

GERSTEL AppNote 244

Pyrolysis GC-MS: Nylon and Nylon-Containing Products

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Keywords

Pyrolysis, nylon, consumer products, smart ramped pyrolysis, GC-MS

Abstract

Nylon is an important class of synthetic polymers used in a variety of products. Nylon polymers are aliphatic polyamides that are classified in two groups according to their composition. These are the Ω -aminocarboxylic acid-type and the diamine-dicarboxylic acid-type. The Ω -aminocarboxylic acid-types consist of a single amine group attached to a carbonyl group. The diamine-dicarboxylic acid-types consist of two amine groups attached to a repeating dicarbonyl group. The thermal degradation products of the two nylon categories are well established [1-3].

Nylon is used in the manufacture of fibers for clothing, stockings, and military equipment as well as in products that contain fine threads, like toothbrushes, paint brushes, and fishing line. Further, nylon resin is used in plastics for packaging and medical supplies.

This work will show pyrolysis fragmentation patterns for seven aliphatic polyamide standards along with the analysis of a few products containing some of these polymeric materials using the GERSTEL PYRO Core System. The GERSTEL pyrolyzer employed in smart ramped pyrolysis (SRP) mode in combination with gas

chromatography mass spectrometry (GC-MS) was used for the analysis. The use of SRP mode eliminates the need for pyrolysis temperature optimization, greatly reducing the time needed to obtain results, especially when determining unknown constituents and polymer mixtures.

Introduction

The GERSTEL pyrolyzer heats the sample using an advanced dual coil platinum wire that allows it to operate in a variety of pyrolysis modes including standard pulsed, sequential, fractionated, evolved gas analysis, and smart ramped pyrolysis. In addition, lower temperatures can be used to perform thermal desorption before pyrolysis. The unique heating system provides uniform sample heating and unmatched reproducibility. The GERSTEL PYRO Core System also has an integrated GERSTEL Cooled Injection System (CIS 4) inlet that can be used to cryofocus analytes in the inlet - or as a hot split interface for direct transfer to the column. The GERSTEL MultiPurpose Sampler (MPS) allows for complete automation of the analysis.

This study describes the use of the GERSTEL PYRO Core System for the analysis of nylon standards and common consumer products containing nylon polymers.

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Experimental

GERSTEL PYRO Core system on Agilent 8890 GC with Agilent 5977B MSD

Analysis Conditions PYRO Core System

Thermal Desorption

Pneumatics mode Splitless
Temperatures 40 °C, 300 °C/min to
300 °C (2.17 min)

Pyrolysis (Smart Ramp)

Lead Time 0.00 min
Follow up Time 0.25 min
Initial Time 0.00 min
Temperatures 300 °C, 5.0 °C/s to 800 °C (0.0 min)

CIS 4

Pneumatics mode Split 100:1
Temperatures -120 °C (0 min), 12 °C/s to
300 °C (3 min)

Analysis Conditions Agilent 8890 GC

Pneumatics He, P_i = 7.1 psi (MSD)
Constant flow = 1.0 mL/min
Column 30 m DB-5MS UI (Agilent)
d_i = 0.25 mm, d_f = 0.25 µm
Oven 40 °C (1.0 min), 10 °C/min to
320 °C (6 min)

Sample Preparation

Nylon standards included Nylon 6, Nylon 11, Nylon 12, Nylon 6/6, Nylon 6/10, Nylon 6/12, and Nylon 6(3)/T. The standards were purchased from Scientific Polymer Products Inc., Ontario, NY. The standards were in pellet form.

Samples analyzed by pyrolysis GC-MS included paint brush bristles, toothbrush bristles, clear fishing line, food packaging, filters, and women's pantyhose.

Approximately one milligram of each standard and sample was placed into an open-ended quartz pyrolysis tube with quartz wool. The quartz tubes were connected to pyrolysis adapters and placed into a 40-position pyrolysis tray.

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Results and Discussion

Figure 1 shows a pyrogram for Nylon 6. The main peak is the monomer, caprolactam. Smaller peaks include 2-propenenitrile, cyclopentanone, and hexanenitrile.

