Evolved Gas Analysis and Multi-step Pyrolysis of Mascara Using the Pyroprobe with GC/MS

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Application Note
Cosmetics

Abstract
This application note demonstrates evolved gas analysis (EGA) and multi-step pyrolysis (MSP) with GC/MS on two different mascara samples.

Introduction
Cosmetics include a wide array of products, such as lipsticks, mascara, eyeshadow, moisturizers, foundations, to enhance the appearance of the face or body. In US alone, the cosmetic industry contributed 1.5% of the gross domestic product (GDP), which is over $250 billion. The chemical formulation of cosmetics is extremely complex, and are grouped into common ingredients and proprietary ingredients. This wide range of substances in complex matrices is challenging for quality control process. The traditional component analyses by wet chemistry require large sample amount and are time-consuming through solvent extraction steps. This application note proposes quicker and easier alternatives by combining EGA and MSP GC-MS analysis to separate ingredients based on volatility.

Experiment Setup
Mascara samples from two different manufacturers were tested. One sample was marked as brand “M”, and the other was brand “C”. For each run, 100µg of samples were added to Drop-In-Sample Chamber (DISC) tubes on a Pyroprobe 6150. EGA and MSP were performed on these samples.

EGA

Pyroprobe Setpoints:		GC-MS	
Initial:	50°C	Column:	fused silica (1m x 0.10mm)
Final:	800°C	Carrier:	Helium 1.25mL/min, 75:1 split
Ramp Rate:	100°C per min	Oven:	isothermal 300°C
DISC Interface:	300°C	Ion Source:	230°C
Transfer Line:	300°C	Mass Range:	35-600amu
Valve Oven:	300°C		

Multi-step Pyrolysis

Pyroprobe		GC-MS	
DISC Chamber:	100°C 1min	Column:	5% phenyl (30m x 0.25mm)
	200°C 1min	Carrier:	Helium 1.25mL/min
	300°C 1min		100:1 split
	400°C 1min	Injector:	360C
	700°C 30sec	Oven:	40°C for 2 minutes
			10°C/min to 320°C
Interface:	300°C	Ion Source:	230°C
Transfer Line:	300°C	Mass Range:	35-600amu
Valve Oven:	300°C		

Results and Discussions
By following the polymer quantification road map, EGA was first tested on the samples. In this fast screening technique, the analytical column in the GC was replaced with a short fused silica and the GC oven was kept hot at 300°.

The sample was then subjected to heating at a ramp rate of 100°C per minute. This quick scan usually leads to a thermal information on samples.

Figure 1 shows the overlay of the EGA runs on samples from two manufacturers. Both of them had two regions of thermal degradation. The peak position of each degradation region from the two samples was identical at 300 °C and 450 °C. The region at 300 °C represented non-polymeric ingredients in the formulation, including waxes and fatty acids, while the second region at 450 °C represents decomposition of the polymeric portion.

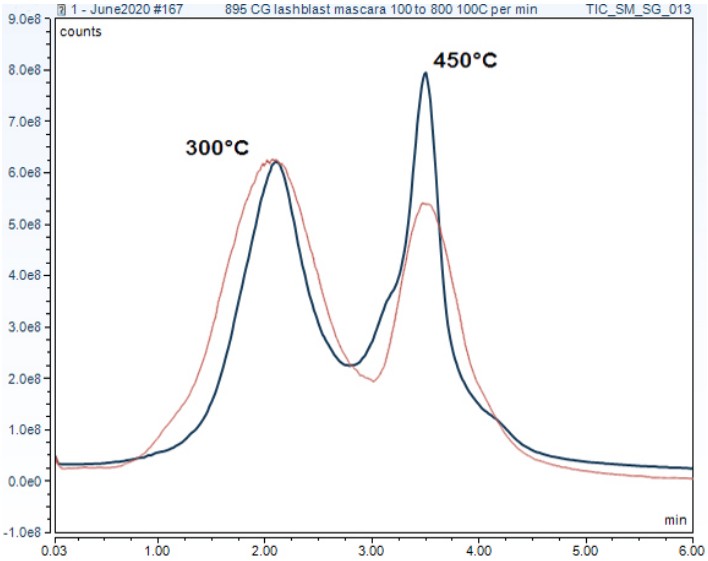

Figure 2. EGA of Mascara “M” (red) and Mascara “C”(blue).

Information gathered from EGA could be generally used to determine setting temperatures for the following MSP analysis. For this application, EGA suggested the MSP temperature could be 300 °C and 450 °C. However, based on the fact that EGA was not sufficient to characterize samples from different brands, more MSP runs were suggested to enhanced the separation. Therefore, MSP temperatures were picked at 200 °C, 300 °C, 400 °C to thermally extract various organic compounds based on volatility, and a single temperature of 700 °C to pyrolyze the remaining polymer.

