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Pyrolysis Gas Chromatography-Mass Spectrometry for the Analysis of Leather and Leather-like Products

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Keywords

Pyrolysis, leather, faux leather, gas chromatography, mass spectrometry

Abstract

Leather and leather-like materials are used in various products such as baseball gloves, furniture, clothing, shoes, car interiors, phone cases, etc. One comes in contact with these types of materials through normal daily activities. Leather is made from animal skin. The skin is composed of a fibrous collagen network. Collagen is a structure-forming protein consisting of three peptide chains in a triple helix structure.

Leather-like materials can comprise different polymers, including polyurethane, nylons, polycarbonate, polyethers, and polyesters. They are often a combination of these materials.

Pyrolysis GC-MS is useful for identifying polymers, such as leather and faux leather. It can easily distinguish between the two types of material.

This study used the GERSTEL pyrolysis system, in combination with gas chromatography-mass spectrometry, to analyze leather and leather-like materials.

Introduction

The GERSTEL PYRO Core system, equipped with an advanced dual coil platinum wire, operates in various pyrolysis modes, including standard pulsed, sequential, and fractionated. Its unique heating system ensures uniform sample heating and unmatched reproducibility. The system also features an integrated GERSTEL CIS 4 inlet, serving as a cryofocusing trap for analytes or a hot split interface for direct transfer to the column. The GERSTEL MPS robotic autosampler enables complete automation of the analysis.

This study details the use of the GERSTEL PYRO system and the GERSTEL MPS robotic autosampler to analyze leather and faux leather using smart ramped pyrolysis. In Smart-Ramped Pyrolysis, a rapid, controlled temperature ramp is applied, enabling continuous pyrolysis of the sample. It produces a pyrogram in a single sample run that is equivalent to, or provides more data, compared to pulsed pyrolysis mode. This mode is ideal for unknown samples and significantly reduces method development time.

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Experimental

Instrumentation

GERSTEL PYRO Core system on Agilent 8890 GC/5977B Inert Plus MSD (Figure 1).

Figure 1: GERSTEL PYRO Core system mounted on an Agilent 8890-5977B GC-MS System

Analysis Conditions PYRO Core System

CIS 4	Split 75:1	
	-120 °C (0 min), 12.0 °C/s, 300 °C (5.0 min)	
TDU	Splitless	
	50 °C (0 min), 300 °C/min, 300 °C (2.02 min)	
Pyro	Lead Time	0.00 min
	Follow up Time	0.25 min
	Initial Time	0.00 min
	Initial Temp	300 °C
	Rate	5 °C/s
	Final Temp	800 °C
	Final Time	0.10 min

Analysis Conditions Agilent 8890 GC

Column	30 m DB-5MS UI (Agilent)
	d_i = 0.25 mm, d_f = 0.25 µm
Pneumatics	He, P_i = 7.1 psi (MSD)
	Constant flow = 1.0 mL/min
Oven	40 °C (2.0 min), 15 °C/min, 300 °C (6 min)

Sample Preparation

Sample types included several brands of golf gloves, a leather glove used in our lab, and a cell phone case. A 1.0 mm Rapid-Core punch (Ted Pella, #15115-3) was used to sample the golf gloves and cell phone case. For the leather glove, an X-acto knife was used to remove a small sample from the glove.

Pyrolysis—the samples were 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 2 shows the total ion chromatogram (TIC) for the pyrolysis of the leather glove. Collagen is made up of proteins, which in turn are made up of amino acids. The TIC shows the pyrolysis of the proteins in the leather, which results in the formation of nitrogen-containing pyrolyzates, including pyrroles, pyridines, and aniline. Collagen also contains some sulfur compounds, which show up as sulfur dioxide and methanethiol at the front end of the chromatogram.

