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Identification of Plastics Used for Disc Golf Discs using Pyrolysis Gas Chromatography-Mass Spectrometry

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Abstract
Disc golf, otherwise known as frisbee golf, has become increasingly popular in the past few years. Invented in the 1960's, it has grown to over 7000 courses in the United States and is played in over 40 countries worldwide. It is played in a manner similar to conventional golf. A disc is thrown from a tee pad at a target. The target is a metal pole in the ground with a cylindrical basket and chains. The chains are present to deflect the disc into the basket.

Discs are 21-30 cm in diameter and weigh no more than 200 g. They vary in the shape of the edge and width of the rim depending on the type of disc; driver, mid-range or putter. There are many manufacturers of disc golf discs and they use a variety of plastics to alter feel (grip), durability, glow-in-the-dark, and floatability of the disc. The same disc mold can be available in different plastics, with one manufacturer listing over ten types of plastics for their discs. The discs are made using injection molding or 3D printing.

Pyrolysis GC-MS is a useful tool for identifying polymers. This study will show how the GERSTEL pyrolysis system and gas chromatography-mass spectrometry can quickly determine a wide range of plastic types with minimal method development. Disc golf discs were analyzed since they provide examples of many plastic formulations.

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 disc golf discs 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 greatly reduces method development time.

Experimental

Instrumentation

GERSTEL PYRO Core system on Agilent 8890 GC/5977B Inert Plus MSD

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 disc golf discs. An X-acto knife was used to remove a small sample from the discs. Twelve discs were sampled from 11 different manufacturers.

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.

Results and Discussion

Figure 1 shows a picture of the instrument used in this study.

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

GERSTEL AppNote 278

Figure 2 shows the total ion chromatogram (TIC) for the pyrolysis of one of the disc samples. The polymer is clearly a polyester based on the terephthalic acid and substituted terephthalate peaks. The lack of a peak for 1,4-butadiene rules out that the polymer is polybutylene terephthalate. It is possibly, a copolymer of polybutylene terephthalate and polybutylene glycol terephthalate or polytetramethylene ether glycol.