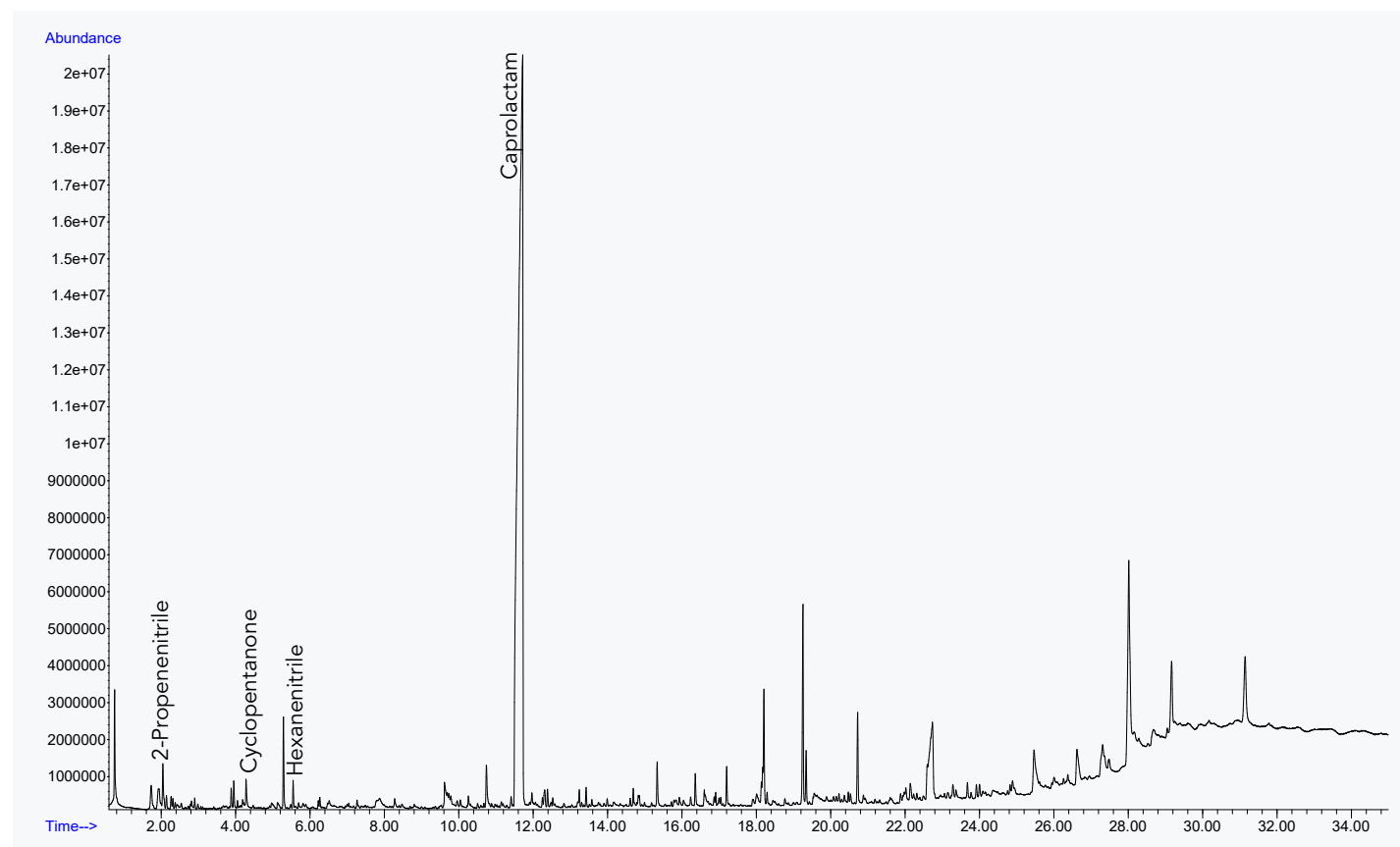


Figure 1: Pyrogram for Nylon 6.

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Figure 2 shows a pyrogram for Nylon 11. Nylon 11 does not exhibit the formation of lactams, rather it thermally degrades into mononitriles and allyl nitriles. The main peak is 10-undecenitrile followed by N-(11-cyanoundecyl)-9-decanamide and 1,13-diazacy-

clotetracosane-2,14-dione eluting at approximately 28 and 30 minutes, respectively, in the pyrogram. Smaller peaks include 11-dodecenenitrile and dodecanenitrile.

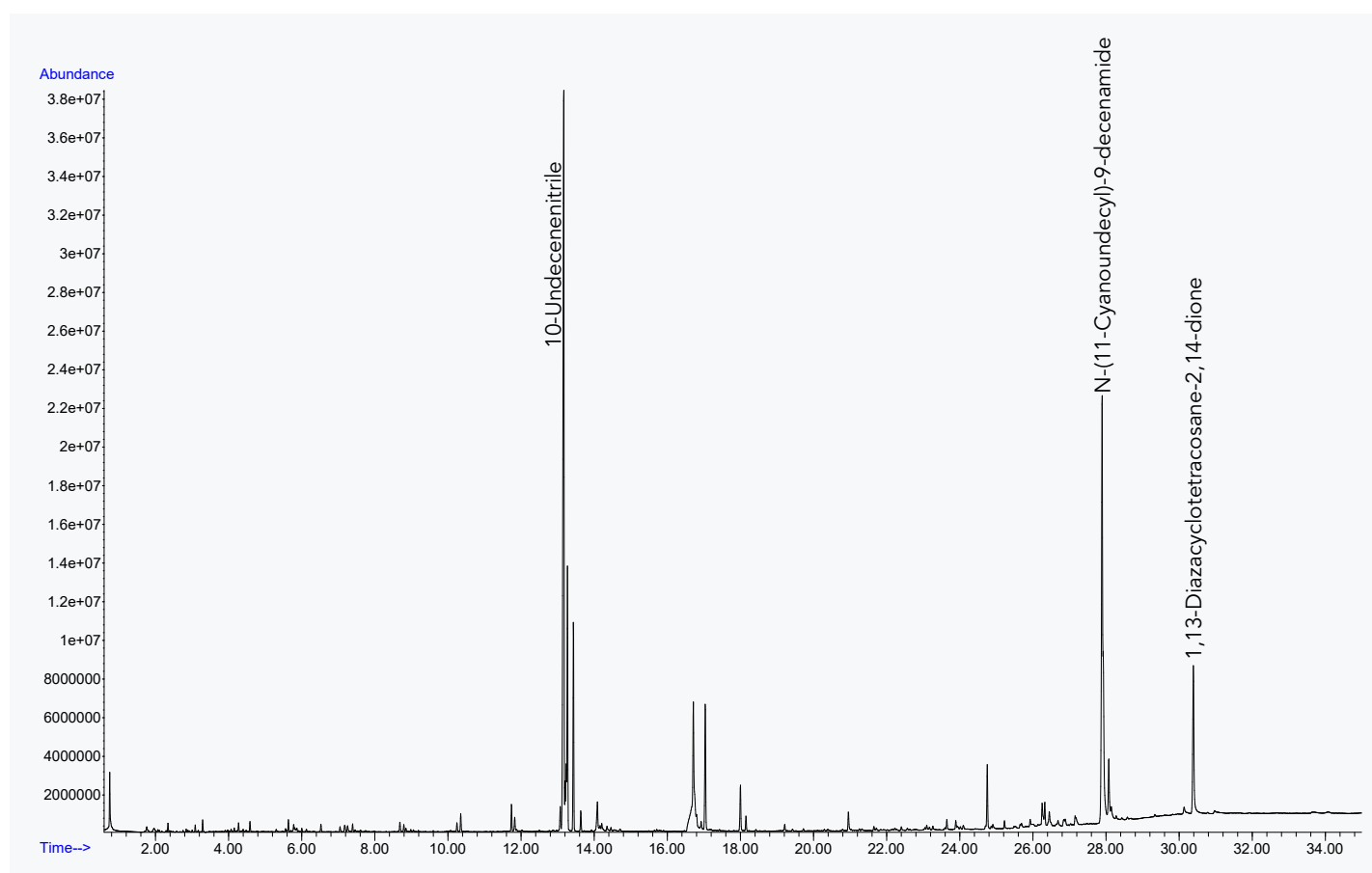


Figure 2: Pyrogram for Nylon 11.

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Figure 3 shows a pyrogram for Nylon 12. Like Nylon 11, Nylon 12 thermally degrades into mononitriles and allyl nitriles, but Nylon 12 also exhibits substituted amides, N-substituted amides,

and dinitriles. The main peak is 11-dodecenenitrile. Other peaks identified include azacyclotridecan-2-one, N-(11-cyanoundecyl)dodec-11-enamide, and 1,14-diazacyclohexacosane-2,15-dione.

