium 1.25mL/min, 80:1 split
Interface: 300°C	Injector: 360°C
Transfer Line: 300°C	Oven: 50°C for 2 minutes
Valve Oven: 300°C	15°C/min to 150°C (1min)
	25°C/min to 280°C (1min)
	Ion Source: 230°C, Mass Range: 35-550amu

Results and Discussion

From the Evolved Gas Analysis of 0.5% MMA in toner, it is observed that degradation begins at 400°C, peaks at 475°C, completes by 600°C (Figure 1).

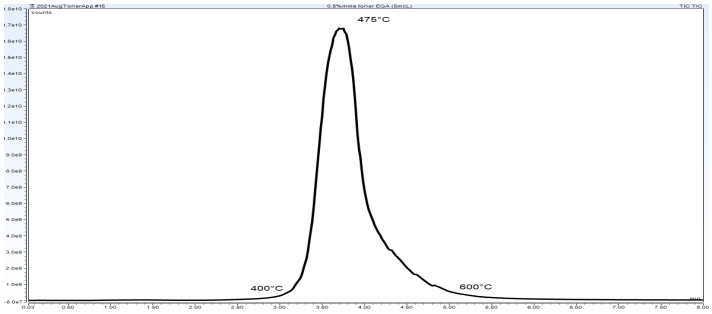


Figure 1. Evolved Gas Analysis of 0.4%MMA toner from 100°C to 800°C at 100°C per minute.

When the spectra under this peak is averaged, the top library match from the CDS polymer library is photocopy toner (Figure 2).

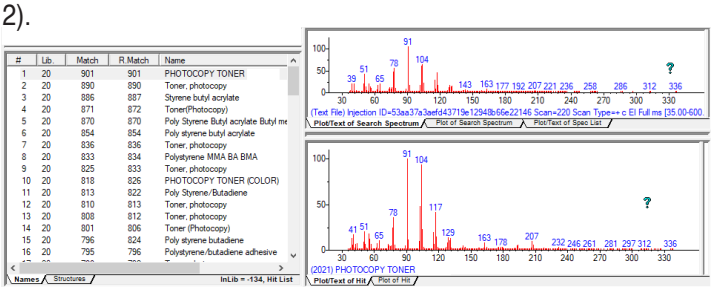


Figure 2. Polymer Library match from toner EGA.

m/z 100 was extracted to isolate the decomposition of the methyl methacrylate portion. This EGA also shows degradation beginning around 350°C, peaking at 460°C, and completing by 600°C (Figure 3).

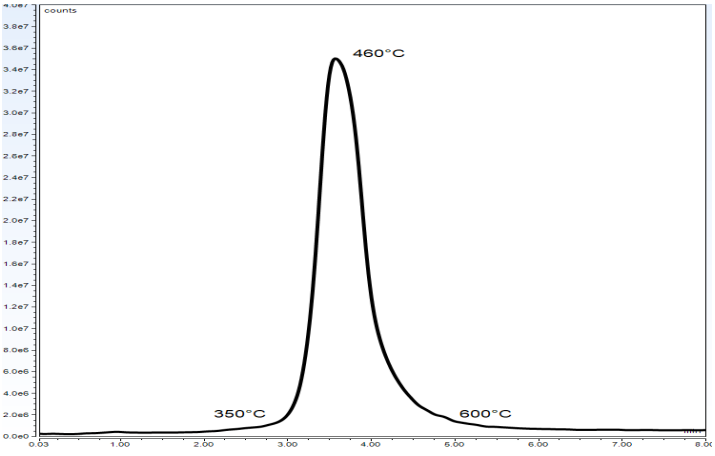
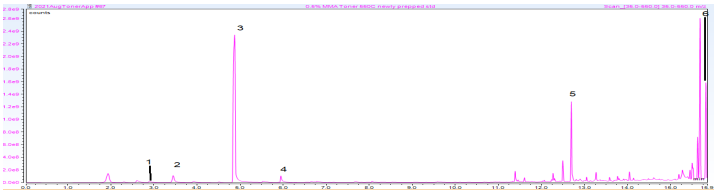


Figure 3. m/z 100 EGA to help isolate methyl methacrylate.

Using this information from the EGA run, 600°C was chosen for pyrolysis GC/MS, and 0.2%, 0.3%, 0.4%, and 0.5% MMA in toner were analyzed for a calibration curve. Each level exhibits pyrolysates of polystyrene (styrene monomer, dimer, and trimer), and a small peak for methyl methacrylate was also seen.

Figure 4 shows the pyrogram for the 0.5% MMA toner.



Peak Identification

1. Methyl Methacrylate
2. Toluene
3. Styrene
4. alpha Methylstyrene
5. Styrene dimer
6. Styrene trimer

Figure 4. Toner with 0.5% MMA, 600°C

A peak area ratio of ions for MMA(100) to Styrene (104) was used for the calibration curve, which resulted in a $R^2$of 0.99 (Figure 5). From this calibration curve, an unknown toner sample was determined to have 0.27% MMA.

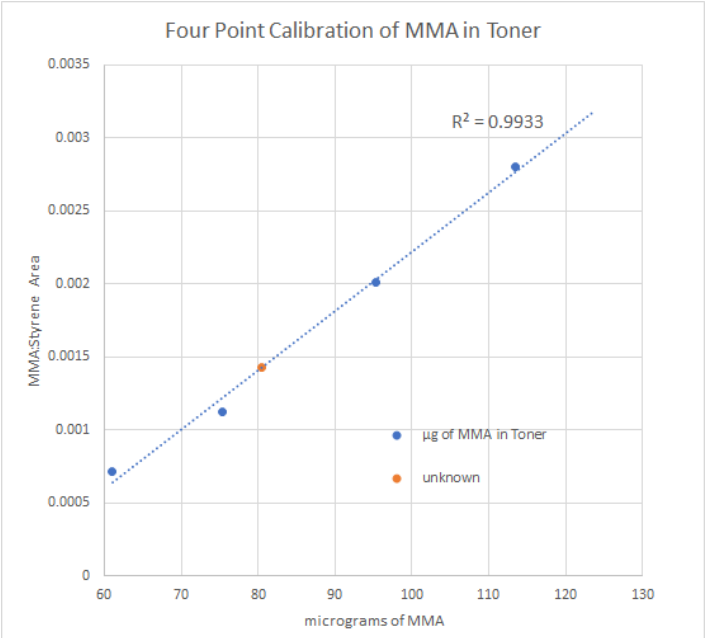


Figure 5. Methyl Methacrylate Linear Calibration and unknown sample.

Conclusions:

A calibration curve for photocopy toner was created, and an unknown sample was quantitatively analyzed in a CDS 6150 Pyroprobe at a sub-percent level.

References

1. Miller, J. Azevedo, D, Interaction Forces between toner surfaces. 2000 TAPPI Recycling Symposium.

2. Pyroprobe Application Decision Making Tree., CDS Analytical, 2021.