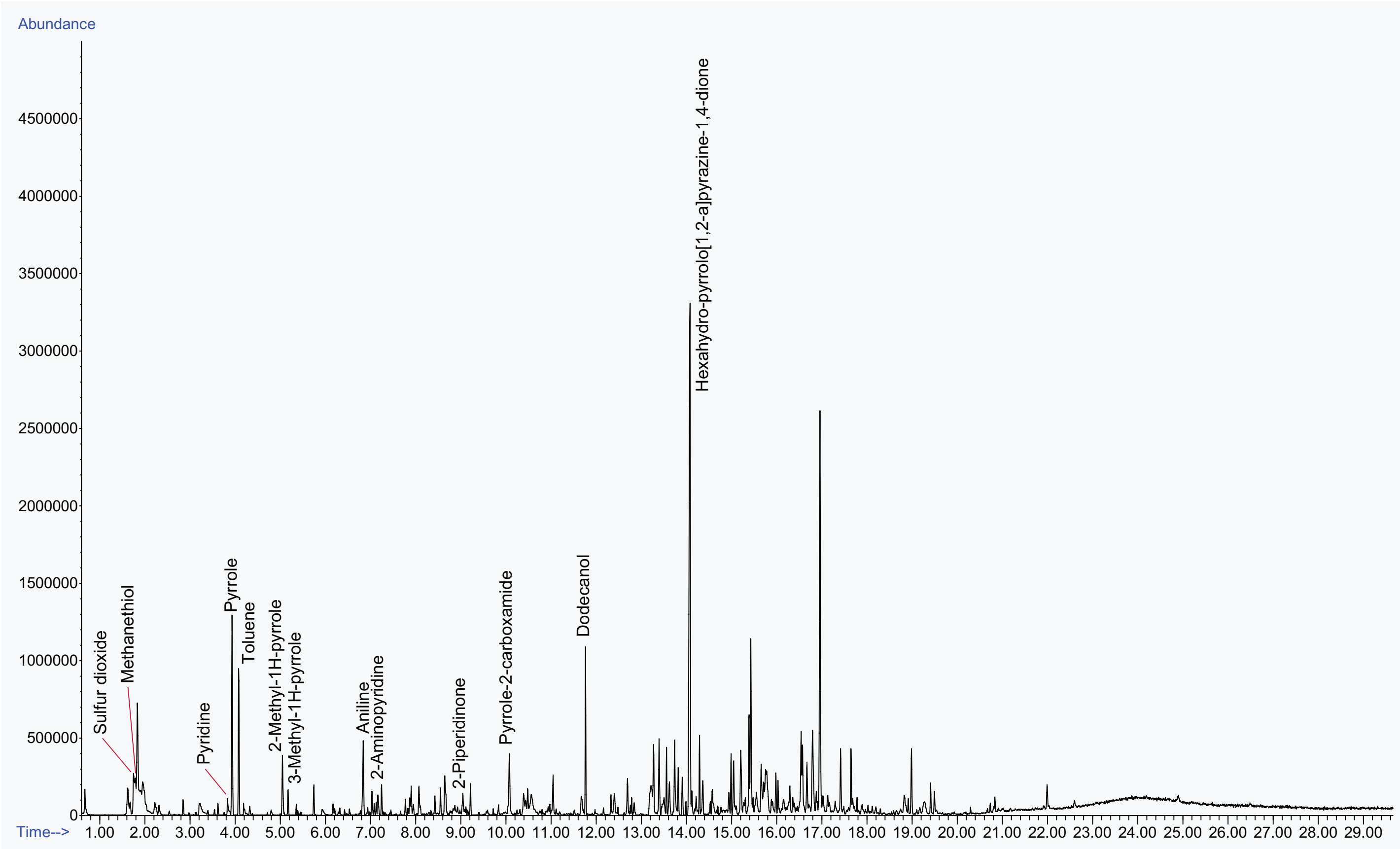

Figure 2: Total ion chromatogram for pyrolysis of leather glove sample.

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Figure 3 shows the resulting TIC for a premium golf glove. The resulting pyrogram is similar to the leather glove, indicating that this golf glove is leather. The sulfur dioxide and methanethiol are present along with a plasticizer, bis (2-ethylhexyl) phthalate.

