

Characterization of the Composition and Thermal Decomposition Profile of Recycled Carpet Samples by TGA-FT-IR, TGA-MS, and TGA-GC-MS

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Introduction

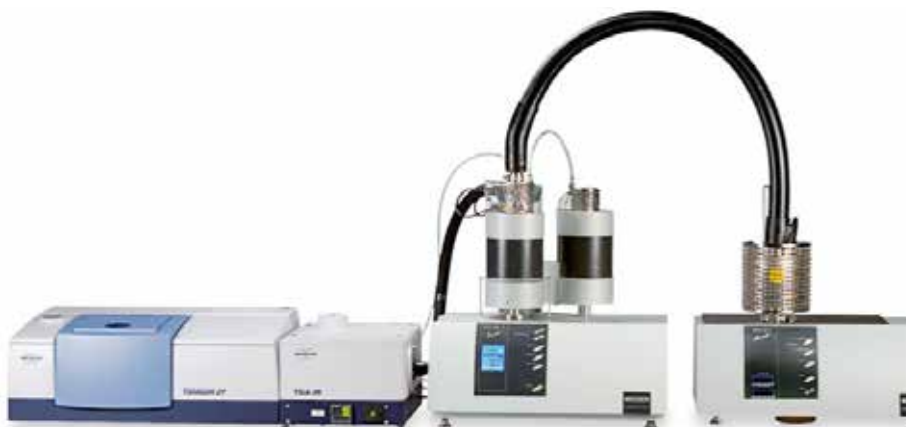
Billions of pounds of carpet are generated annually worldwide, a large percentage of which ends up in landfills, which is problematic because nylon is non-biodegradable. Limitations in landfill capacity and the environmental impact of disposing of carpet waste in this manner have made recovering nylon from carpet waste an increasingly important enterprise. As carpet compositions vary and can contain Nylon-6 and/or Nylon-6,6 along with variety of other materials, such as other polymer fibers (e.g. PP, PE, polyester), latex adhesive, dyes, and inorganic fillers (e.g., CaCO_3 and BaSO_4),¹ the characterization of waste carpet composition and its thermal decomposition profile is essential for the recycling process. Thermogravimetric analysis (TGA) coupled with evolved gas analysis (EGA) by FT-IR, MS, or GC-MS enables the simultaneous analysis of a material's thermal mass loss profile and identification of the gaseous species evolved during the decomposition.

In this study, material recovered from carpet waste was analyzed by TGA-FT-IR, TGA-MS, and TGA-GC-MS in order to compare the capabilities of the three combined thermal

analysis/evolved gas analysis methods for identifying the composition of the recycled carpet.

Experimental

TGA-FT-IR and TGA-MS were performed using a NETZSCH TG 209 **F1 Libra**® thermogravimetric analyzer (TGA) coupled to a BRUKER Optics TENSOR™ FT-IR spectrometer and a NETZSCH QMS 403 **Aëolos**® quadrupole mass spectrometer (Figure 1). For TGA-GC-MS measurements, the NETZSCH TG 209 **F1 Libra**® was coupled to an Agilent Technologies 7890A gas chromatograph equipped with an Agilent 5975C quadrupole mass spectrometer (QMS) (Figure 2).



1 NETZSCH STA 449 **F3 Jupiter**® instrument simultaneously coupled to a BRUKER Optics TENSOR™ FT-IR spectrometer and a NETZSCH QMS 403 C **Aëolos**® quadrupole mass spectrometer

¹C. Mihut, D. K. Captain, F. Gadala-Maria, and M.D. Amiridis. "Review: Recycling of Nylon from Carpet Waste", Polymer Eng. Sci., Vol. 41(9), pp. 1457-1470, 2001.