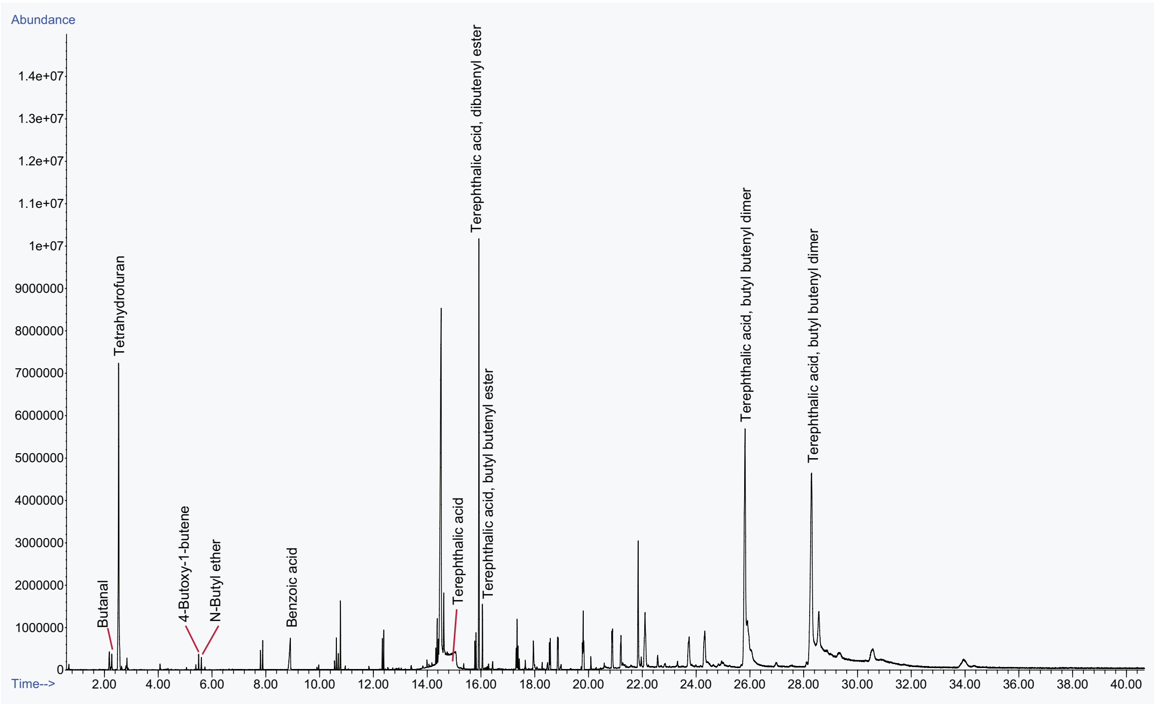

Figure 2: Total ion chromatogram for pyrolysis of a disc sample.

Figure 3 shows a stacked view of three different discs all made from similar copolymers. In all three pyrograms, 2,4-dimethyl-1-heptene is seen which is a marker peak for polypropylene. A pattern of peaks for polypropylene are also seen in the chromatogram. Styrene, alpha-methylstyrene, styrene dimer and styrene trimer appear in all three pyrograms indicating the presence of polystyrene in all three discs. The bottom chromatogram shows a peak for 4-vinylcyclohexene which is a marker compound for butyl rubber. The disc sampled for this pyrogram has a "grippier" feel which may be due to butyl rubber in the disc. The center pyrogram has a peak for benzoguanamine, which is used as a crosslinker. The top chromatogram has a large peak for 2-propenylbenzene which may be a third monomer used in the plastic for this disc.