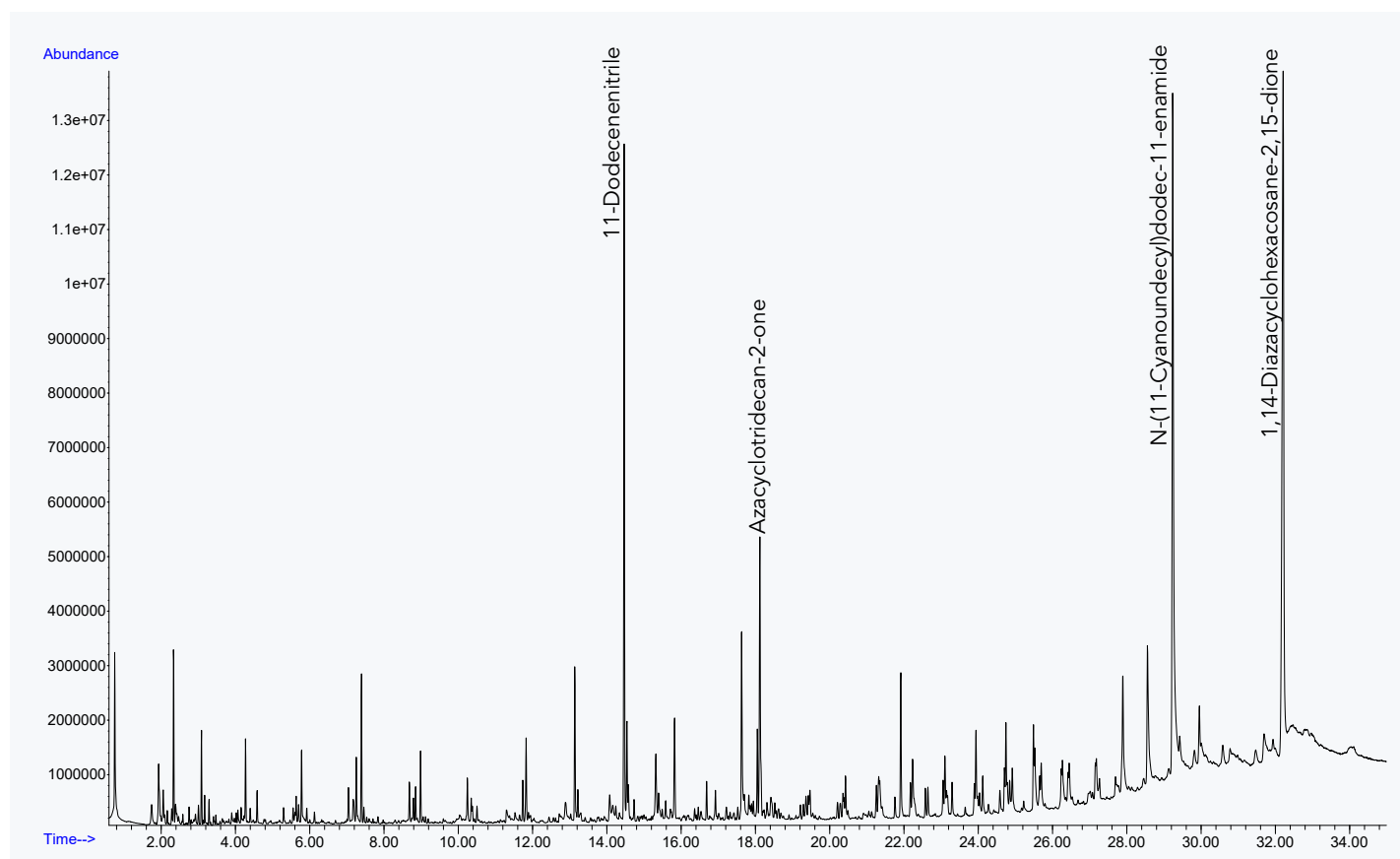


Figure 3: Pyrogram for Nylon 12.

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Figure 4 shows a pyrogram for Nylon 6/6. Thermal degradation of Nylon 6,6 generates some caprolactam, but the main peak is cyclopentanone along with other diamines.