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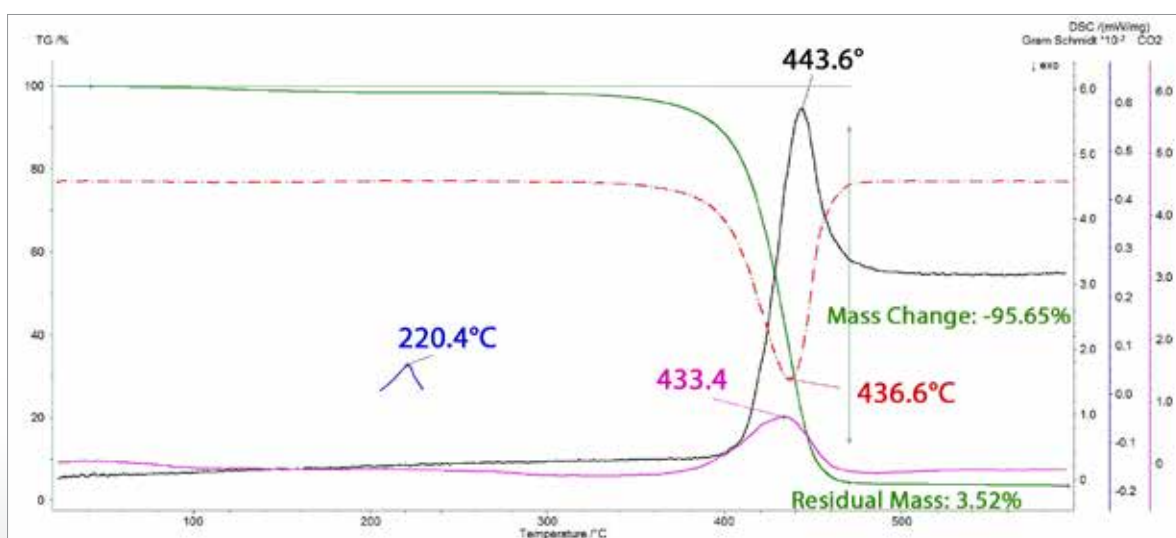
2 NETZSCH TG 209 **F1 Libra**® TGA instrument coupled to the Agilent 7890A gas chromatograph equipped with an Agilent 5975C quadrupole mass spectrometer (QMS)

The recycled carpet samples were heated in the thermobalance from 25 to 600°C at 10 K/min under either nitrogen (40 mL/min; TGA-FT-IR and TGA-MS) or helium (65 mL/min; TGA-GC-MS). Evolved gases were passed from the thermobalance to the EGA analysis instrument via a transfer line heated at 220°C for the FT-IR and MS coupling or 300°C for the GC-MS coupling. For the GC-MS analysis, the gases were sampled every four minutes and injected onto an Agilent HP-5MS column held at 150°C and eluted with a helium gas flow of 2 mL/min. For FT-IR and MS measurements the gases were introduced continuously into an IR gas cell held at 200°C or directly into the MS analyzer.

Results and Discussion

TGA-FT-IR

Mass loss (TGA) and mass loss rate (DTG) curves are plotted in Figure 3 along with curves for the total integrated IR absorption (Gram Schmidt) and the integrated intensity of the CO₂ asymmetric stretching band. A single mass loss step was observed that peaked in rate at 436.6°C. The peaks in the DTG and CO₂ curves are nearly coincident, followed closely by the peak in the Gram Schmidt curve. Also shown is a melting endotherm at 220.4°C determined with the NETZSCH patented c-DTA® analysis.