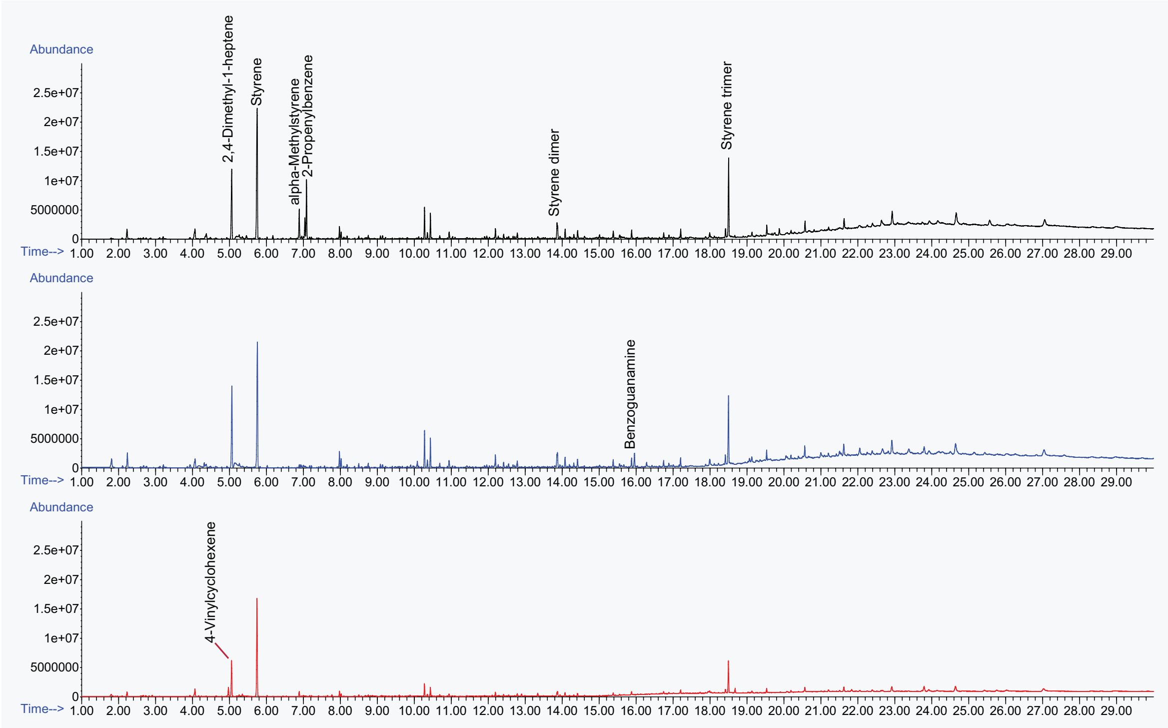

Figure 3: Stacked view of three total ion chromatogram for pyrolysis of three disc samples containing polystyrene/polypropylene.

Figure 4 shows the total ion chromatogram (TIC) for the pyrolysis of another disc sample. Marker peaks for polyurethane; tetrahydrofuran and 1,4-butanediol, are present in the chromatogram. The diisocyanate is methylene 4,4'-diisocyanate (MDI). Tinuvin 234, a UV stabilizer, was found at retention time 25.6 min. The diols used is most likely a combination of 1,4-butanediol and tetramethylene ether glycol (polytetrahydrofuran) or polybutylene glycol.

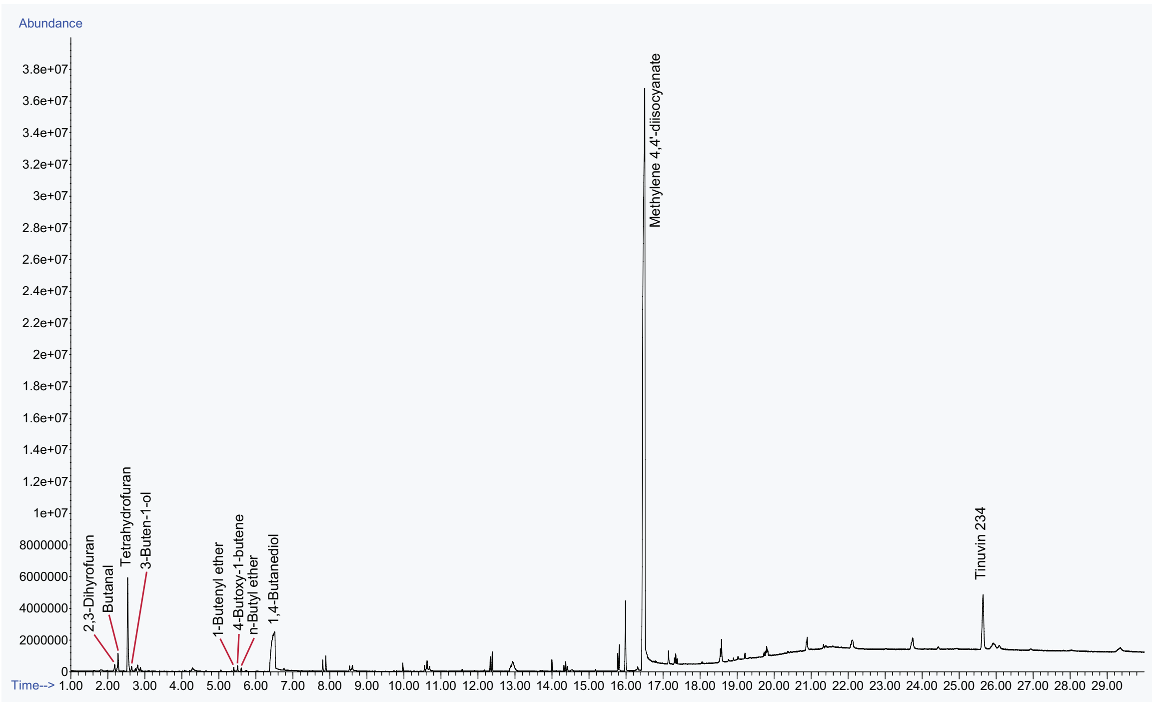

Figure 4: Total ion chromatogram for pyrolysis of a disc sample containing polyurethane.

