Quantitative Analysis of Flame Retardant TDCPP in Cushion Foam by Pyroprobe

Application Note

Environmental, Polymer

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Abstract

This application note demonstrates quantitative analysis of a toxic flame retardant Tris(1,3-dichloro-2-propyl)phosphate (TDCPP) in polyurethane foam by Evolved Gas Analysis (EGA) and Multi-step Pyrolysis (MSP) with GC/MS method.

Introduction

Flame retardants are often added to industrial and consumer products to meet flammability standards for furniture, textiles, electronics, and insulation products. Polybrominated diphenyl ethers (PBDEs), particularly penta-BDE and octa-BDE, were introduced in 1970s and quickly became the largest product on the flame retardant market[1] until they were officially banned in the EU from August 2004 and listed as pollutant in the Stockholm Convention[2] due to various health risks[3]. As an alternative to PBDEs, tris(1,3-dichloro-2-propyl) phosphate (TDCPP) emerged from the market and became the major flame retardant used for the polyurethane foam in furniture and automobiles[4]. Even though the European Union considered TDCPP safe for its intended uses[5], animal studies have suggested that TDCPP is neurotoxic, an endocrine disruptor, and a reproductive toxicant[6].

In this application note, a polyurethane foam sample was quantitatively tested against TDCPP on the trace level. The analysis was performed on a CDS 6150 Pyroprobe that was connected to a GC-MS.

Experiment Setup

The polyurethane foam sample was obtained from a furniture cushion. The bulk sample was further cut down to 100 μg and then loaded into a DISC tube. TDCPP standard was purchased from Sigma-Aldrich. A 1-meter long fused silica transfer line was used to connect the GC inlet to the MS detector for EGA analysis. In subsequent GC/MS analyses, a 30-meter long 5% phenyl capillary column was adopted in the MSP. A vent-free adapter was installed to enable an easy switch between the two columns without losing vacuum in the mass spectrometer.

EGA

Pyroprobe	
Initial:	100°C
Final:	800°C
Ramp Rate:	100°C per min
DISC Interface:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

Multi-step Pyrolysis

Pyroprobe:	
DISC:	250°C 1 min
	360°C 1 min
	460°C 1min
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
	80:1 split
Injector:	360°C
Oven:	300°C
Ion Source:	230°C
Mass Range:	35-600amu

GC-MS	
Column:	5% phenyl (30m x 0.25mm)
Carrier:	Helium 1.25mL/min
	80:1 split
Injector:	360°C
Oven:	40°C for 2 minutes
	12°C/min to 320°C, 10 min
Mass Range:	35-600amu

TDCPP Quantification

Pyroprobe:		GC-MS	
DISC:	300°C 5min	Column:	5% phenyl
Interface:	300°C		(30m x 0.25mm)
Transfer Line:	300°C	Carrier:	Helium 1.25mL/min
Valve Oven:	300°C		80:1 split
		Injector:	360°C
		Oven:	40°C for 2 minutes
			20°C/min to 320°C, 10 min
		Mass Range:	35-600amu

Results

Based on the Pyroprobe Application Roadmap, EGA was first performed on the foam sample. In this fast screening technique, the DISC temperature was ramped up at 100 °C/min from 100 °C to 800 °C and the GC oven was kept isothermal at 300°C.

Figure 1 shows the EGA data, where two regions of thermal degradation were observed. The peak position of each degradation region was 360°C and 460 °C respectively. The mass spectra integration under the first peak resembled toluene diisocyanate (TDI), whereas the second peak resembled polyol. This was consistent with the composition of polyurethanes, which are made by reacting diisocyanate with polyols.

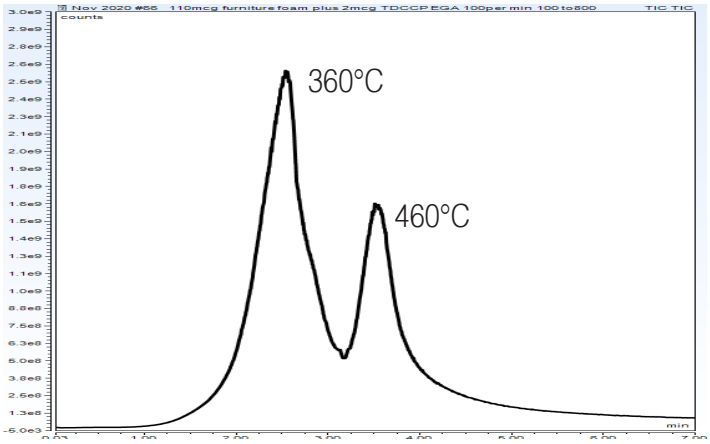

Figure 1. EGA run of a foam sample from a chair cushion.

