Performance Fabric Identification using Evolved Gas Analysis and Multi-step Pyrolysis GC-MS with MSChrom + CDS EGA and Py Databases

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Application Note
Fabrics

Abstract
This application note demonstrates the use of a Pyroprobe 6150 to characterize an elastomeric fabric using Evolved Gas Analysis (EGA) plus Multi-Step Pyrolysis (MSP), along with CDS's EGA and Pyrolysis Databases on Mestrelab's Mnova MSChrom + DB and CDS plugins

Introduction
Performance clothing is often designed for specific needs. For example, they can be durable and provide physical and comfort benefits such as managing moisture, resisting stains, or offering sun protection. They can be waterproof yet "breathable," or a combination of soft, stretchy and form-fitting. Here, evolved gas analysis (EGA) plus multi-step pyrolysis (MSP) and database searches in Mestrelab's Mnova MSChrom plus CDS Plugin was performed on soft and stretchy fabric from work-out gear, providing valuble information for both failure and competitive analysis.

Experiment Setup
A small piece of soft and stretchy fabric from workout clothing, 200 µg, was loaded into a DISC tube for analysis. A fused silica transfer line was used to connect the GC inlet to the MS detector for the EGA. After which, a 30 meter long 5% phenyl capillary column was used on a fresh piece of fabric for multi-step pyrolysis. A vent-free adapter (CDS p/n 6203-5069) was installed to enable a fast switch between the fused silica and the column without losing vacuum in the mass spectrometer.

EGA

Pyroprobe 6150 Autosampler
Initial: 50°C
Final: 1000°C
Ramp Rate: 100°C per min
Interface: 300°C
Transfer Line: 325°C
Valve Oven: 300°C

Thermo Trace 1310 GC ISQ MS
Column: Fused silica (1m x 0.10mm)
Carrier: He 1.25mL/min 75:1 spl
Injector: 360°C
Oven: 300°C
Ion Source: 230°C
Mass Range: 35-600amu

Multi-Step Pyrolysis

Pyroprobe 6150 Autosampler
350°C 40 sec
450°C 40 sec
600°C 40 sec

Interface: 300°C
Transfer Line: 325°C
Valve Oven: 300°C

Thermo Trace 1310 GC ISQ MS
Column:
5% phenyl (30m x 0.25mm x 0.25µm)
Carrier:
He 1.25mL/min, 75:1 spl
Injector: 360°C
Oven: 40°C for 2 minutes
12°C/min to 320°C (10min)
Ion Source: 230°C
Mass Range: 35-600amu

Results and Discussion
For the EGA, the analytical column was replaced with a piece of fused silica and the GC oven was kept at 300°C. The DISC temperature was ramped up at

100 °C/min from 50°C to 1000 °C. In this preliminary step, thermal desorption and thermal degradation information is gathered with respect to time, instead of a traditional chromatogram. To better understand at what temperature the material decomposes, the retention time on the x-axis was converted to temperature using the Temperature Conversion function in the CDS toolbar of MSChrom. The resulting EGA is shown in Figure 1. An initial region of outgassing began just after 300°C (circled in blue), and a second, larger region occured between 450°C and 800°C (circled in green).