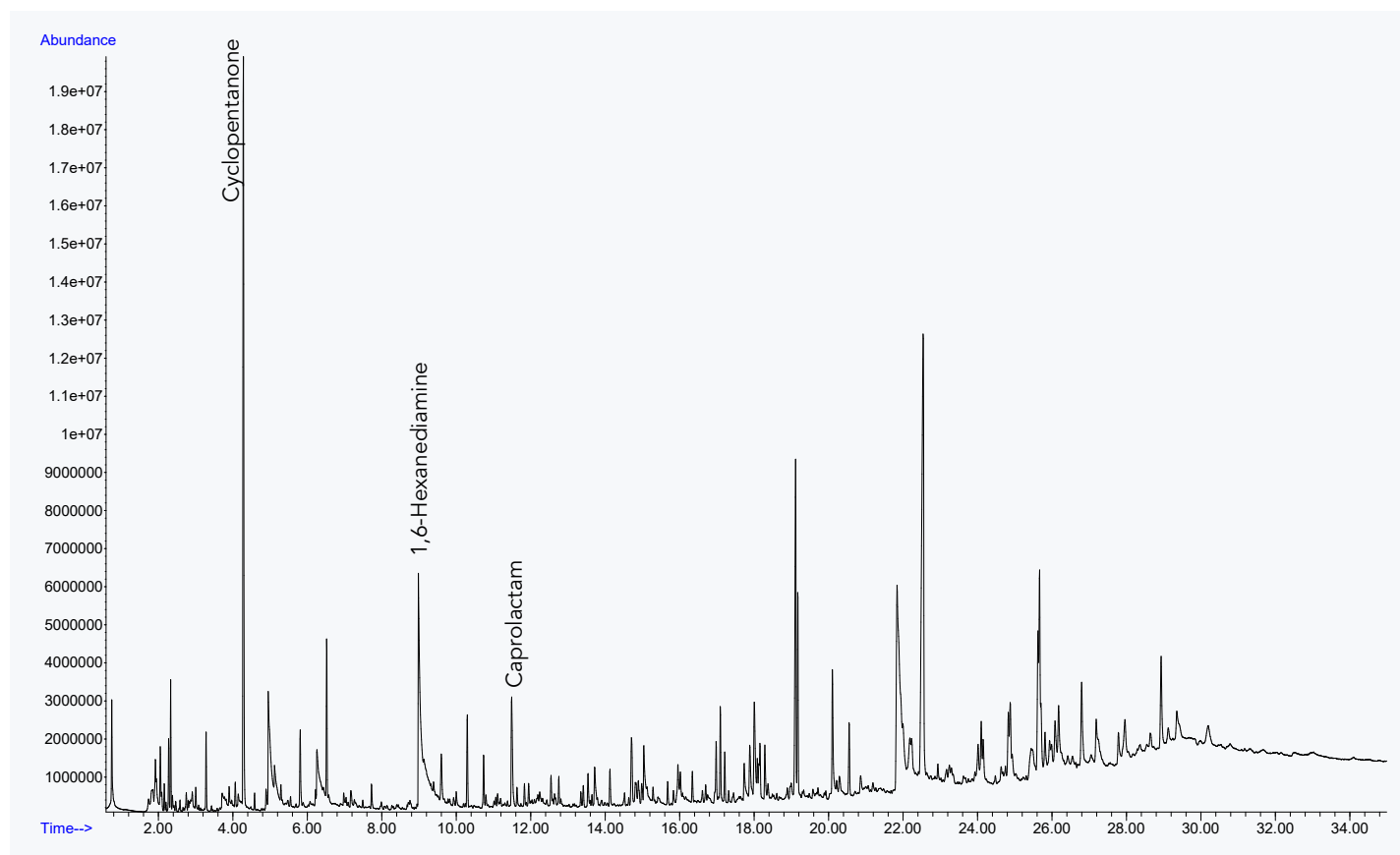


Figure 4: Pyrogram for Nylon 6/6.

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Figure 5 shows a pyrogram for Nylon 6/10. Thermal degradation of Nylon 6/10 shows 1,8-diazacyclooctadecane-9,18-dione as the

main component. Smaller peaks included 7-octenenitrile, caprolactam, decanedinitrile, and 9-cyano-N-hexylnonamide.

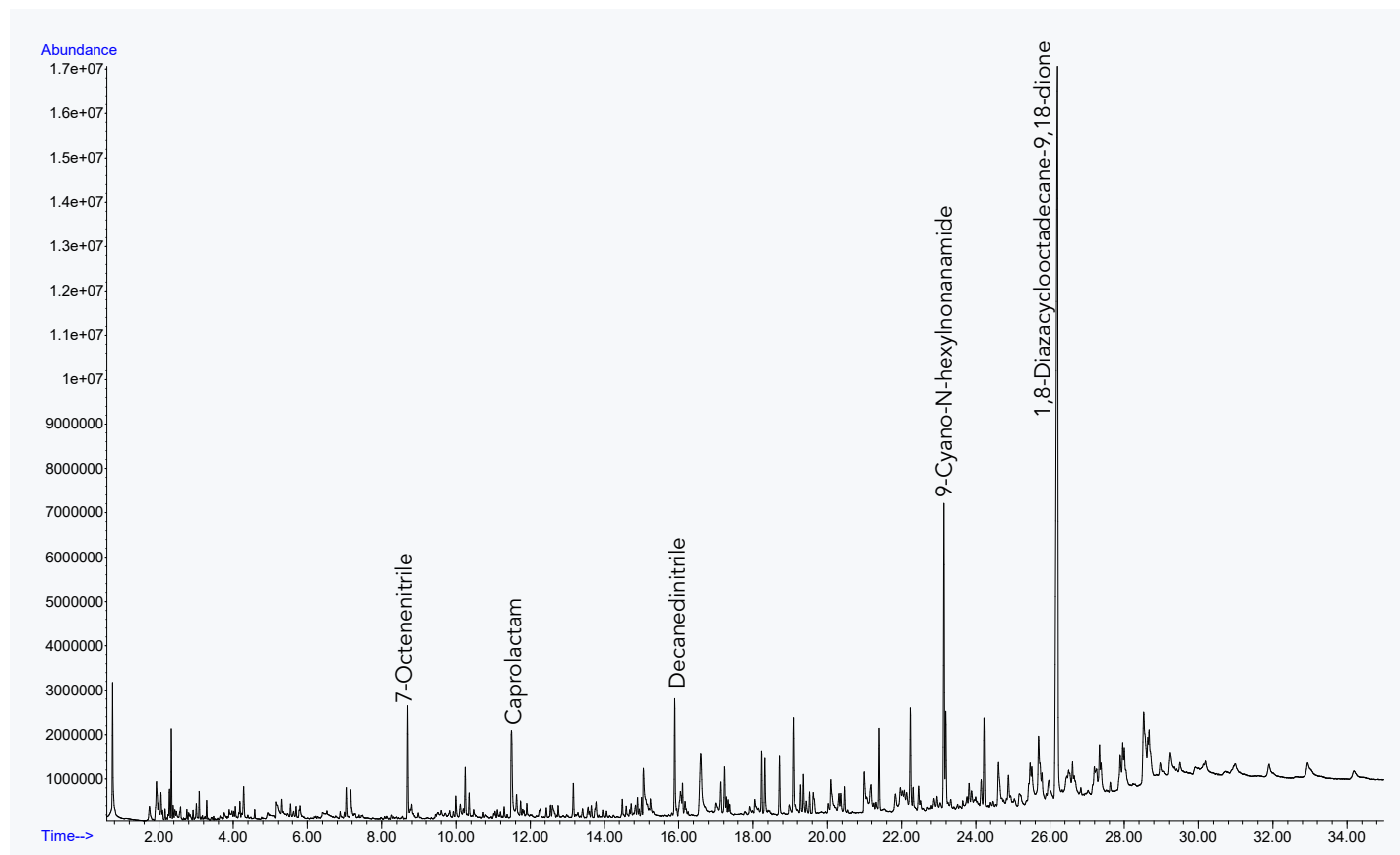


Figure 5: Pyrogram for Nylon 6/10.

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Figure 6 shows a pyrogram for Nylon 6/12. Thermal degradation of Nylon 6/12 produces an even distribution of several dinitriles, mononitriles, and amides. These include 10-undecenenitrile, 1,10-dicyanodecane, and a small caprolactam peak. The main

components elute at 24.8 and 27.6 minutes and represents the Nylon 6/12 monomer unit with a loss of water and the monomer itself with parent peak 310 m/z, respectively.