Except the TDI and Polyol peaks, no separate additive peak was observed in Figure 1. The extracted ion technique was further used to filter the EGA data by tracing ion m/z=381 to isolate the TDCPP as shown in Figure 2, where a EGA peak position at 350 °C was obtained. This data indicated the possibility of TDCPP, which has a lower extracting temperature than the TDI.

Using the EGA results as a guide, the sample was then tested by multi-step temperatures at 250°C, 360°C, and 460°C respectively. The resulting chromatograms are shown in Figure 3. At 250°C, TDCPP was confirmed. At 360°C, more TDCPP, as well as TDI, which is one of the degradation product of polyurethane, were observed. At 460°C, polyol ether oligomers were present.

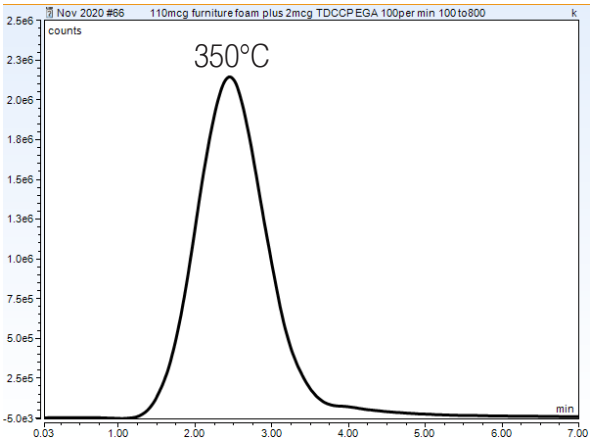

Figure 2. Extracted ion on m/z=381 from EGA.

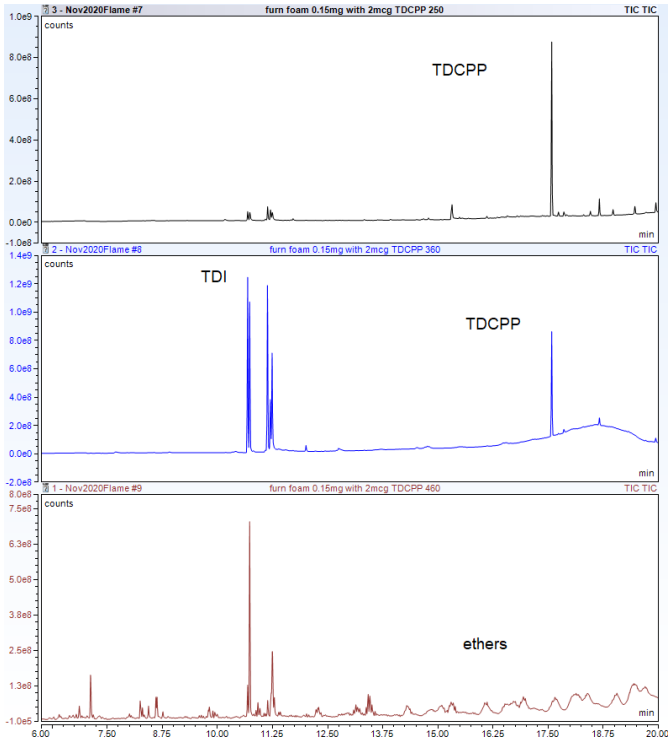

Figure 3. Multi-step pyrolysis of the sample at 250 °C (top), 360 °C (center), and 460 °C (bottom).