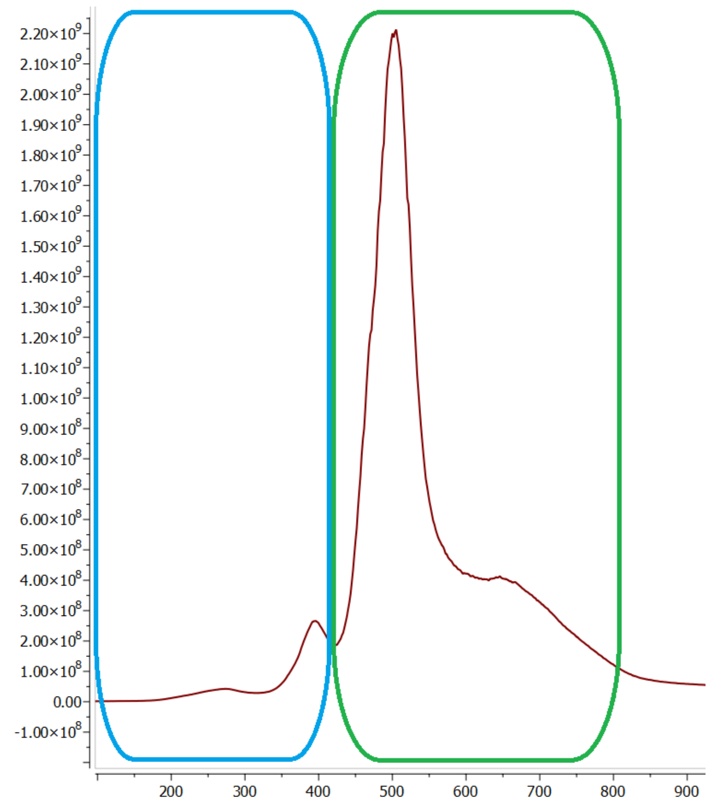


Figure 1. Fabric EGA, 100°C per minute from 50°C to 1000°C

An EGA can serve as a quick screening technique, less than 10 minutes, to initially understand the polymer type by using the CDS EGA database that works with MSChrom. The initial step to using this database is to sum the mass spectra within the entire EGA temperature range by choosing the Crosshair Manual Tool, and performing a left-click hold, and drag across the TIC. The second step is to search this combined mass spectrum against the database using MSsearch, which returns a list of potential matches to the mass spectrum (Figure 2). Here, the top matches in the database were forms of poly(ethylene) terephthalate (PET), with match qualities of over 900 (out of 1000) (Figure 3).

These match results give a strong indication that PET is a major component of the fabric. Therefore the top database entry's EGA was compared to the fabric to uncover any additional components (Figure 4). Most of the outgassing in each dataset occurred along the same temperature region. However, the unknown fabric contained an additional region between 300°C and 425°C (circled in Figure 4).

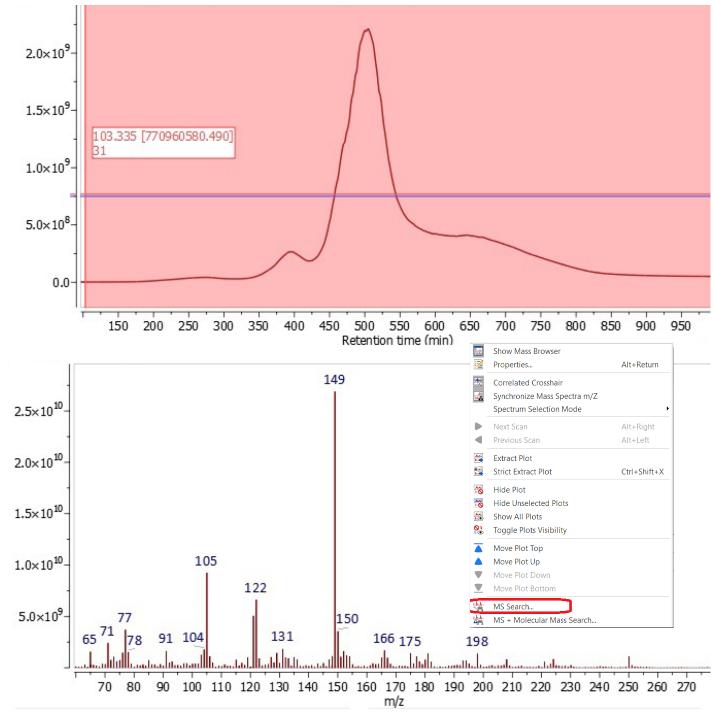


Figure 2. Summing EGA Spectra and Performing Database Search

	Database	Score	Polymer Name
1	CDS-EGA	976	Poly(ethylene terephthalate)
2	CDS-EGA	974	PET unmodified
3	CDS-EGA	974	Carpet with Stain Treatment 1
4	CDS-EGA	972	PET 1.77% DEG
5	CDS-EGA	972	Carpet with Stain Treatment 2
6	CDS-EGA	971	Poly(ethylene terephthalate) with Tinuvin 1577
7	CDS-EGA	969	PET 1.7% I.A.
8	CDS-EGA	968	Carpet, polyester
9	CDS-EGA	967	PET 0.57% DEG
10	CDS-EGA	967	Amorphous Pellet Recycle PET