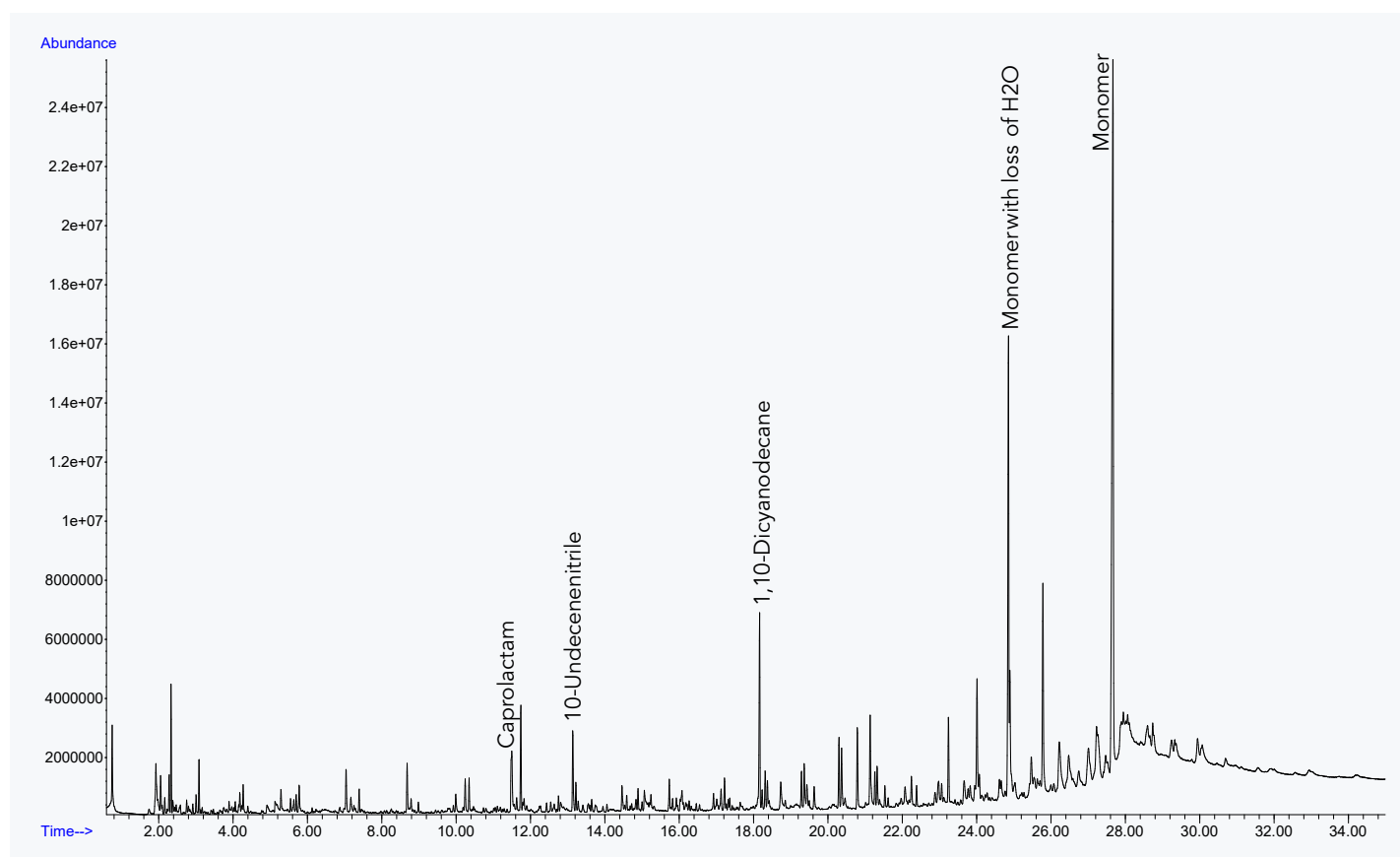


Figure 6: Pyrogram for Nylon 6/12.

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Figure 7 shows a pyrogram for Nylon 6(3)/T. Nylon 6(3)/T is an aromatic polyamide making it differ greatly from the latter nylon standards. Thermal degradation of Nylon 6(3)/T results in several

aromatic nitriles; the predominant being 4-methylbenzonitrile and isophthalonitrile along with some aromatic amides.

