

Instrument: Pegasus® BTX 4D

The Utility of Pyrolysis with Enhanced Chromatography–Time-of-Flight Mass Spectrometry for the Characterization of Nylon

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Introduction

Nylon is an engineered polymer that is synthesized through the reaction between dicarboxylic acid and diamine. It consists of a series of repeated amide groups that result in a polymer that has superior strength, durability, and abrasion resistance. Also featuring a low molecular weight and low cost of production, nylon is a popular choice within the world of polymers. Originally used as an alternative for silk, it quickly found many applications when WWII started in 1939, where it was used in textiles to create parachutes, ropes, and clothing for the war. Now, nylon can be found in anything from instruments like guitar strings to self-care products like toothbrushes.

Modern-day consumers are given a variety of options for toothbrushes. They can pick a toothbrush with medium, soft, or even extra soft bristles. Having different options for bristle types allows consumers to make choices that are closely tailored to their oral health needs. Most consumer toothbrushes use nylon for their bristles, the exception being premium or biodegradable toothbrushes that use polybutylene terephthalate (PBT) or polyethylene terephthalate (PET). In this application note, we utilized TD/Py-GCxGC-TOFMS for the characterization of nylon in typical consumer toothbrush bristles (Figure 1).

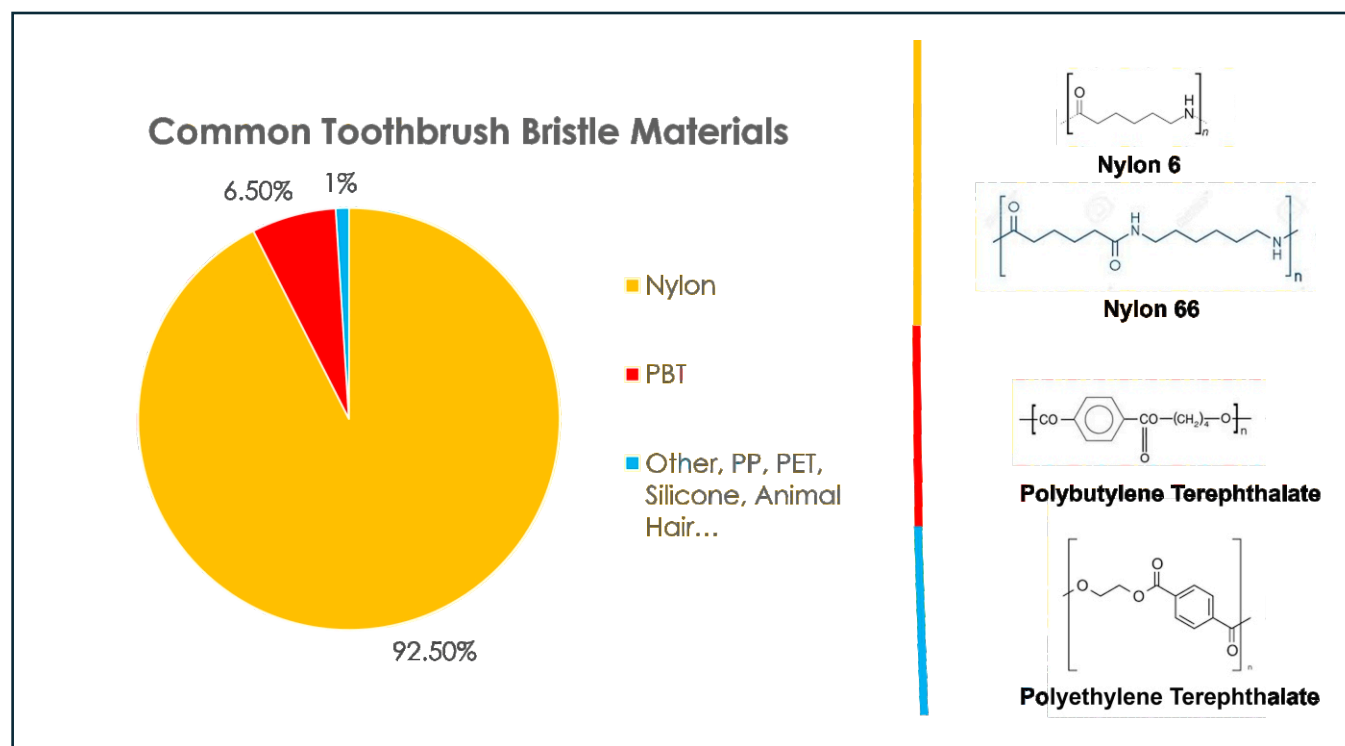


Figure 1. Common polymers used for toothbrush bristles.

