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

Application Note
Food

Author:

Karen Sam

Abstract
This application note demonstrates Evolved Gas Analysis (EGA) and Multi-step Pyrolysis (MSP) with GC/MS on two different tea bag samples..

Introduction
Tea is the second most consumed drink in the world. According to the UK Tea and Infusions Association, over 60 billion cups of tea are consumed every year, and 96% of the tea-drinkers steep tea in a tea bag rather than brewing loose tea leaves. The common consumer misconception has been that the tea bag is made from filter paper and remains plastic free, until a recent media coverage by BBC News on research work from McGill University, which concluded that a single tea bag released about 11.6 billion microplastic and 3.1 billion smaller nanoparticles into the hot water[1].

Evolved Gas Analysis in conjunction with Multi-step Pyrolysis is a powerful tool set in identifying unknown polymer compounds. In this application note, two 100 μg of tea bag samples from different manufacturers were tested to unveil the chemical composition by a CDS Pyroprobe 6150, which is a multi-function thermal extraction instrument for GC/MS analysis.

Experiment Setup
Two tea bag samples, named W and C by their brand, were cut from center of the tea bag to avoid sampling in the sealing area where glue may be applied. Then each sample was further trimmed down to 100 μg before loading into the Drop-In-Sample-Chamber(DISC) tube for analysis. A fused silica transfer line was used to connect the GC inlet to the MS detector in the EGA run. A 30 meter long 5% phenyl capillary column was adopted in the Multi-step Pyrolysis. A vent-free adapter was installed to assist a fast switch between two columns without losing vacuum in the mass spectrometer.

EGA

Pyroprobe:		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		
DISC Interface:	300°C	Oven:	isothermal 300°C
Transfer Line:	300°C	Ion Source:	230°C
Valve Oven:	300°C	Mass Range:	35-600amu

Multi-step Pyrolysis

Pyroprobe:		GC-MS	
DISC:	300°C 1 min	Column:	5% phenyl (30m x 0.25mm)
	400°C 1 min	Carrier:	Helium 1.25mL/min
	500°C 1 min (W)		75:1 split
	550°C 1 min (C)	Injector:	320°C
Interface:	300°C	Oven:	40°C for 2 minutes
Transfer Line:	300°C		10°C/min to 300°C
Valve Oven:	300°C		hold 15 min
		Mass Range:	35-600amu

Results and Discussions

By following the polymer quantification road map, EGA was first performed on both samples. In this fast screening technique, the DISC temperature was ramped up at 100 °C/min from 50 °C to 800 °C and the GC oven was kept isothermal at 300°.

Figure 1 shows the EGA data on sample W, where two regions of thermal degradation were observed. The peak position of each degradation region was 400 °C and 500 °C. When the mass spectra under the first peak was averaged and compared against the polymer library, the top match was paperboard, whereas the second peak was a styrene acrylic blend.

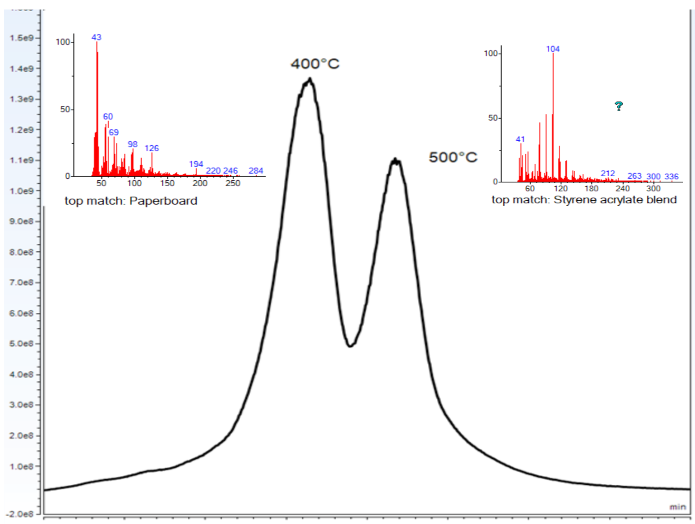

Figure 1: EGA of tea bag W from 50 °C to 800 °C at 100 °C per minute. The mass spec library top match from each peak region is shown in the figure.

Tea bag C also showed two regions of thermal degradation in Figure 2. The peak position of the 2nd degradation region shifted to 550 °C compared to sample W, which indicated a different polymer. The mass spectra under the first peak matched paperboard again, while the second peak yielded polypropylene.

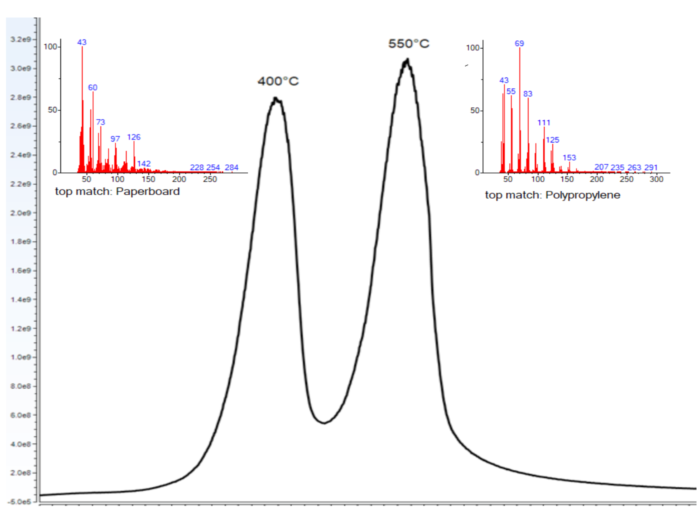

Figure 2: EGA of tea bag C from 50 °C to 800 °C at 100 °C per minute. The mass spec library top match from each peak region is shown in the figure.