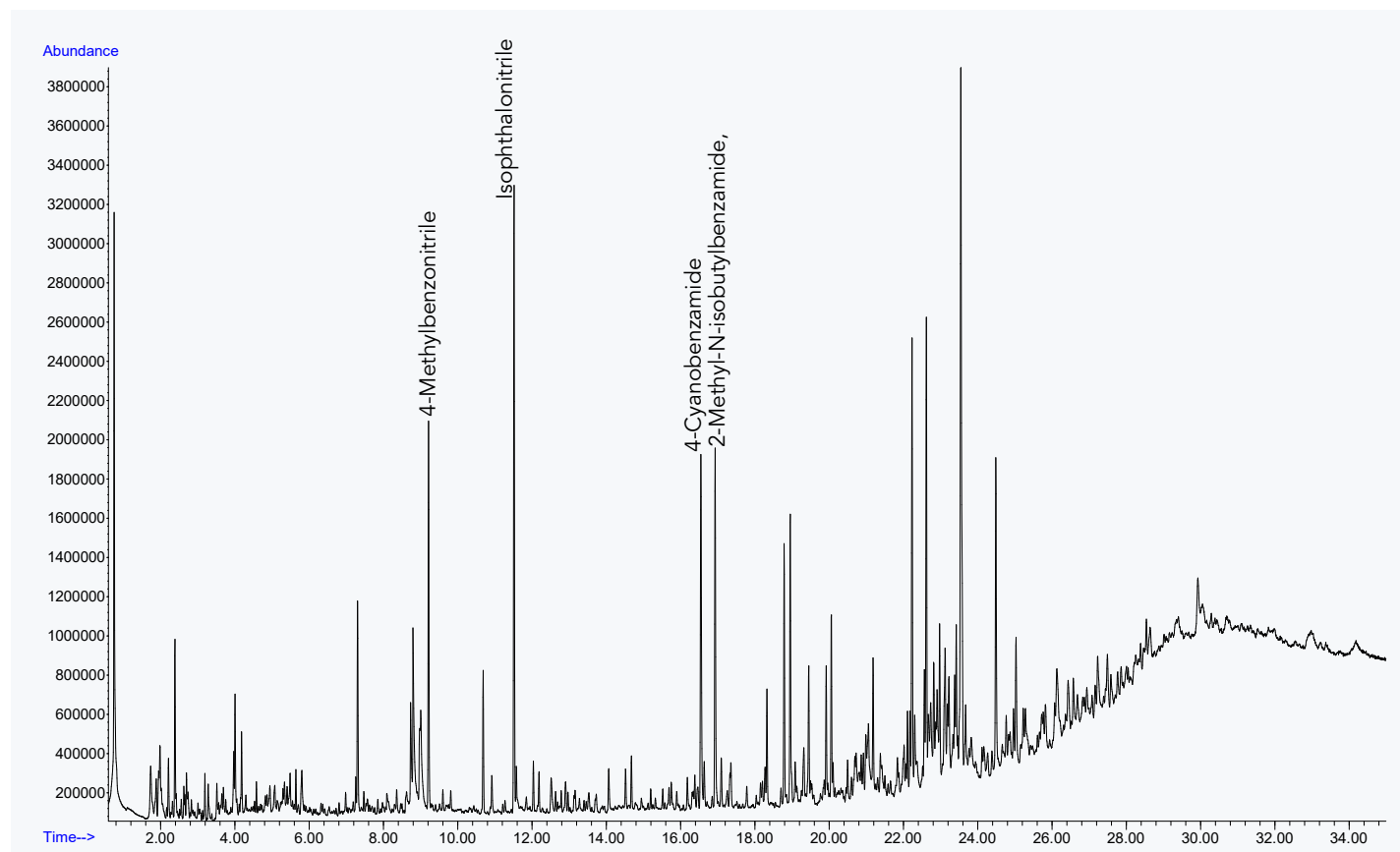


Figure 7: Pyrogram for Nylon 6(3)/T.

The pyrograms for the standards compare well with those found in the references cited (1, 2, 3). This demonstrates the ability of the

smart ramped pyrolysis mode to produce optimized pyrograms without the need for method optimization.

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Figure 8 shows pyrograms for the paint brush and toothbrush samples, respectively. The bristles from each are made from Nylon

6/12, as the marker peaks for this nylon, the monomer, caprolactam and 1,10-dicyanodecane are present in the pyrograms.

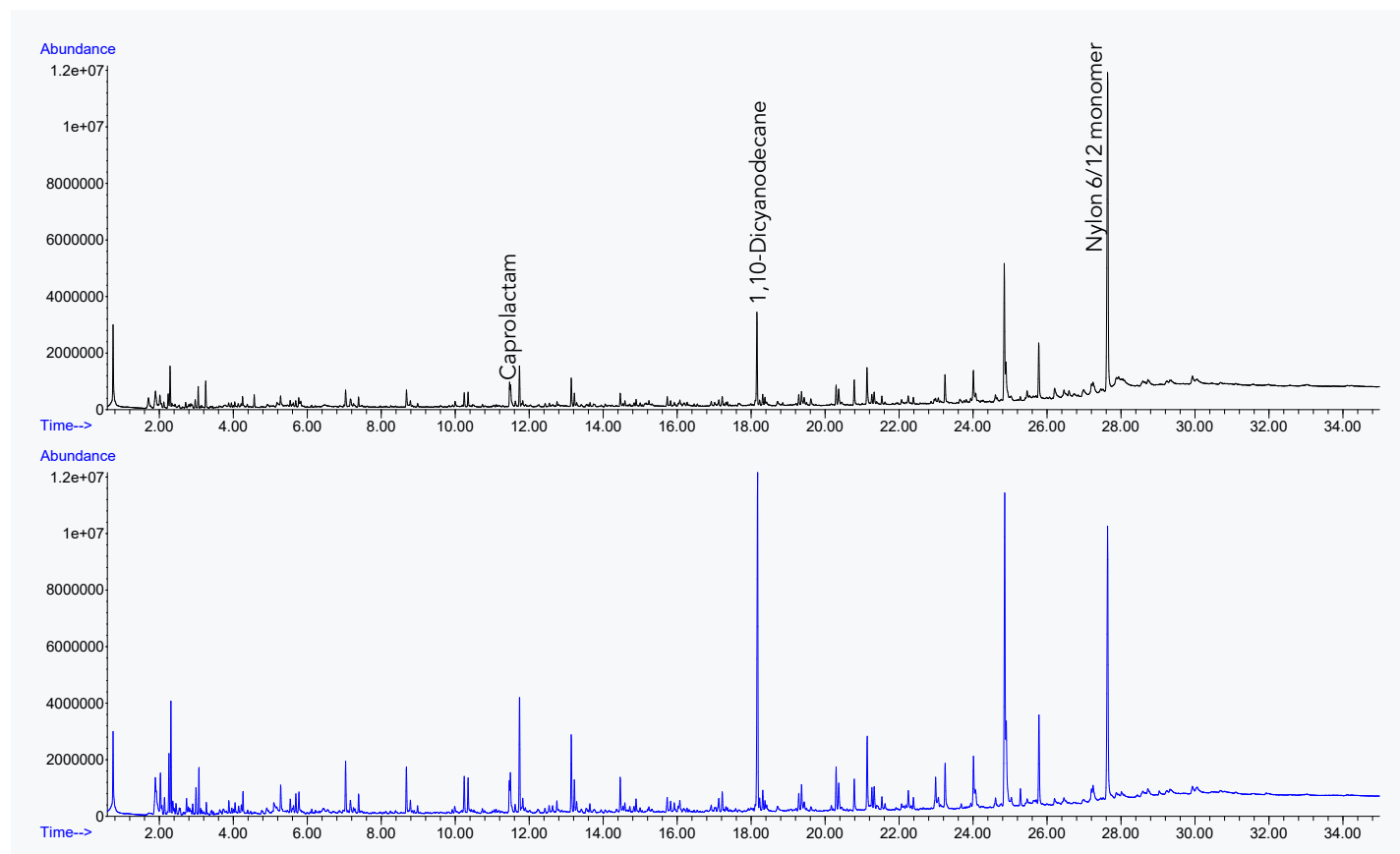


Figure 8: Pyrograms for paint brush (upper trace) and toothbrush (lower trace).

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Figure 9 shows the pyrogram for the clear fishing line. The predominant peak is caprolactam with smaller peaks present such

as cyclopentanone and hexanenitrile. These are all indicative of Nylon 6.