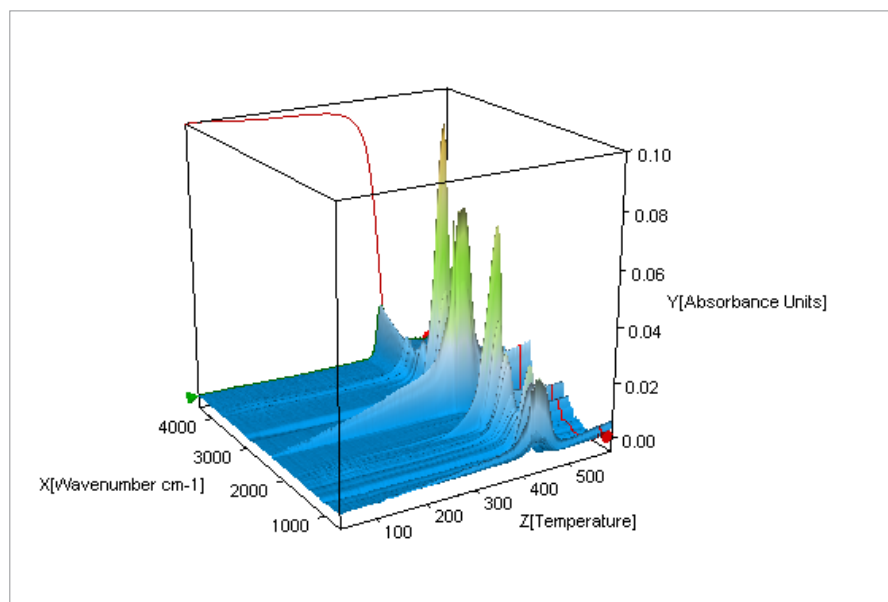


3 Results of the TGA-FT-IR analysis showing TGA (green), DTG (red), Gram Schmidt (black), and CO₂ IR absorption (pink) curves, and melting peak (blue) determined with c-DTA®

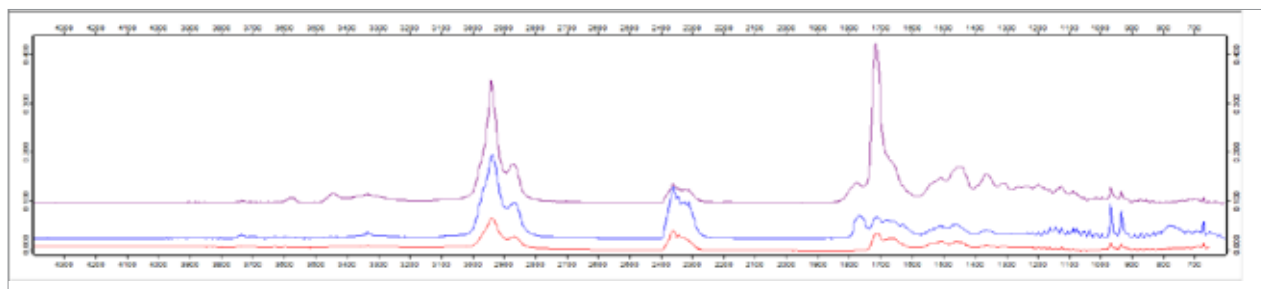
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A 3-dimensional plot of the FT-IR spectra of the evolved gases over the duration of the thermal decomposition is shown in Figure 4. Individual extracted spectra were compared with a database of IR spectra in order to identify

species evolved at different temperatures during the thermal decomposition. As shown in Figure 5, the FT-IR spectra of gases evolved at 460°C were consistent with that of Nylon-6,6 (PA66) and with Nylon-6 (PA6).



4 3-D plot of FT-IR spectra of evolved gas from the sample pyrolysis



30 Hits	Hit Quality	Compound Name	Entry No.	Molecular formula	Molecular weight	CAS number
<input checked="" type="checkbox"/> 1.	844	PA66 polyamide 66	15			
<input checked="" type="checkbox"/> 2.	547	PA6 polyamide 6	7			
<input type="checkbox"/> 3.	503	1-Cyclohexanol-1-butanone	453	C10H18O1	154.25	1462-27-7
<input type="checkbox"/> 4.	494	trans-Cyclododecene	5147	C12H22	166.31	1486-75-5
<input type="checkbox"/> 5.	492	1-Cyclohexyl-1-propanone	461	C9H16O1	140.23	1123-86-0
<input type="checkbox"/> 6.	483	10-Eicosanone, 11-hydroxy-	1453	C20H40O2	312.54	4443-65-6
<input type="checkbox"/> 7.	481	Cyclohexane, (1,1-dimethylethyl)-	3375	C10H20	140.27	3178-22-1
<input type="checkbox"/> 8.	478	Cyclohexane, 1,1-dimethyl-	3378	C8H16	112.22	590-66-9