Experimental

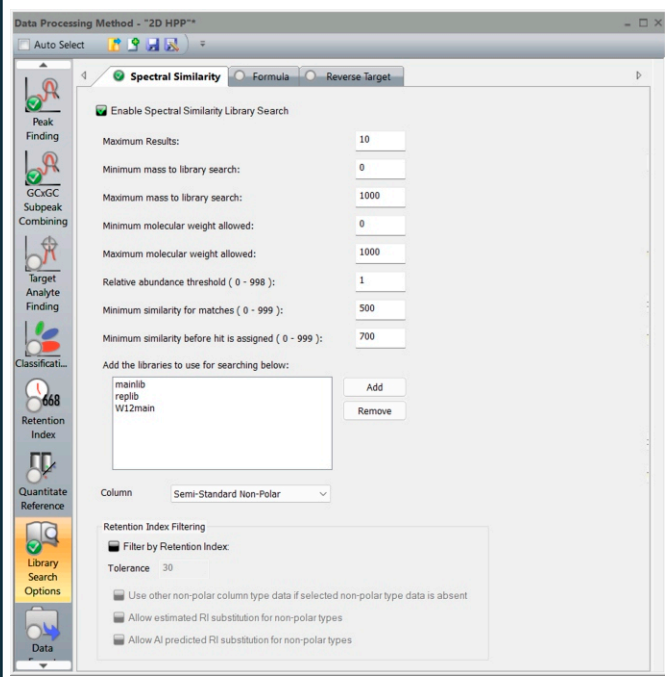
Toothbrushes were purchased from local pharmacies. Sample preparation involved cutting the bristles near the base using wire cutters without removing material from the toothbrush handle. One or two bristles (approximately 5 mm in length) were placed into 60 μ L quartz microtubes, which were then transferred to quartz inlet liners for analysis.

Pyrolysis was carried out using a Pegasus BTX 4D instrument equipped with a GL Sciences Optic 4 inlet.¹ GC-TOFMS and GCxGC-TOFMS data were processed using ChromaTOF[®] software with automated peak finding and spectral deconvolution for untargeted workflows, including spectral similarity searches against extensive reference libraries and mass delta (ΔM) calculations for molecular ion evaluation.

Table 1. Instrument Parameters

Gas Chromatograph	Agilent 8890 with GL Sciences Optic-4 Inlet
Inlet	Pyrolysis, 45 °C to 600 °C at 60 °C/s
Carrier Gas	He @ 1.5 mL/min, Constant Flow
Primary Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 μ m
Secondary Column	Rxi-17sil ms 0.6 m x 0.25 mm i.d. x 0.25 μ m
Temperature Program (GCxGC, 3s Modulation)	45 °C (1.5 min) ramp to 300 °C at 10 °C/min (hold 23 min) Secondary oven maintained +5 °C relative to primary oven Modulator maintained +15 °C relative to secondary oven
Transfer Line Temperature	300 °C
Mass Spectrometer	LECO Pegasus BTX 4D
Source Temperature	250 °C
Ionization	El
Mass Range (m/z)	35-1000
Acquisition Rate	10 sps (GC-TOFMS), 200 sps (GCxGC-TOFMS)

The TOFMS data were processed using automated Peak Find (Non-Targeted) processing, which included deconvolution, spectral similarity searches of large spectral databases (e.g., NIST, Wiley libraries), and mass delta calculations for molecular ions (Figure 2).





- ✓ Non-Targeted Data Processing
- ✓ Deconvolution
- ✓ Database Comparisons
- ✓ BTX 4D, Mass Error

Mass Delta ($M\Delta$)

$$\Delta M = m/z_{\text{obs}} - m/z_{\text{calc}}$$

Figure 2. Non-Targeted Peak Find data processing method.

Results and Discussion

GC-TOFMS and GCxGC-TOFMS analyses were conducted on the toothbrush bristle samples. The enhanced chromatographic performance provided by GCxGC provided improved compound separation, resulting in higher peak signal to noise ratios and increased spectral similarity scores. These advantages are illustrated for a selected set of pyrolytic marker compounds listed in Table 2. Transitioning from GC-TOFMS to GCxGC-TOFMS enabled the resolution of compounds that coeluted in the first dimension GC-TOFMS analysis and increased the number of selected annotated compounds from 10 of 19 to 19 of 19. In addition, the average spectral similarity score from automated Peak Find database comparisons improved from 863 to 897 (out of 1000).