Figure 3. Fabric EGA search results

Figure 5 shows summed mass spectrum of the fabric and the database match, which were similar. For example, both files showed a strong presence of m/z 149, (circled in blue) which is indicative of a phthalate structure and is a known monomer of PET. This further supports the matches identified by MSsearch in Figure 3. However, there were also subtle differences, such as an increased presence of both m/z 250 and m/z 71 (circled in red) in the fabric, which indicate additional components unrelated to PET. m/z 250, 71, and 149 were extracted and overlayed in Figure 6. From there, it could be seen that each m/z occurred in different temperature regions, one between 325°C and 425°C a second region from 425°C to 475°C, and a final region from 475°C to 600°C.

Using these findings as a temperature guide, the analytical column was re-installed and a multi-step pyrolysis sequence was performed at 350°C, 450°C and 600°C to thermally isolate and favor the characteristic components for data analysis (Figure 6).

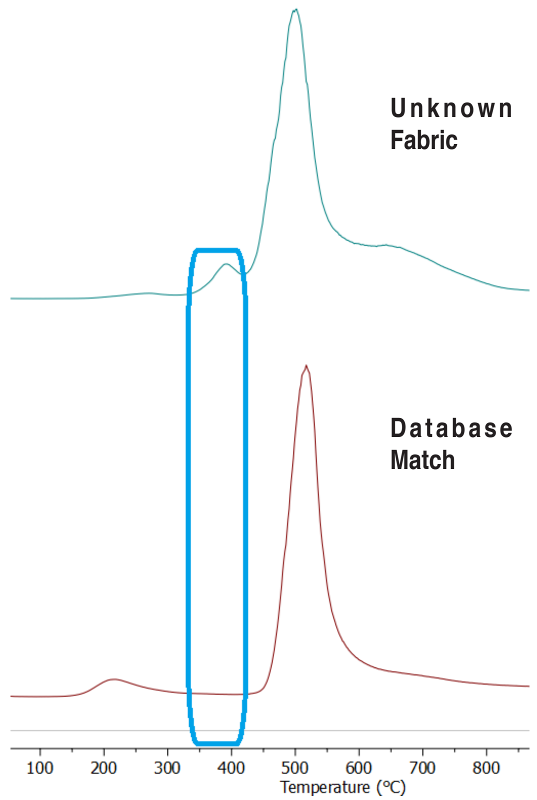


Figure 4. EGA of Fabric (top) and top database match, PET (bottom)

