#252

# Evolved Gas Analysis and Multi-step Pyrolysis of Waterproof Breathable Fabric

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## Application Note
Polymer

## Abstract
This application note demonstrates Evolved Gas Analysis (EGA) and Multi-step Pyrolysis (MSP) with GC-MS on a high-tech waterproof breathable textile.

## Introduction
High-performance breathable, waterproof textiles found in clothing make outdoor activities more enjoyable. The secret to this high-tech textile is expanded polytetrafluoroethylene (ePTFE) invented by Wilbert and Robert Gore[1]. The microporous structure of an expanded polytetrafluoroethylene membrane is able to resist large drops of water, while allowing water vapor to pass through, therefore making it both waterproof, yet breathable. As ePTFE is fragile on its own, it is used in conjunction with other materials to give the membrane structure.

As a useful tool in both failure analysis and competitor analysis of finished products like high performance waterproof breathable textiles, Evolved Gas Analysis together with Multi-step Pyrolysis can be invaluable for uncovering different components in finished materials. In this application note, high-tech fabric was analyzed to reveal its polymeric composition using a CDS Pyroprobe 6200.

## Experiment Setup
Using the Pyroprobe Application Decision Making Tree[2] as our guide, a small piece of multi-layered high performance fabric was trimmed down with scissors to 100$\mu$g and loaded into a DISC tube for analysis. A fused silica transfer line was used to connect the GC inlet to the MS detector in a preliminary EGA run. After which, a 30 meter long 5% phenyl capillary column was used for multi-step pyrolysis. A vent-free adapter was installed to enable a fast switch between the fused silica and the column without losing vacuum in the mass spectrometer.

### EGA
Pyroprobe 6200 Autosampler
Initial: 100°C
Final: 1000°C
Ramp Rate: 100°C per min
Interface: 300°C
Transfer Line: 325°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

### Multi-Step Pyrolysis
Pyroprobe 6200 Autosampler
DISC:
400°C 1 min to trap
550°C 1 min to GC
650°C 30 sec to GC
Trap Contents: Tenax
Trap Rest: 40°C
Trap Final: 300°C 3 min
Interface: 300°C
Transfer Line: 325°C
Valve Oven: 300°C

GC-MS
Column: 5% phenyl (30m x 0.25mm)
Carrier: Helium 1.25mL/min, 50:1 split
Injector: 360°C
Oven: 40°C for 2 minutes
12°C/min to 320°C (10min)
Ion Source: 230°C
Mass Range: 35-550amu

## Results and Discussion

EGA was first performed on the fabric as a screening technique. In this fast screening technique, the DISC temperature was ramped up at 100 °C/min from 100°C to 1000 °C and the GC oven was kept isothermal at 300°C. The results are shown in Figure 1. Three regions of interest were seen, a small peak at 350°C, then large peak at 500°C, followed by another small peak at 600°C. When the mass spectra were averaged in the first region and compared against a NIST library, top matches included toluene diisocyanate, a component of polyurethane. A polymer library search of the averaged mass spectra in the second region at 500°C had matches for nylon (Figure 3). The third peak at 600°C had top matches for fluorinated ethylene propylene copolymer, and Teflon®, a trade name for polytetrafluoroethylene (Figure 4).

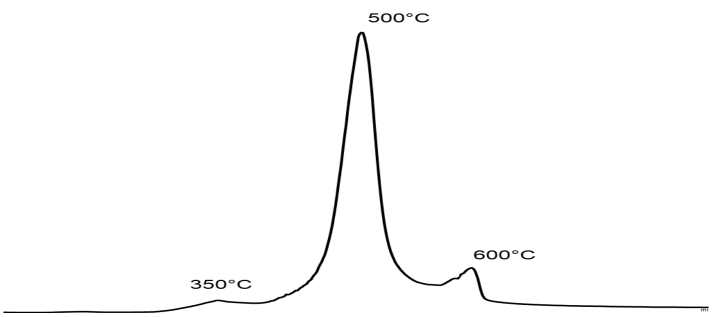



Figure 1. Evolved Gas Analysis of high performance from 100°C to 1000°C at 100°C per minute.

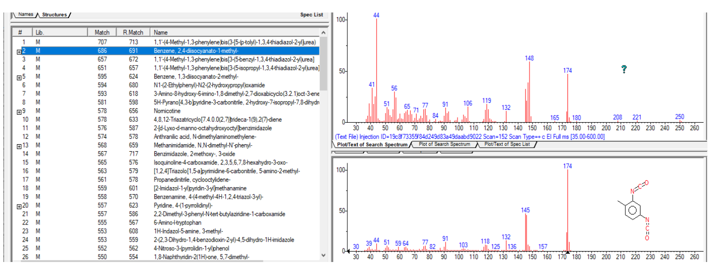


Figure 2. NIST Library match from center Peak of the EGA. in Figure 1.