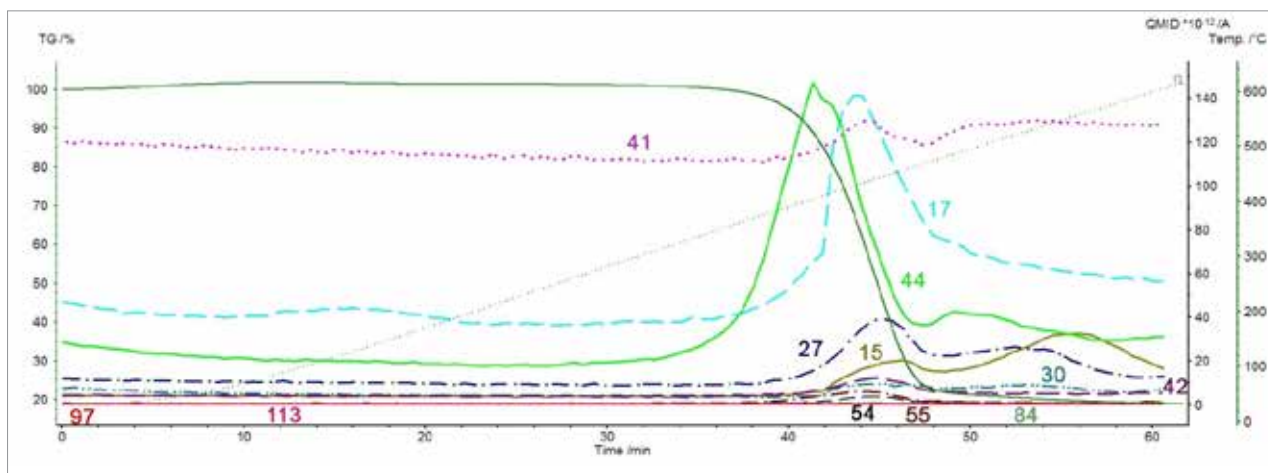
5 Results of database search of extracted FT-IR spectrum (red) of gases evolved at 460°C showing matches with PA66 (blue) and PA6 (purple)

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TGA-MS

The evolution of CO₂ was identified by MS analysis, but organic species were not identified with any confidence by searching extracted mass spectra from the acquisition in the NIST mass spectral library. Nevertheless, peaks in the ion currents (Figure 6) for mass numbers 15, 41, and 55, are consistent with Nylon-6, and peaks in the ion currents for mass numbers 17 and 54 are consistent with Nylon-6,6.

Currents for ion masses 27, 30, and 44 are also shown. These also exhibit peaks during the decomposition, but the product ions are common to both polymers. No peaks were observed in the ion current for mass 113 (caprolactone) or 84 (cyclopentanone); however, these ions are not expected with electron impact mass spectrometric (EIMS) analysis.²