Based on the data from the multi-step pyrolysis, an optimal extraction temperature for TDCPP should be between 250 °C and 360 °C to maximize the effectiveness of extraction on TDCPP and minimize the interference from foam degradation. A setpoint of 300 °C for 5 minutes was picked in the middle point. To verify the extraction effectiveness, a foam sample was tested at the picked setpoint, and then tested again at the same setpoint for carryover. The data is shown in Figure 4. From the data, over 99% of the TDCPP was extracted in the first step, only 0.11% of the TDCPP remained in the seconds step.

To quantify the concentration of TDCPP in the foam, a calibration curve was drawn. 4 mg of TDCPP was dissolved into 1 mL of methanol as standard. 0.1, 0.2, 0.3, 0.4, and 0.5 μL of such standard was loaded into five DISC tubes individually, resulting in an

absolute mass of 0.4, 0.8, 1.2, 1.6, and 2.0 μg TDCPP respectively in each of the DISC tube. Then each sample was thermally extracted at the setpoint. The five-point calibration was shown in Figure 5 with a linear regression greater than 0.99.

From plugging the foam sample data into the calibration curve, the sample was calculated to contain 1.50 μg of TDCPP, which is equivalent to a weight percent at 1.50%.

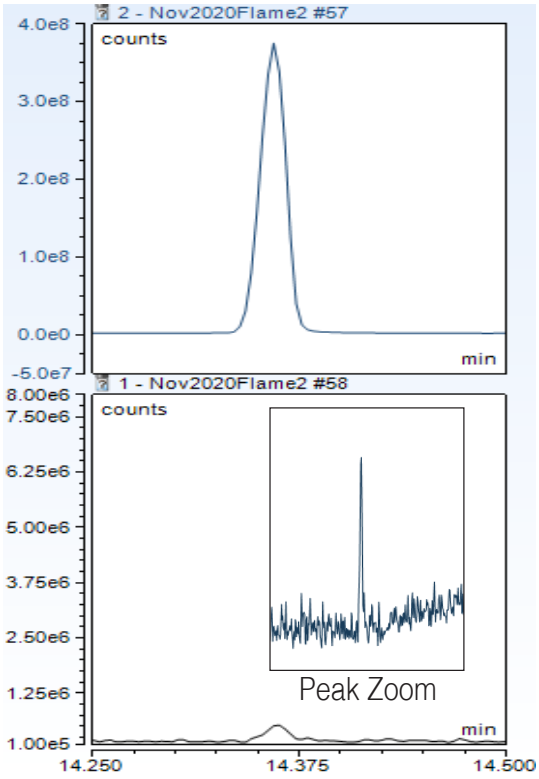

Figure 4. Extraction of TDCPP in foam at 300 °C for 5 minutes (top) then again (bottom).

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. Combining these tools, this application note built a quantitative thermal extraction method to test the concentration on one of the widely used flame retardants - TDCPP in unknown samples using a Pyroprobe.

References

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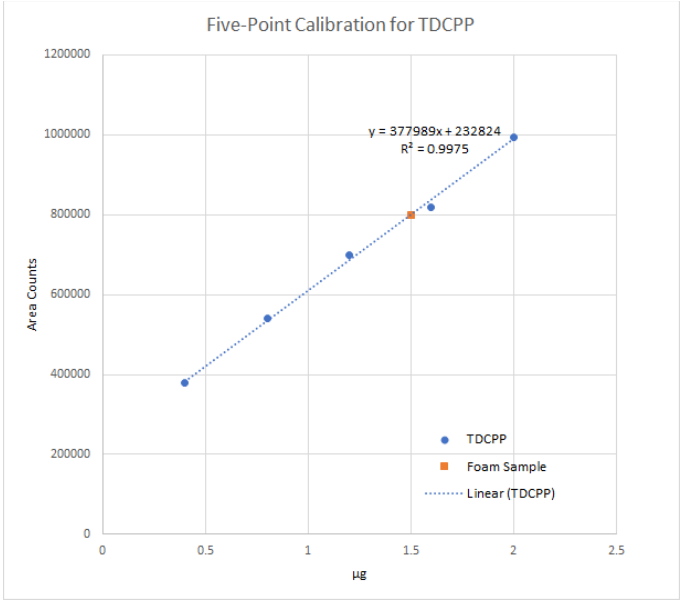

Figure 5. TDCPP Calibration Plot

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