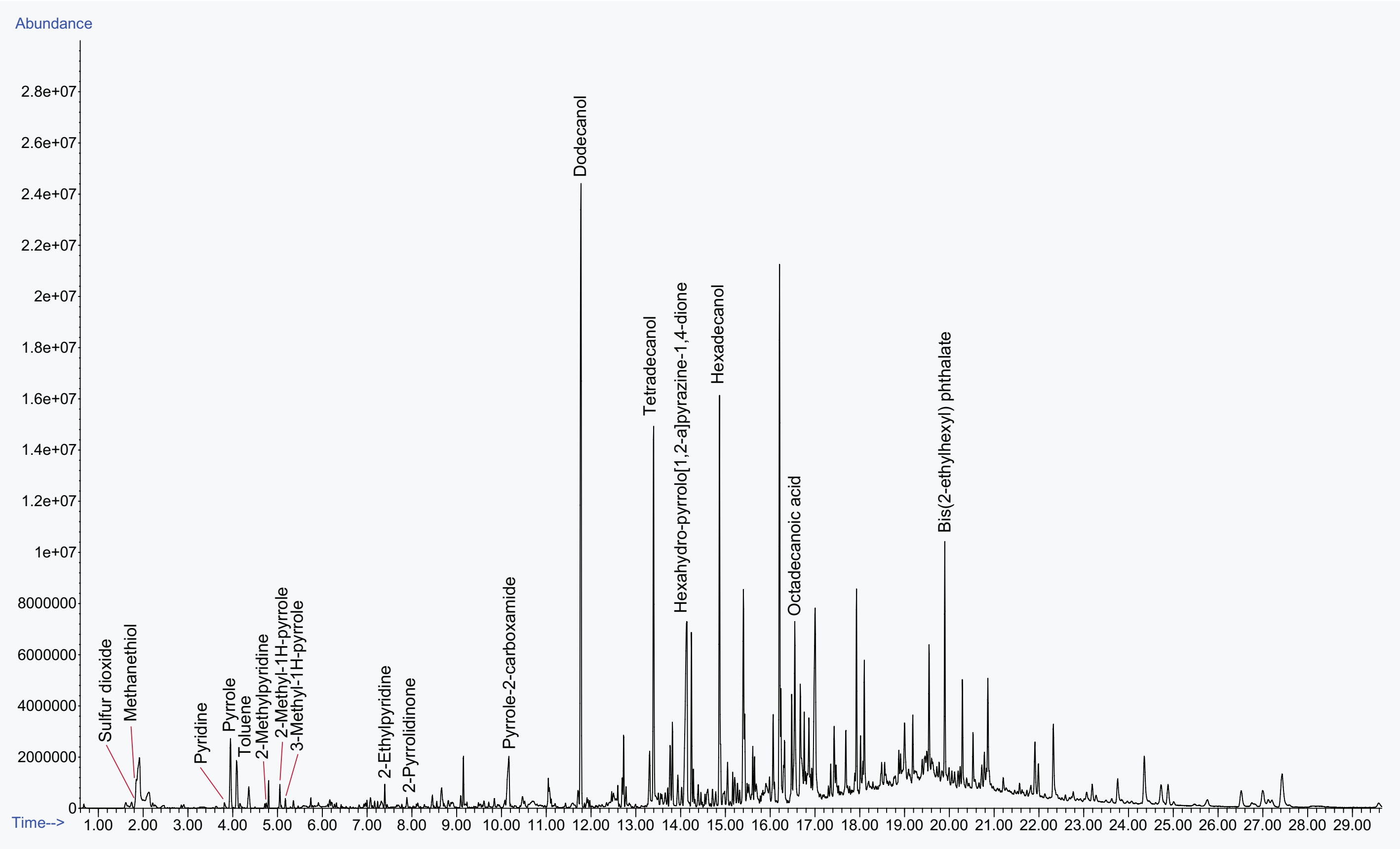

Figure 3: Total ion chromatogram for pyrolysis of premium leather golf glove sample.

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Figure 4 shows a second golf glove sample's total ion chromatogram (TIC). Marker peaks for polyurethane: tetrahydrofuran, cyclopentanone, and 1,4-butanediol are present in the chromatogram. Marker peaks for polyethylene terephthalate include benzene, benzoic acid, biphenyl, and terephthalic acid. Other peaks present in the chromatogram are substituted benzoic and terephthalic acid compounds. The pyrogram indicates a faux leather made of PET, possibly with a polyurethane coating. The polyurethane makes the glove water-resistant and provides the feel of natural leather.