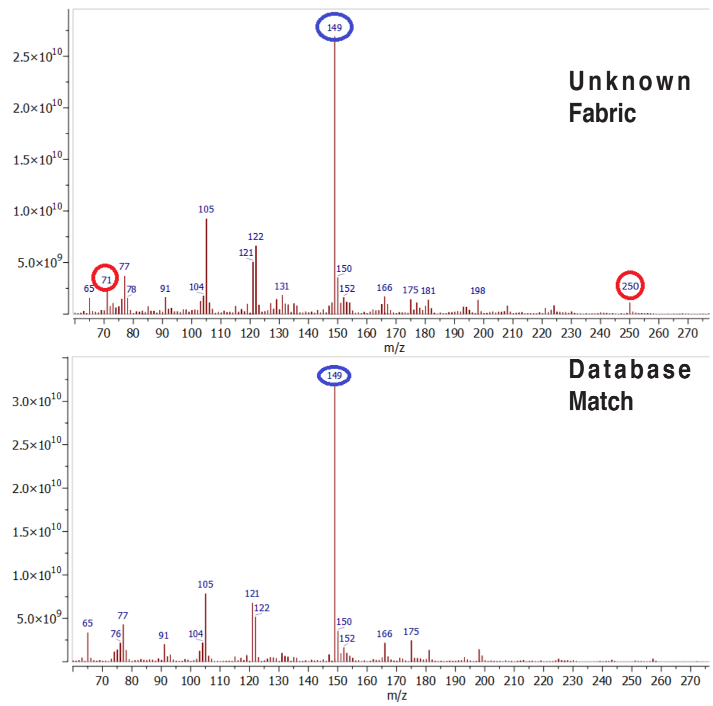


Figure 5. Summed EGA Spectrum of Fabric (top) and top database match, PET (bottom).

After each quick heating cycle of the multi-step sequence, the DISC quickly cooled to an ambient temperature while the sample remained in the chamber waiting for the GC to become ready for the next analysis.

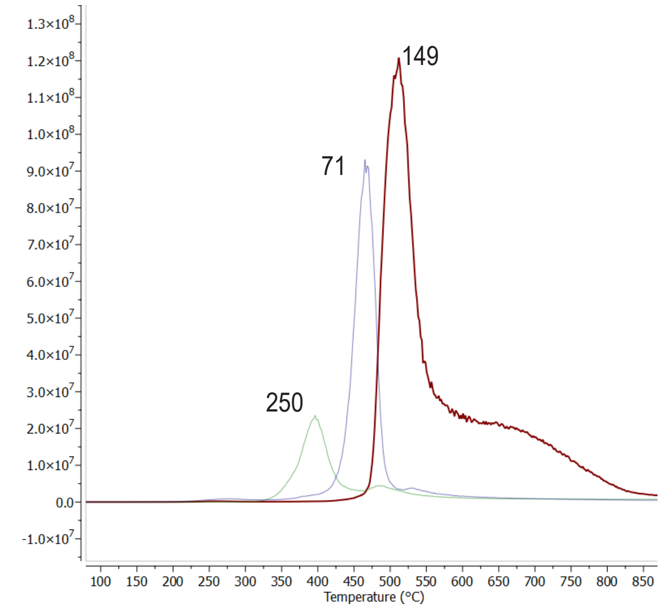
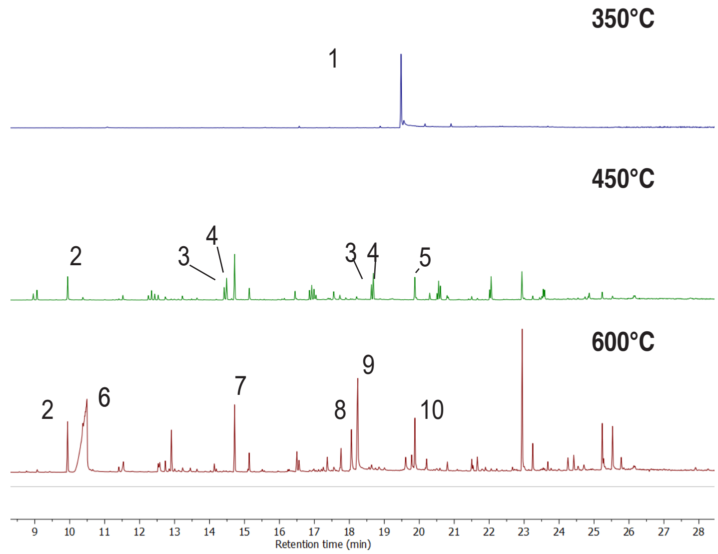


Figure 6. EIC overlay of m/z 250 (green), m/z 71 (blue), and m/z 149 (maroon).