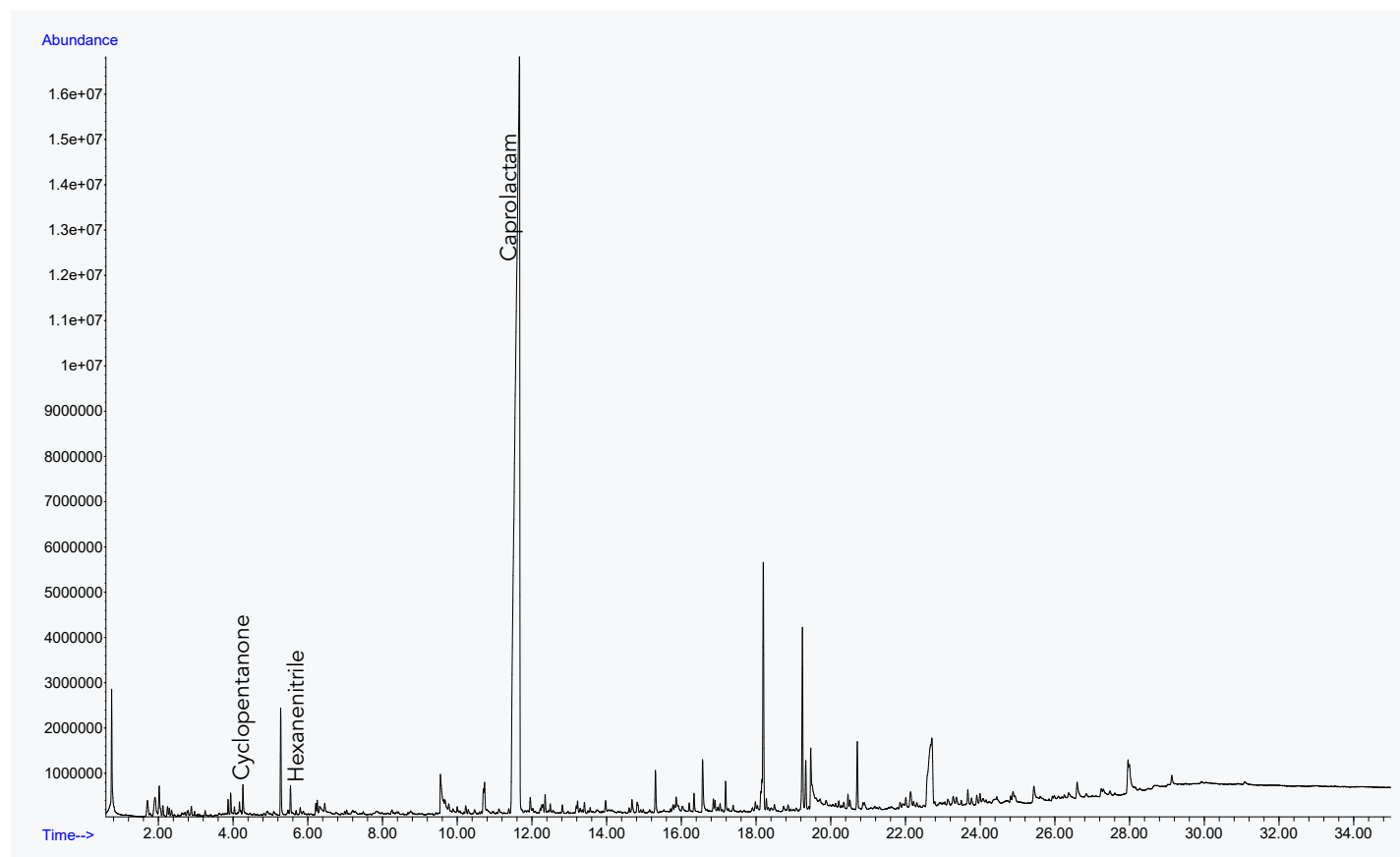


Figure 9: Pyrogramm for fishing line.

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Figure 10 shows the pyrogram for the food packaging. Food packaging can be complex consisting of several layers bonded together. The multilayer construction is used to give strength, barrier properties and storage stability for food products. In this sample, a large caprolactam peak is seen, indicating the sample is

composed of Nylon 6. The repeating triplet pattern of alkyl diene, alkene, and alkane indicates the presence of polyethylene in the sample. Also present are styrene (polystyrene), methyl methacrylate and isobutyl methacrylate (polymethacrylate), and two siloxanes (polysiloxane).