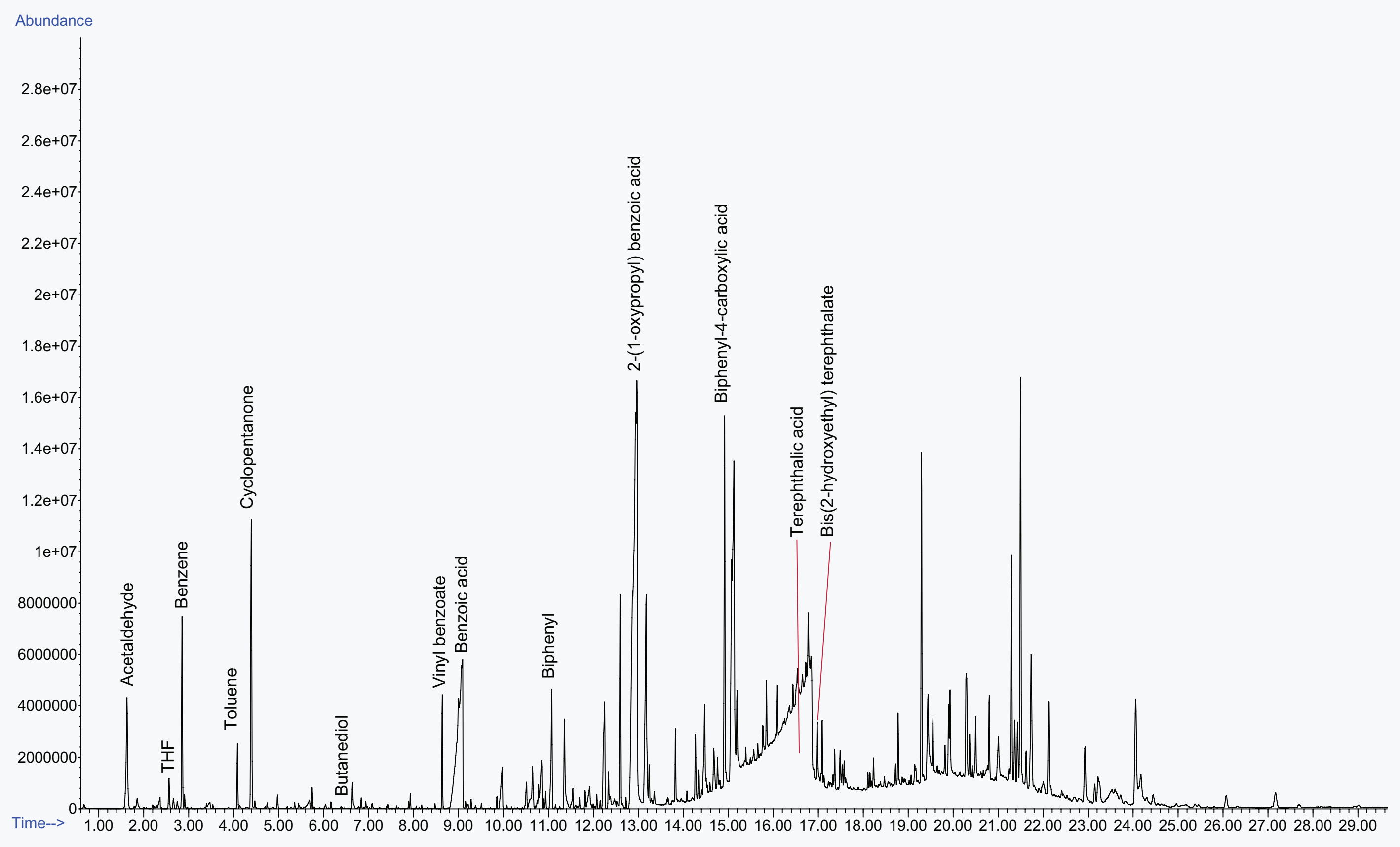

Figure 4: Total ion chromatogram for pyrolysis of golf glove sample 2.

Figure 5 shows a third golf glove sample's total ion chromatogram (TIC). Caprolactam and caprolactam dimer indicate the presence of Nylon 6 in the sample. Polyurethane is in the sample as indicated by the peaks for cyclopentanone, tetrahydrofuran and 1,4-butanediol. Peaks for Bis(butenyl) adipate, butenyl butanediol adipate, and butanediol adipate indicate the presence of polybutylene adipate in the glove. This polymer is used as a water-resistant coating.