6 Overlay of TGA curve and MS ion currents for mass numbers 15, 17, 30, 41, 42, 44, 54, 55, 84, 97, and 113

TGA-GC-MS Analysis

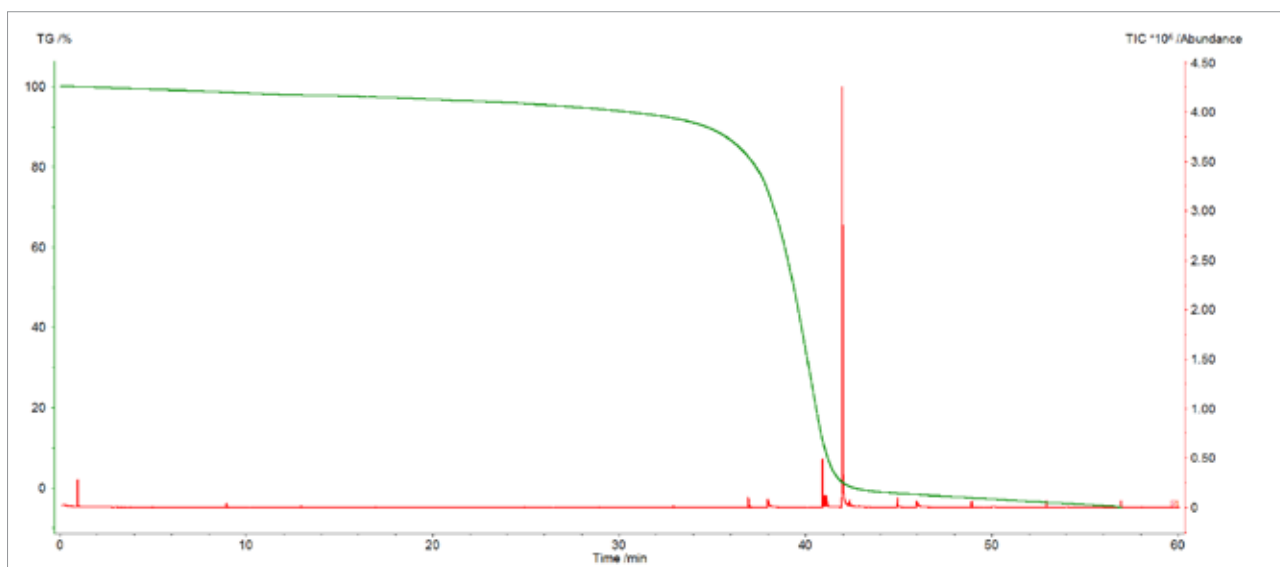
The TGA-GC-MS analysis was performed in a quasi-continuous mode by sampling the gases evolved during the pyrolysis of the sample every four minutes. Figure 7 displays an overlay of the total ion chromatogram (TIC) from the GC-MS measurement with the thermal mass loss curve. Figure 8 shows an expanded view of the TIC with peak identifications that were determined from library searches of the extracted mass spectra. Caprolactam, a primary decomposition product of Nylon-6, was the major component of the evolved gases. It started to appear in the

gas sampling around 400°C and continued to appear in pulses up to around 500°C. The appearance of CO₂ in the gas samplings between 400°C and 480°C was also consistent with both TGA-FT-IR and TGA-MS findings. Chromatographic separation of the gaseous components during the GC-MS analysis allowed the identification of a variety of other organic species that were not identified by either FT-IR or MS analysis (Figure 9). Cyclopentanone is a thermal decomposition product most characteristic of Nylon-6,6.³