The chromatograms of the multi-step sequence at 350°C, 450°C and 600°C are stacked in Figure 7. In the 350°C chromatogram (Figure 7 top), the top match for peak #1 appearing at 19 min was for 1,1'-methylenebis[4-isocyanato-benzene (MDI), a diisocyanate

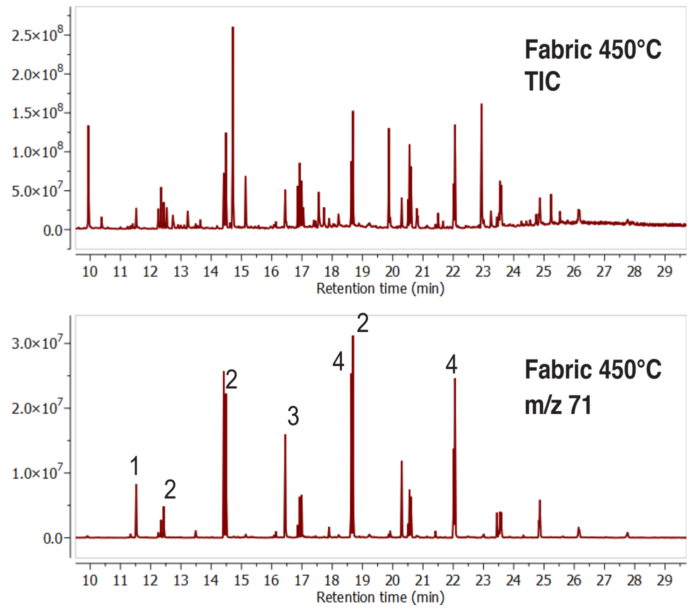


Peak	Top Match
1	1,1'-Methylenebis[4-isocyanato-benzene (MDI)
2	Vinyl benzoate
3	2-Butoxy-2,4-dimethyl-1-pentene
4	1,4-Diglycidyloxy butane
5	1,2-Ethanediol, dibenzoate
6	Benzoic Acid
7	Biphenyl
8	cis-9-Hexadecanoic acid, heptyl ester
9	n-Hexadecanoic acid
10	1,2-Ethane diol, dibenzoate

Figure 7. Fabric at 350°C (top), 450°C (center), and 600°C (Bottom).

commonly used in polyurethanes. Reacting a disocyanate with a polyol or a polyester and creates urethane linkages, and when a polyurethane thermally decomposes, the diisocyanate portion of the polymer is first released, followed by the polyol/polyester portion[1]. So, the presence of MDI diisocyanate at 350°C indicates that an MDI polyurethane is part of the fabric.

The top of Figure 8 contains the 450°C TIC chromatogram that is also shown in the center of Figure 7. Figure 8 also has an EIC of 71 of the 450°C chromatogram (bottom). That EIC exhibits a



Peak	Top Match
1	4-Heptanone
2	1,4-Diglycidyloxybutane
3	2,3,4-Triethyl 1,2-pentanediol diisobutyrate
4	3-Butoxy-2,4-dimethyl-1-pentene

Figure 8. Fabric at 450°C, TIC (top), m/z 71 (bottom).

repeating pattern. Peaks indicated with a "2" each have mass spectra so similar that the top match is the same: 1,4-diglycidyloxybutane, a linear ether compound. Likewise, the peaks labeled as "4" all have a top match for 2,3,4-triethyl 1,2-pentanediol diisobutyrate, a branched ether compound. These findings may represent the polyol portion of the MDI polyurethane, with oligomers of increasing size along the retention time axis. The matches with both branched and linear ethers could mean that the polyol portion of the polyurethane has both branched and linear portions. Additionally, searching the mass spectra of the co-added peaks m/z 71 peaks against the CDS Pyrolysis database reveals a top match was for Poly(tetramethylene ether glycol), an ether polymer, with a match quality of 913/1000 (Figure 9), further supporting the idea that a polyether polyurethane is present.