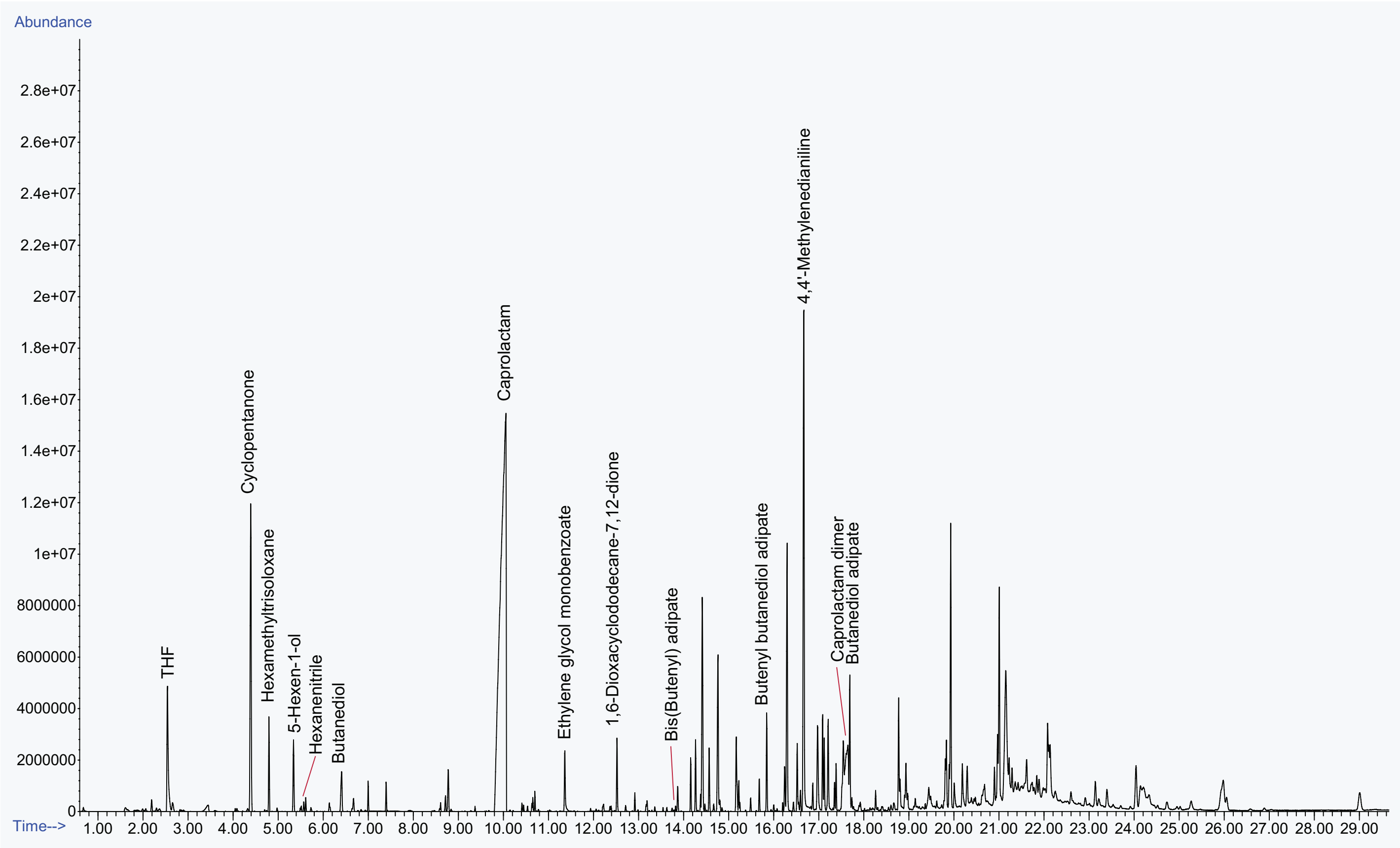

Figure 5: Total ion chromatogram for pyrolysis of golf glove sample 3.

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Figure 6 shows a total ion chromatogram (TIC) of a faux leather phone case. Several polymers are indicated by marker peaks. Polystyrene is present as styrene, α-methylstyrene, styrene dimer, and styrene trimer are found in the chromatogram. Acrylonitrile is seen early in the chromatogram. Markers for PET: ethyl benzoate, benzoic acid, and biphenyl are found in the chromatogram. Phthalic anhydride is also indicative of a polyester being present in the sample. Tetrahydrofuran, cyclopentanone, and biphenyl indicate polyurethane is present in the sample. 4,4'-Methylenediamine is seen in the chromatogram. It is commonly used as a polyurethane precursor.