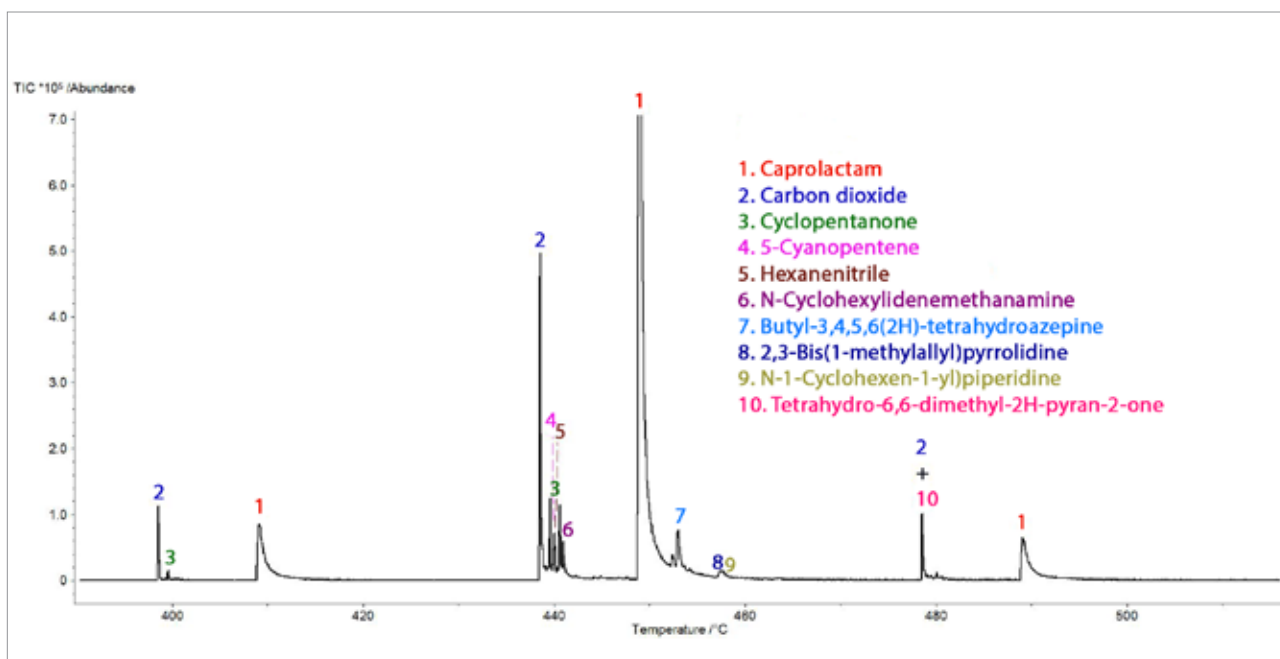
² T. Arai, K. Motomura, and S. Otake. "Evolved Gas Analysis Using Photoionization Mass Spectrometry, EGA-PIMS: Characterization of Pyrolysis Products from Polymers", J. Mass Spectrom. Soc. Jpn., Vol. 59(1), pp. 5-11, 2011.

³ S. V. Levchik, E. D. Weil, and M. L. "Review: Thermal decomposition of aliphatic nylons" Polym. Int., 48(7), pp. 532-557, 1999.