Table 2. Pyrolytic markers for Nylon 6 (N6), Nylon 66 (N66), and Polyethylene (PE)

Name	Formula	GC-TOFMS			GCxGC-TOFMS		
		R.T. (s)	Mass Delta (Da)	Similarity	R.T. (s)	Mass Delta (Da)	Similarity
Cyclopentanone	C ₅ H ₈ O				250.006, 1.010	0.02	877
Pentanedinitrile	C ₅ H ₆ N ₂				418.013, 1.727	N/A	901
1,10-Undecadiene	C ₁₁ H ₂₀	521	N/A	849	523.017, 0.766	0.04	905
1-Undecene	C ₁₁ H ₂₂	529	0.05	898	529.017, 0.743	0.04	939
N-Methylvaleramide	C ₆ H ₁₃ NO	527	N/A	848	529.017, 1.250	0.03	884
Undecane	C ₁₁ H ₂₄	442	N/A	869	538.018, 0.715	0.04	939
Hexanamide	C ₆ H ₁₃ NO				583.019, 1.264	0.03	931
8-Nonene-1-nitrile	C ₉ H ₁₅ N	607	0.04	924	607.02, 1.108	0.03	917
Hexanedinitrile	C ₆ H ₈ N ₂				613.021, 1.927	N/A	961
Caprolactam	C ₆ H ₁₁ NO	682	0.03	859	682.023, 1.598	0.03	901
9-Decene-1-nitrile	C ₁₀ H ₁₇ N	697	0.05	961	697.024, 1.087	0.07	842
Decanenitrile	C ₁₀ H ₁₉ N	702	0.04	851	703.024, 1.021	0.04	908
β-Methylcaprolactam	C ₇ H ₁₃ NO				733.025, 1.499	0.03	882
Octanamide	C ₈ H ₁₇ NO	837	N/A	854	757.026, 1.223	0.04	863
ω-Enantholactam	C ₇ H ₁₃ NO	770	0.04	720	772.027, 1.579	0.03	917
Dodecanenitrile	C ₁₂ H ₂₃ N				865.031, 1.009	0.05	924
Pentadecanenitrile	C ₁₅ H ₂₉ N				1081.04, 0.994	0.05	906
ω-Lauroactam	C ₁₂ H ₂₃ NO				1081.04, 1.479	0.05	913

The pyrolysis of toothbrush bristles produced markers for polyethylene (PE) and two different types of nylon polymers (N6, N66), as shown on the contour plot in Figure 3. Markers for Nylon 6 consisted of lactams such as caprolactam, as well as a series of αω-nitrilealkenes, amides, and alkanedinitriles. The markers were characterized using a combination of spectral similarity searches and mass delta calculations ($M\Delta$) as illustrated for caprolactam and 8-nonene-1-nitrile in Figure 4. Nylon 66 markers included cyclopentanone and hexamethylenediamine. Pyrolysis of polyethylene produced a sequence of alkanes, alkenes, and αω-dienes (Figure 5).