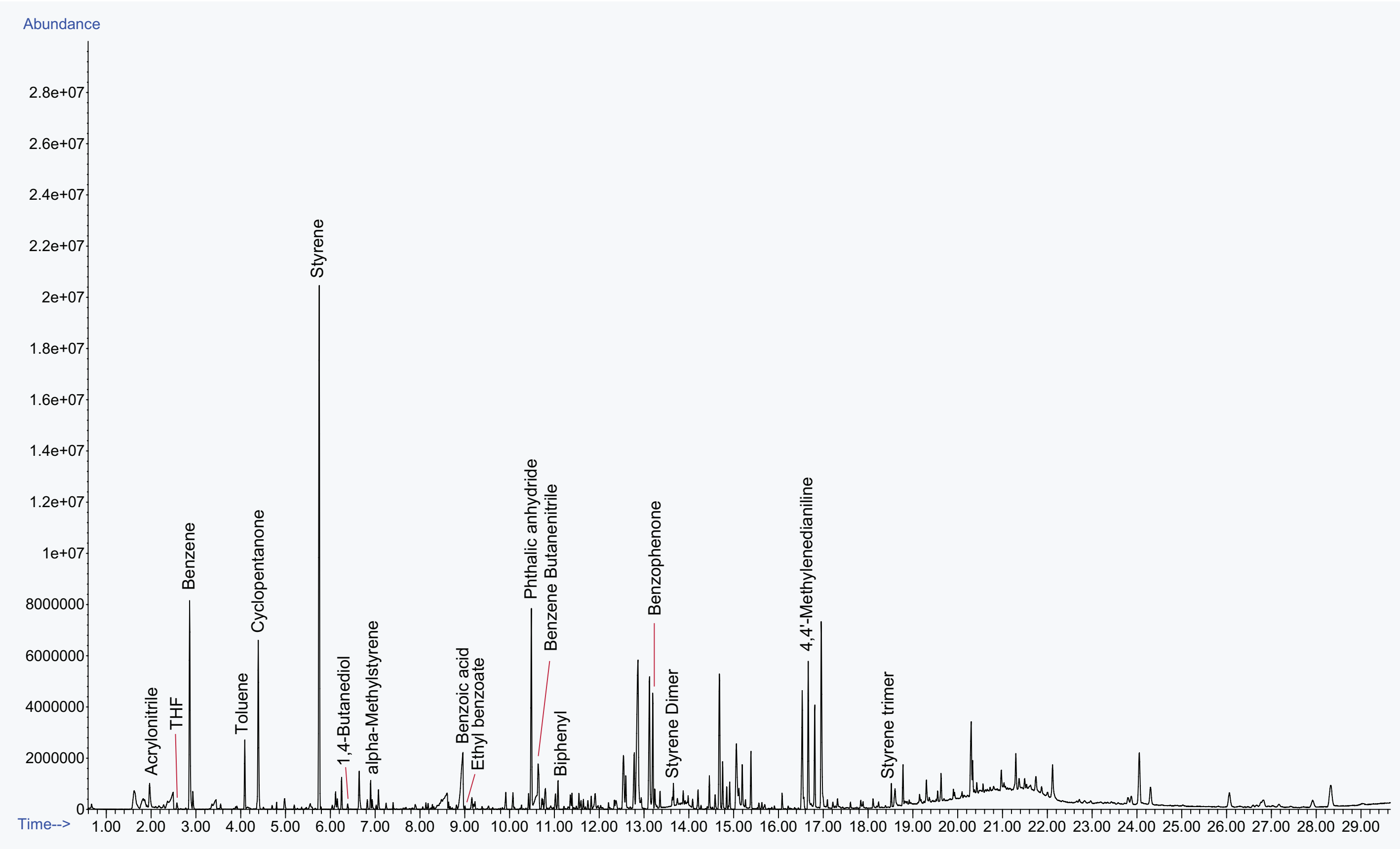

Figure 6: Total ion chromatogram for pyrolysis of phone case.

Conclusion

This study used Smart Ramped Pyrolysis to produce an optimized pyrogram without needing method development for unknown leather and leather-like samples. Several polymer types were identified in the leather-like samples. Using pyrolysis, it was easy to distinguish between leather and non-leather samples.

The GERSTEL Pyrolysis system enables highly flexible and efficient automated pyrolysis of solids and liquids up to 1000 °C combined with thermal decomposition products using GC-MS. It provides an excellent tool for analyzing polymers and polymer additives.