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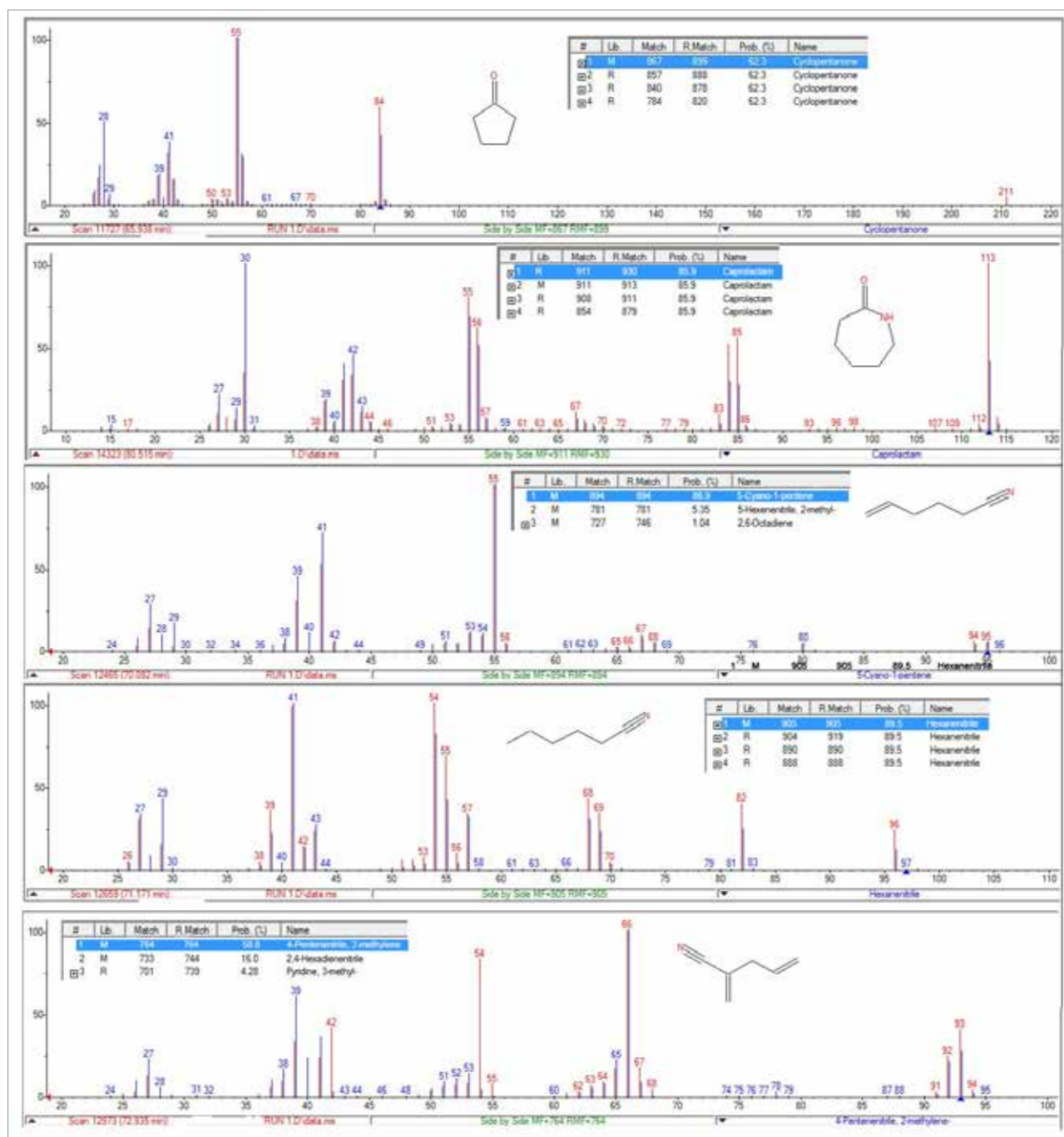