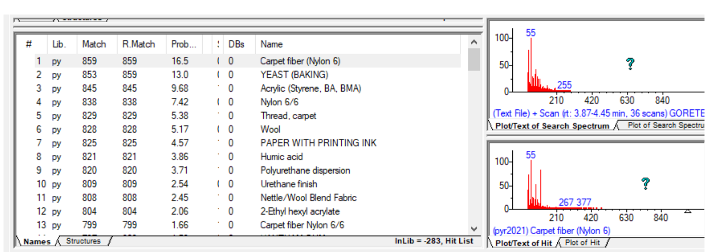


Figure 3. Polymer Library match from center Peak of the EGA. in Figure 1.

The information from this EGA was used to determine setpoint temperatures for multi-step pyrolysis. Temperatures chosen were to the right of each peak to be sure adequate energy was applied to thermally release each component. Therefore, 400°C, 550°C, and 650°C temperatures were chosen for multi-step pyrolysis GC-MS. The sequence was run so the 400°C method was in trapping mode. This was found to improve the peak shape of the analytes at 400°C. The Pyroprobe 6200 can automatically switch between non-trapping methods and trapping methods in a single sequence.

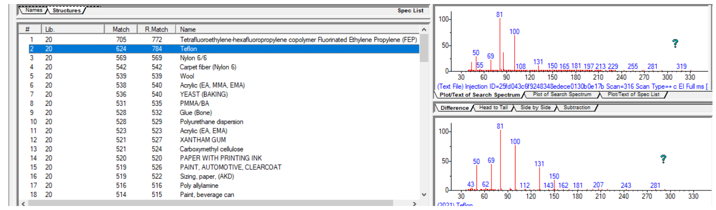
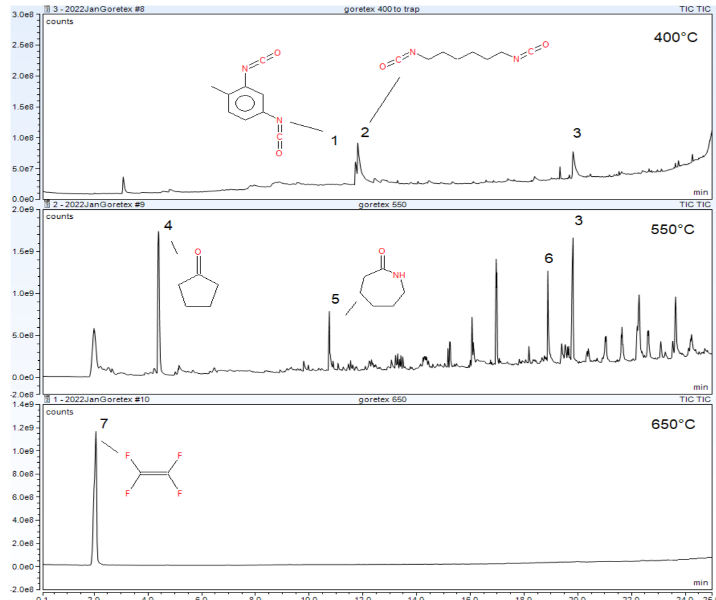


Figure 4. Polymer Library match from last peak of EGA in Figure 1.




| Peak | Identification |
|---|---|
| 1 | toluene diisocyanate |
| 2 | hexamethylene diisocyanate |
| 3 | 1,8-diazacyclotetradecane-2,7-dione |
| 4 | cyclopentanone |
| 5 | caprolactam |
| 6 | 4,4'-methylenebis-benzeneamine |
| 7 | tetrafluoroethylene |

Figure 5. Multi-step pyrolysis of fabric at 400 °C (top), 550 °C (center) and 650 °C (bottom).

Multi-step pyrolysis of the fabric is shown in Figure 4. At 400°C consistent with the EGA findings, there were two small peaks for diisocyantes, toluene diisocyanate (Peak 1) and hexamethylene diisocyanate (Peak 2). This indicates there is a small amount of polyurethane present which uses those diisocyanates. At 550°C, caprolactam (Peak 5), a marker for polycaprolactam (nylon 6 ) was present. 1,8-diazacyclotetradecane-2,7-dione (Peak 3), and cyclopentanone (Peak 4), markers for poly(hexamethylene adipamide) (nylon 6/6) were also present. Finally at 650°C, tetrafluoroethylene (Peak 7), the monomer of polytetrafluoroethylene, was present. This is produced from the depolymerization (unzipping) of ePTFE. Finally, the presence of 4,4'-methylenebis benzeneamine (Peak 5) at 550°C could be an indication that this polyurethane crosslinker was also used.

Therefore, this high-tech fabric, consisting of multiple layers, is made of nylon 6, nylon 6/6, polytetrafluoroethylene, and polyurethane.

## Conclusion

EGA plus Multi-step Pyrolysis GC-MS was useful in determining that this fabric contains polyurethane, two different nylons, and ePTFE. It could also thermally separate analytes of one material into 3 individual chromatograms.These two techniques provide essential information for polymer identification. An EGA screening step provides quick information and serves as a guide for multi-step pyrolysis, which in turn provides in-depth information of polymeric materials.

## References

1. Bennett, D., “The GORE-TEX Eye,” Bloomberg Businessweek, May 2019.

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