Finally, after removing the contribution from the polyurethane in the lower temperature steps, the 600°C chromatogram (Figure 7, bottom) was searched against the CDS Pyrolysis database. Top matches were all forms of PET (Figure 10). Figure 11 has the

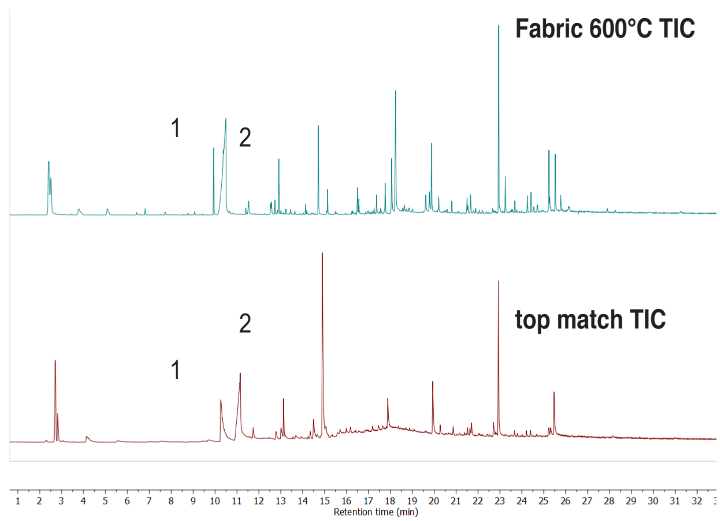
	Database	Score	Polymer Name
1	CDS-PY	913	Poly(tetramethylene ether) glycol
2	CDS-PY	889	Hytrel
3	CDS-PY	716	Poly(tetrahydrofurfuryl methacrylate)
4	CDS-PY	707	Poly(tetrahydrofurfuryl acrylate)
5	CDS-PY	662	Poly(vinyl stearate)
6	CDS-PY	626	pOLY(2,3-dihydrofuran)
7	CDS-PY	615	Ethylene Propylene Rubber 40.1% C2
8	CDS-PY	607	Coal 1
9	CDS-PY	599	fast food wrapper
10	CDS-PY	589	Poly[butylene terephthalate-co-poly(alkylene glycol)terephthalat

Figure 9. Search Results for 450°C, m/z 71 peaks of fabric.

	Database	Score	Polymer Name
1	CDS-PY	929	Amorphous Pellet Recycle PET
2	CDS-PY	922	Flake Recycle PET
3	CDS-PY	907	Poly(ethylene terephthalate) with Tinuvin 1577
4	CDS-PY	906	Poly(ethylene terephthalate) with Tinuvin 1577
5	CDS-PY	889	PET unmodified

Figure 10. Search Results for 600°C chromatogram.

600°C chromatogram (top) and the database match (bottom). The similarities in the chromatograms of both the unknown and the database match provide further confirmation that PET is another major component in the fabric.



Peak	Match
1	vinyl benzoate
2	benzoic acid

Figure 11. Fabric at 600°C (top), and top database match (bottom).

Conclusion

In this application, EGA and MSP were combined with CDS's MSChrom Polymer identification databases to analyze the elastomer formulation of fabric used in commercially available performance workout clothing. The initial EGA screening revealed that the presence of PET as one component while providing insight on how to further investigate the other components that were not related to

PET. The platinum coil and chamber design of the Pyroprobe 6000 Series, using a proprietary energy reserve system, provides fast and flexible temperature ramping capabilities. This allows an Evolved Gas Analysis to be finished in under 10 minutes, as compared to a furnace design, which may only have a maximum heating rate of 20°C per minute, thus completing the same analysis in 45 minutes.

Finally, when supplementing the EGA analysis with MSP and the CDS MSChrom Pyrolysis Identification database, the analysis revealed a second elastomer component that was a polyurethane with possibly branched and linear isomers of a polyol. MSP with the 6000 Series chamber design easily allows pyrolysis to be done step-wise at multiple temperatures, as rapid heating and cooling of the sample chamber is possible, with no need to remove the sample from the chamber between temperature steps. This is a different approach from furnace pyrolysis which requires the sample to be removed from the furnace as a new temperature is set. Using this application of identifying elastomers in fabrics as an example, the CDS 6000 Series Pyroprobe solutions are powerful tools for deconvoluting the identity of polymers used in different materials.

References

1. Sam, Karen D. “Chapter 11 - Pyrolysis-gas chromatography “ in Gas Chromatography (Second Edition) Handbooks in Separation Science ,2021, Pages 325-342.