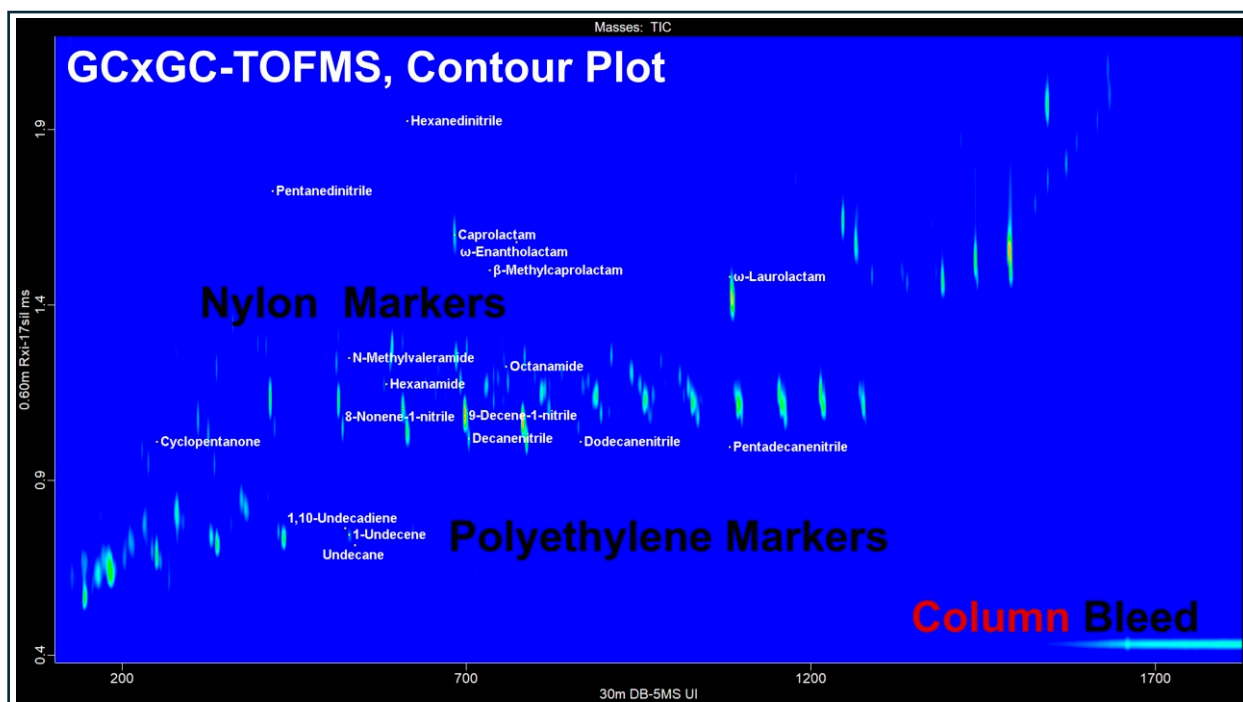


Figure 3. GCxGC-TOFMS contour plot of toothbrush bristles with pyrolytic markers annotated.