Figure 3 shows chromatograms of mascara “M” using a multi-step sequence of 200 °C, 300 °C, 400 °C and 700 °C, separating components among 4 chromatograms. At 200 °C, the mascara “M” released siloxanes, as well as an aliphatic alcohol. The sample run at 300 °C produced a series of n-alkanes from thermally extracting waxes. At 400 °C, as waxes continued to desorb, the polymer portion began to be revealed as butyl methacrylate monomer broke free from the polymer chain. Finally, at 700 °C only polymer remains. The presence of butyl methacrylate, 2-ethylhexyl acrylate, and styrene indicate the mascara was a copolymer containing these 3 monomers.

Figure 4 shows MSP runs of mascara “C” at 200 °C, 300 °C, 400 °C and 700 °C. At 200 °C, mascara “C” released squalene and siloxanes. MSP at 300 °C showed fatty acids and monoglycerols.

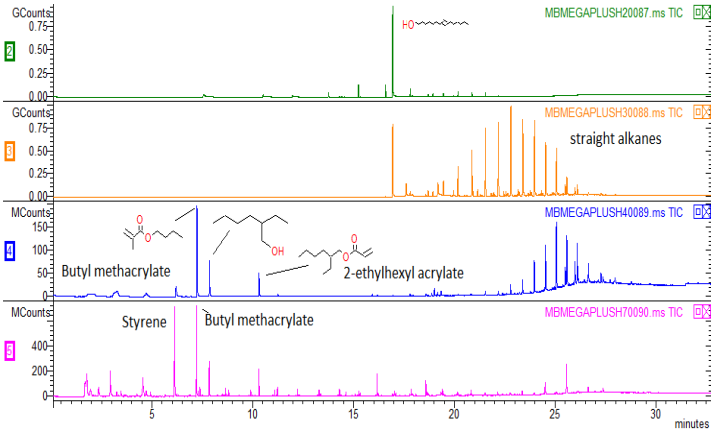

Figure 3. MSP of mascara “M” at 200 °C, 300 °C, 400 °C and 700 °C.

At 400°C, there were fatty acid methyl esters and the diglycerol, dipalmitin. Finally, at 700°C, only the polymeric portion of the mascara remained. Peaks for methyl methacrylate, butyl acrylate and styrene indicated this mascara’s base polymer is a styrene acrylic composed of methyl methacrylate, butyl acrylate.

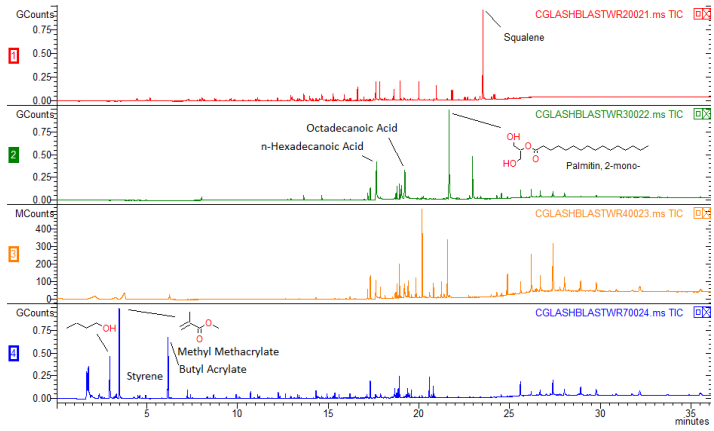

Figure 4. MSP of mascara “C” at 200 °C, 300 °C, 400 °C and 700 °C.

Figure 5 compared the 700 °C run of both mascaras to illustrate two polymer formulations. Both brands contained styrene and acrylic monomers, but the type of acrylic was different. Mascara “M” used butyl methacrylate and 2-ethyl hexyl acrylate, while mascara “C” contained methyl methacrylate and butyl acrylate.

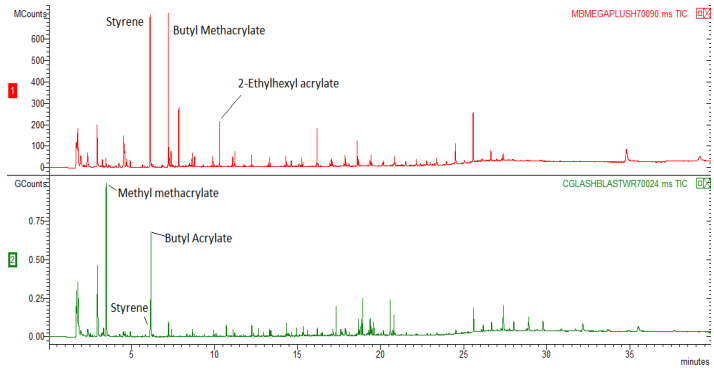

Figure 5. Mascara “M” (top), and Mascara “C” at 700 °C after 200 °C, 300 °C, 400 °C.

Conclusion

EGA and MSP are two powerful tools in polymer identification. The first tool is emphasizing on screening speed, whereas the second tool could provide more in depth information. This application note presented an example that both tools yield valuable information to support each other.