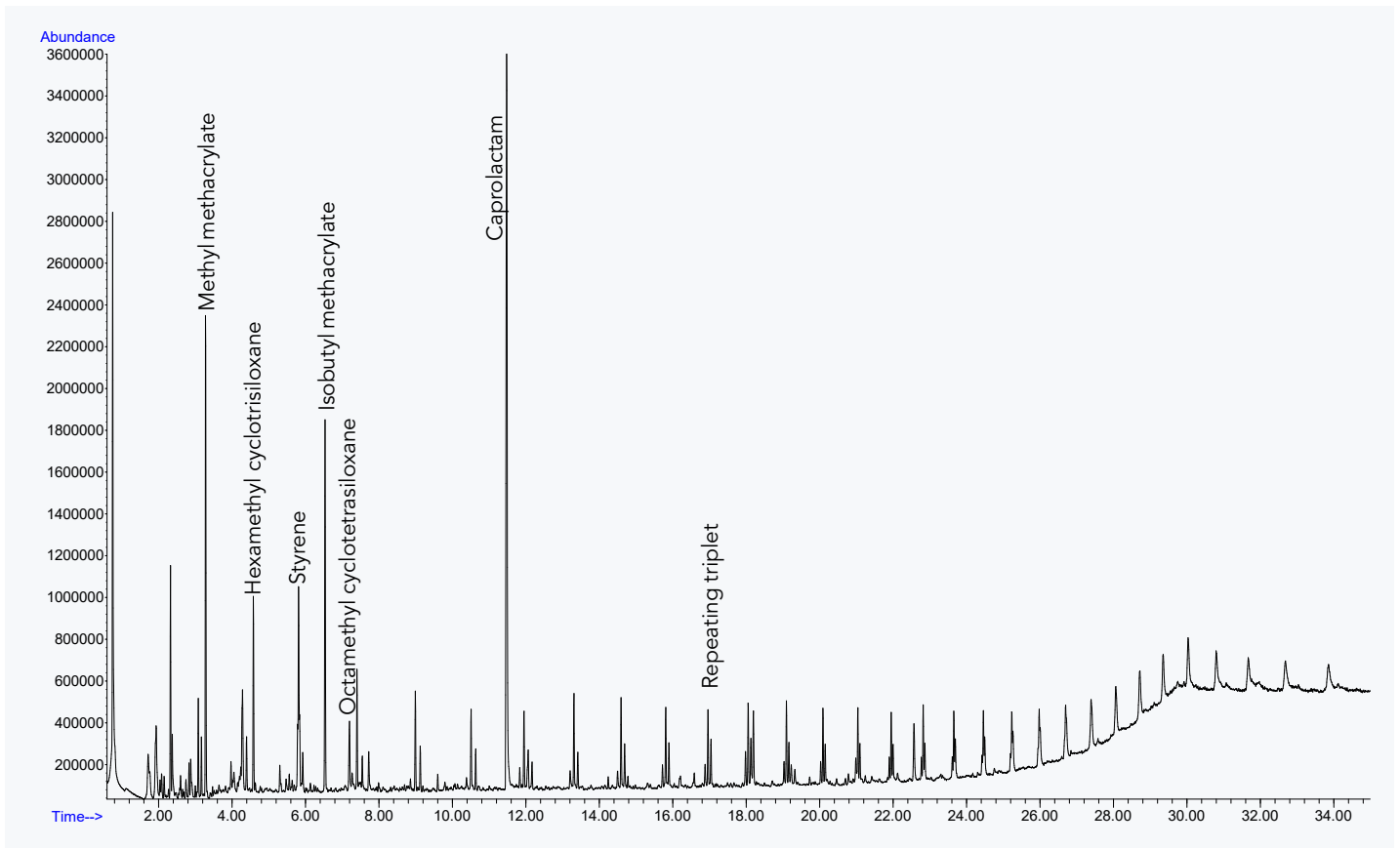


Figure 10: Pyrogramm for food packaging.

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Figure 11 shows pyrograms for a filter membrane and black panty hose samples, respectively. Both consumer products' pyro-

grams showed cyclopentanone as the main thermal degradation component, therefore, they are made from Nylon 6/6.

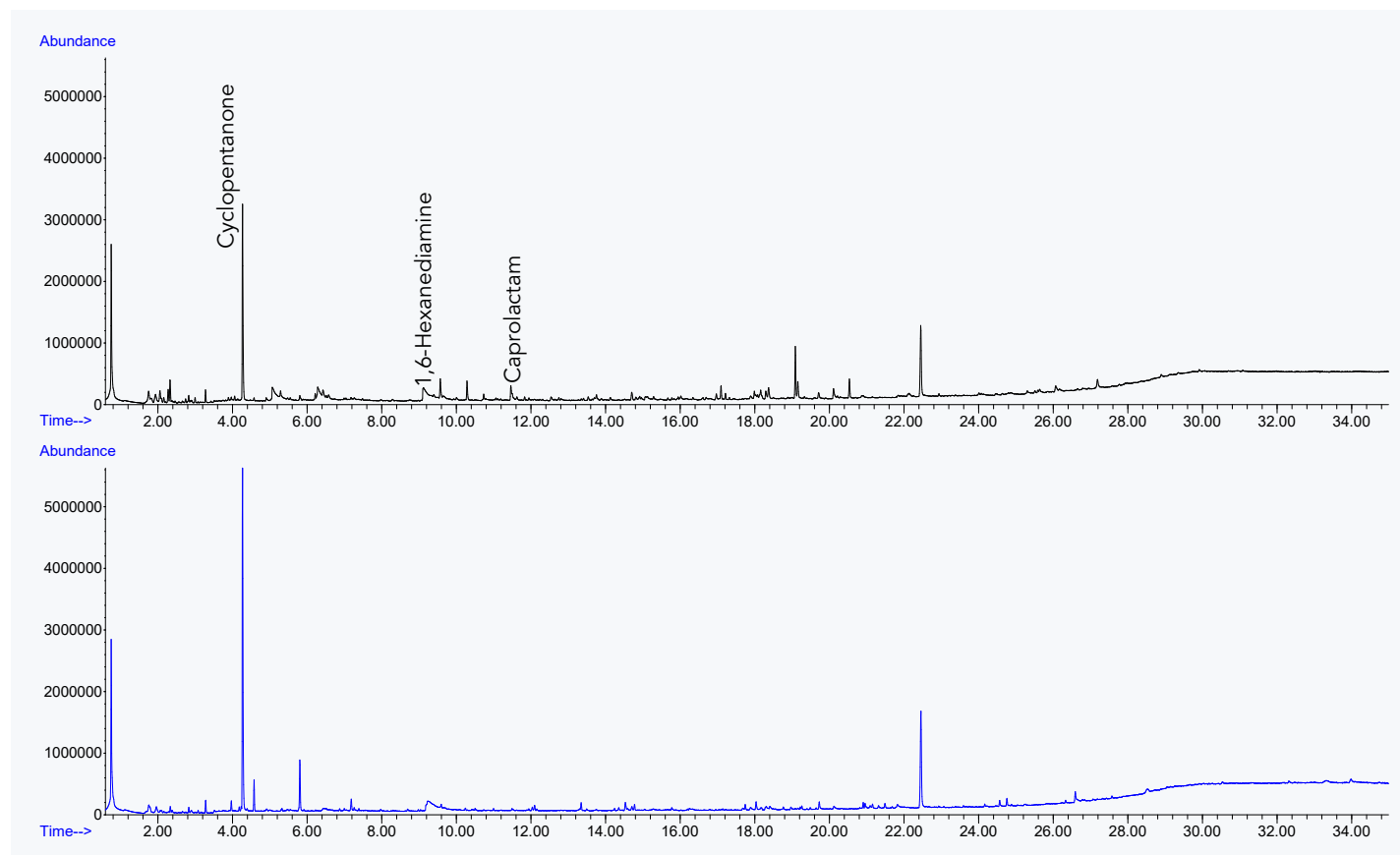


Figure 11: Pyrograms for filter (upper trace) and panty hose (lower trace).

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Conclusions

Pyrolysis of the Nylon 6 standards showed monomer reversion, to caprolactam. Nylon 6/6, 6/10, and 6/12 also produced caprolactam, but not as the main component. Cyclopentanone was found to be the main thermal degradation product of Nylon 6/6. Other common compounds produced due to thermal degradation included mononitriles, dinitriles, and amides. Nylon 6(3)/T was the exception to the other standards in that it produced an abundance of aromatic nitriles.

Pyrolysis GC-MS was used to identify nylon polymers in several sample types. Nylon 6, 6/6, and 6/12 were only found in the consumer products.

Smart Ramped Pyrolysis combines a slow heating rate with a quick transport rate to apply a broad temperature range to a sample without overheating its components. This results in an optimized pyrogram for a sample without having to determine the optimal pulsed pyrolysis temperature. This is especially important for unknown samples or whenever the amount of sample is limited. It was applied in this study and greatly reduced method development time, while improving the accuracy of compound identification. The GERSTEL PYRO Core system enables highly flexible and efficient automated pyrolysis of solids and liquids up to 1000 °C combined with GC-MS determination of the thermal decomposition products. It provides an excellent tool for the analysis of polymers, polymer mixtures, and polymer additives.

References

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