Information gathered from EGA was used to determine the setting temperatures for the following Multi-step Pyrolysis. Tea bag W was thermally tested at 3 temperatures sequentially: 300 °C, 400 °C, and 500 °C. As shown in Figure 3, at 300 °C, a tiny caffeine peak, which was adsorbed from the tea, was observed. Besides caffeine, no trace of plasticizers was detected, which implied that a food grade polymer was used in the manufacturing process. At 400 °C, levoglucosan, which is the pyrolysis marker for cellulose, indicated the presence of cellulose fibers. At 500 °C, the data unveiled the synthetic portion of the tea bag as styrene and acrylic fibers, namely methyl methacrylate and butyl methacrylate.

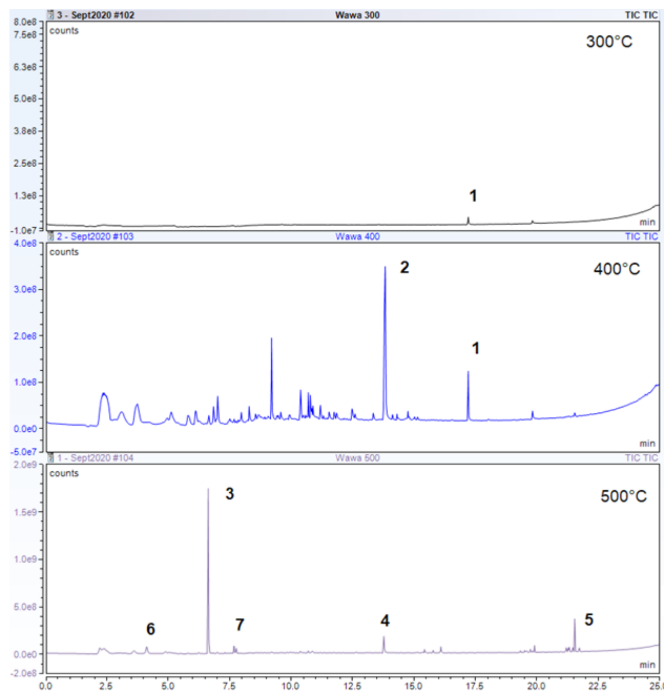

Figure 3: Multi-step pyrolysis of tea bag W at 300 °C(top), 400 °C (center) and 500 °C (bottom). Peak # Identification:
1 Caffeine, 2 Levoglucosan, 3 Styrene, 4 Styrene Dimer, 5 Styrene Trimer, 6 Methyl Methacrylate, 7 Butyl Methacrylate

Figure 4 showed the data where tea bag C was thermally treated at 3 temperatures that were determined by the EGA, At 300 °C, neither caffeine nor plasticizer was identified, which indicated better storage condition and/or shorter storage time, as well as using virgin polymer without additives. Consistent with tea bag W, cellulose fibers were unveiled at 400 °C. At 550 °C, the pyrogram matched the plastic portion of the tea bag to polyethylene, which has higher thermal degradation temperature than the polymer used in tea bag W.

Conclusion

Evolved Gas Analysis and Multi-step Pyrolysis 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 a hot environmental topic to further bring public awareness in the widespread use of plastics into the areas that even impact the food safety.

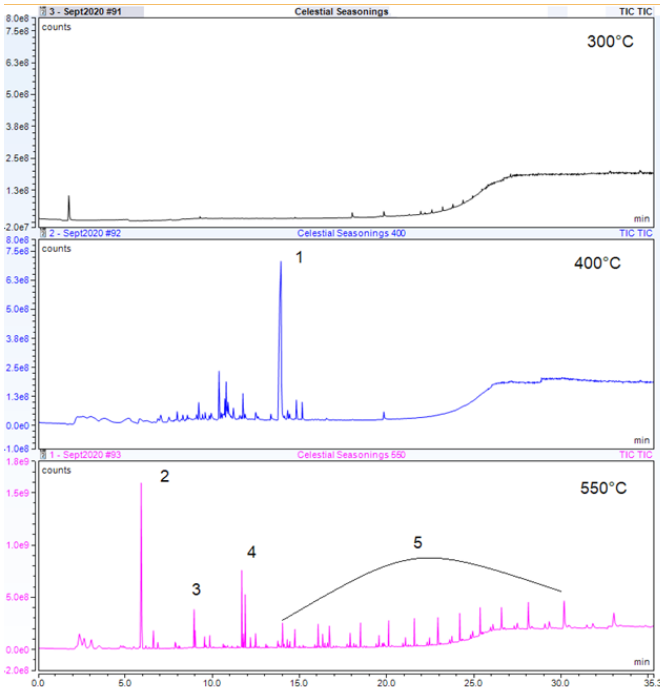

Figure 4: Multi-step pyrolysis of tea bag C at 300 °C(top), 400 °C (center) and 550 °C (bottom). Peak # Identification:
1 Levoglucosan, 2 Polypropylene Trimer, 3 Polypropylene Tetramer, 4 Polypropylene Pentamer, 5 Polypropylene Oligomers

References

(1) Hernandez, Laura M., et al. “Plastic teabags release billions of microparticles and nanoparticles into tea.” Environmental science & technology 53.21 (2019): 12300-12310.