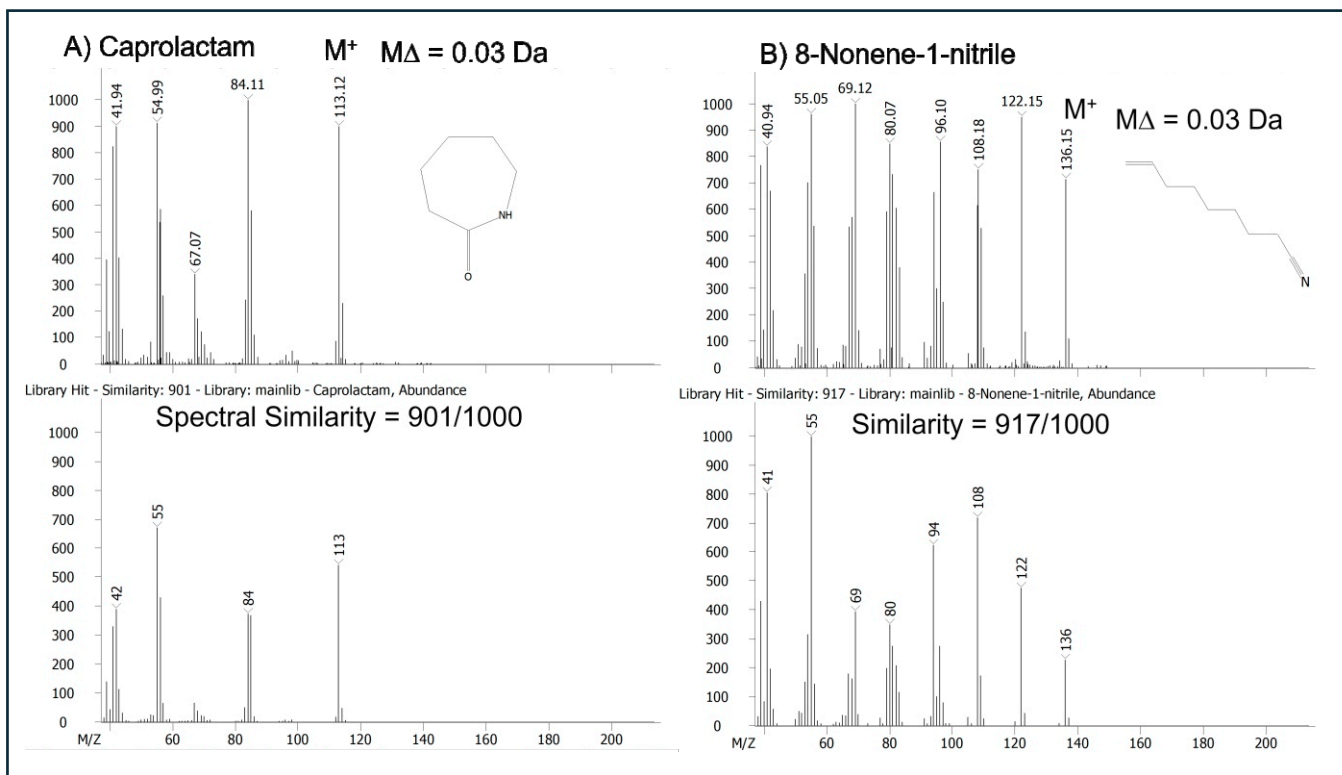


Figure 4. A) Peak True deconvoluted (Top) and library (Bottom) mass spectra for A) Caprolactam, and B) 8-Nonene-1-nitrile.

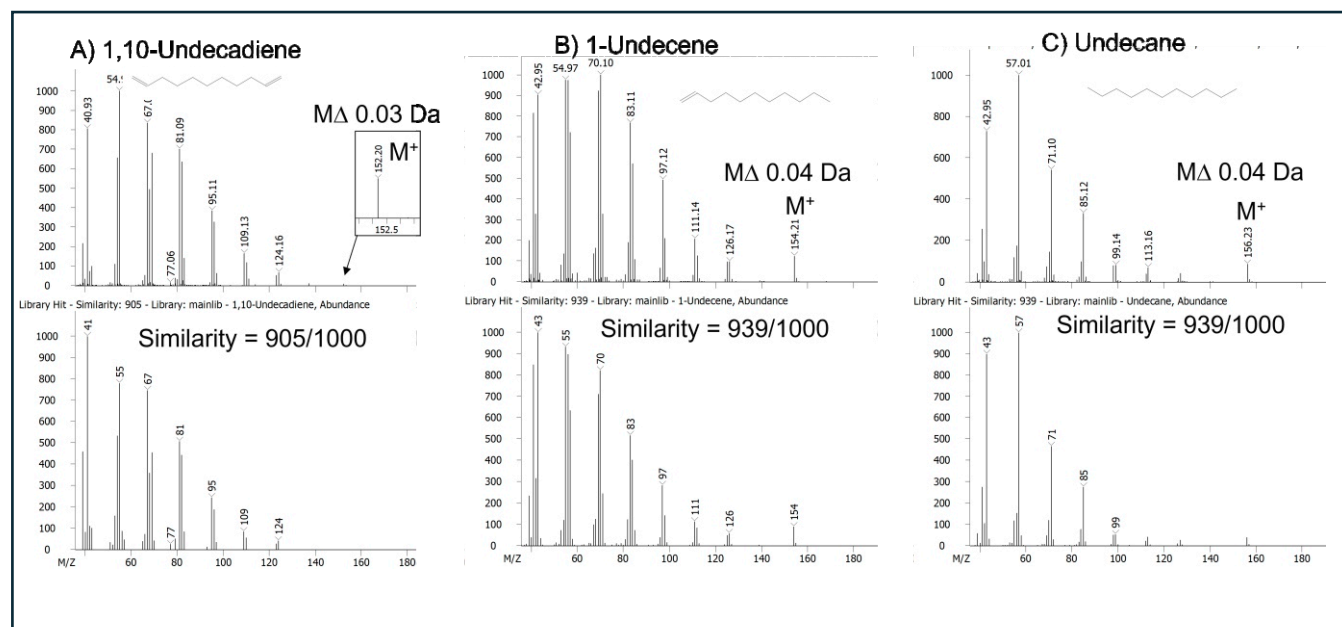


Figure 5. A) Peak True deconvoluted (Top) and library (Bottom) mass spectra for A) 1,10-undecadiene, B) 1-undecene, and C) undecane.

Conclusion

The LECO Pegasus BTX 4D demonstrates exceptional capability for the characterization of polymeric materials, particularly when leveraging GCxGC-TOFMS. The enhanced chromatographic resolution and sensitivity provided by GCxGC generated rich, high quality pyrolysis spectral data, enabling robust and unambiguous characterization of key polymeric markers. In this study, characteristic markers associated with Nylon 6, Nylon 66, and polyethylene were confidently annotated from toothbrush bristles, underscoring the instrument's suitability for real world industrial applications involving complex polymer matrices and consumer product analysis.

References

¹GL Sciences Optic-4: <https://www.glsciences.eu/html/intro-optic-4.html>