7 TGA curve (green) and TIC (red) from quasi-continuous mode GC-MS analysis of evolved gases



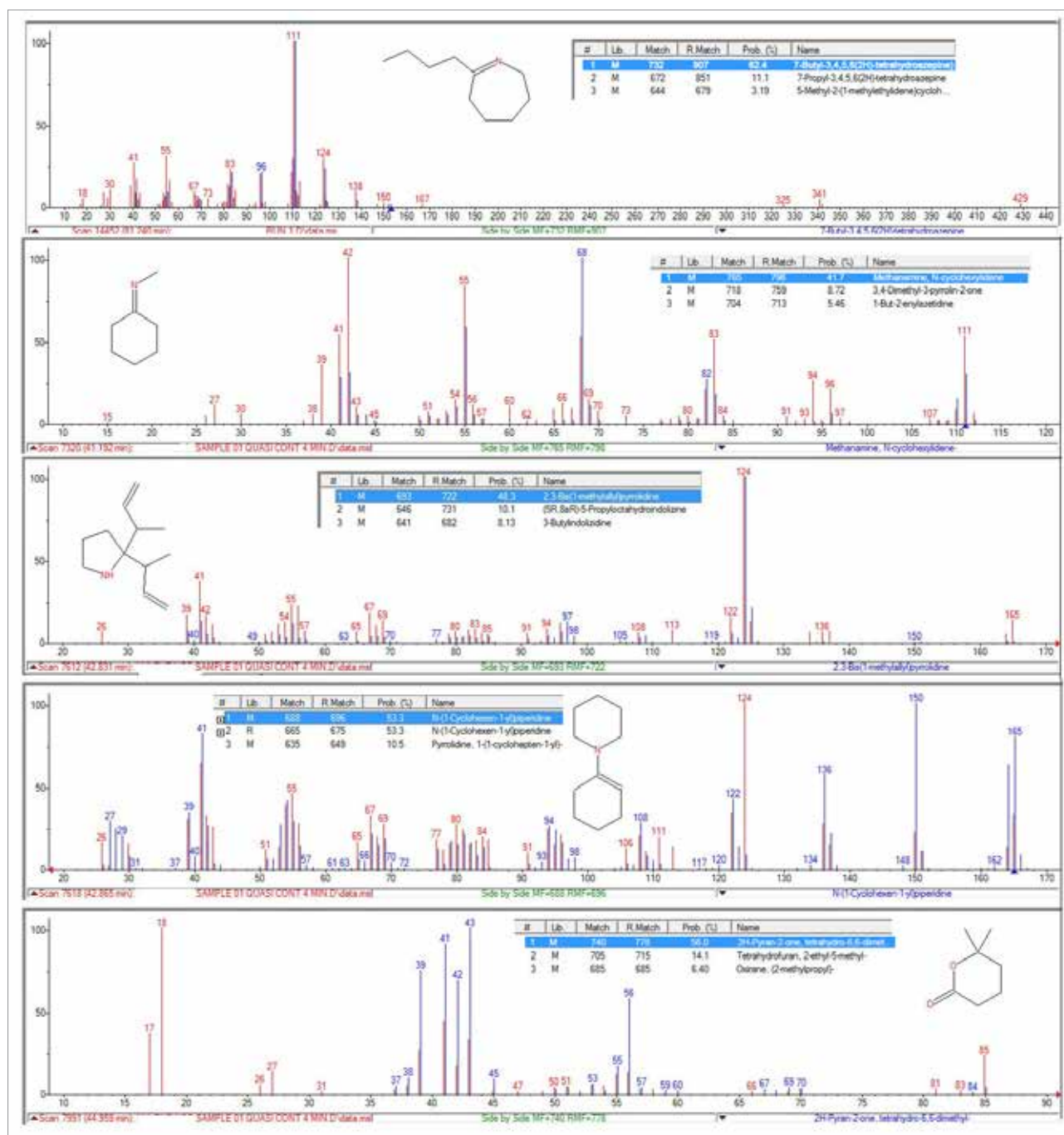
8 Expanded view of TIC from GC-MS analysis with labeling of identified peaks

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9 Results of library searches of mass spectra extracted from peaks in GC-MS. Extracted spectra are in red and library spectra are in blue.

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Conclusion

Each evolved gas analysis method has specific strengths and weaknesses that normally lend each one to specific applications. GC-MS is generally the most informative of the three methods due to the chromatographic separation of gaseous components, allowing their individual identification. In this study, GC-MS offered the clearest identification of caprolactam, confirming that the material consisted primarily of Nylon-6. It also identified cyclopentanone and nitrile products that are more characteristic of Nylon-6,6. A variety of other cyclic organic species, possibly products of Nylon-6,6, were identified for the first time in this study. EIMS (electron impact mass spectrometry) and FT-IR results confirmed the presence of both nylon polymers in the recycled carpet material. Molecular ion masses characteristic of both Nylon-6 and Nylon-6,6 were

identified by EIMS. Although FT-IR identified both polymers as potential components of the material, due to the similarities between the spectra, this evolved gas analysis method was the least definitive with respect to which specific nylon polymer(s) were actually present.

As demonstrated in this study, thermogravimetric analysis coupled with evolved gas analysis (TGA-EGA) methods is an informative and time-saving analytical tool that is useful not only for simultaneously determining the thermal decomposition profile and chemical composition of materials, but also for elucidating the chemical processes responsible for thermal mass loss by identifying the corresponding evolved gas species.