GERSTEL AppNote 278

Figure 5 shows a stacked view for extracted ion chromatograms (m/z = 129) for the polyester shown in Figure 2 (bottom) and the polyurethane in Figure 4 (top). The two EICs are very similar indicating that the same polyol was used in the polyester and polyurethane samples.

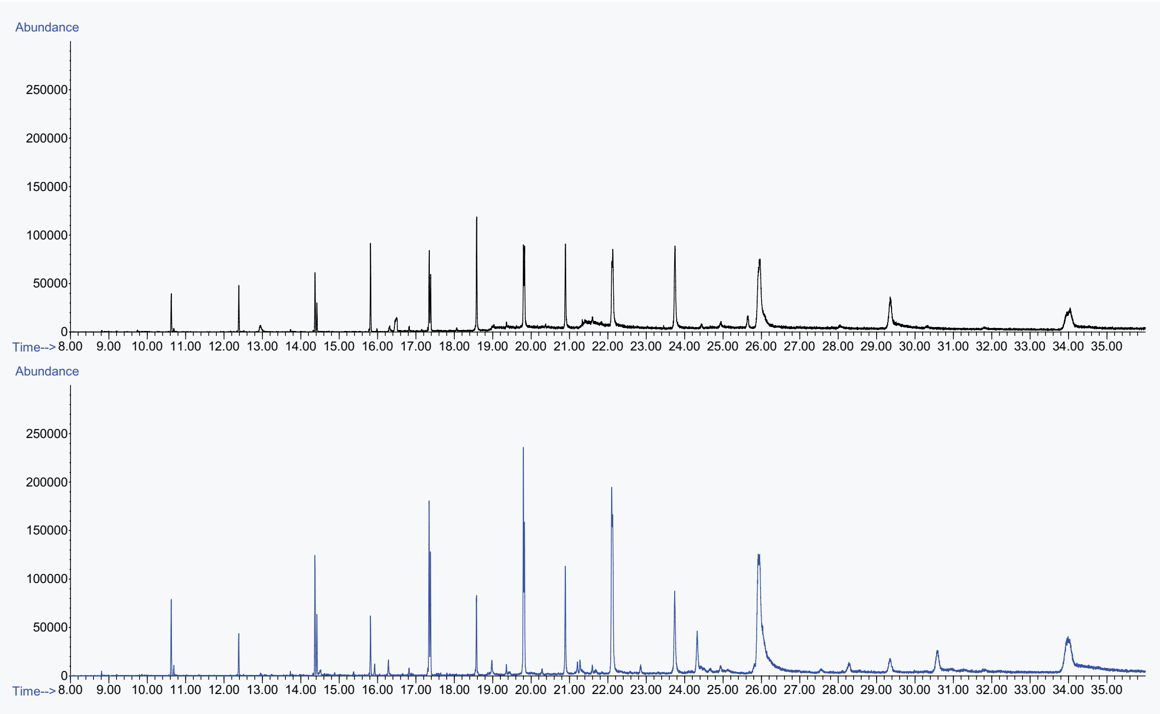

Figure 5: Extracted ion chromatograms (m/z=129) for the polyurethane sample (top) and polyester sample (bottom).

Figure 6 shows a stacked view of the total ion chromatograms (TIC) for two discs from the same manufacturer. The top chromatogram is a low cost disc which are, typically, not as durable as higher end discs. The resulting pyrogram shows a classical pattern for polyethylene. Polyethylene is the most widely produced plastic in the world making it a cheaper alternative to other types of plastics. The lower pyrogram of a higher end disc from the same manufacturer shows that it is made from polyurethane. MDI was used as the diisocyanate. Cyclopentanone is indicative of an adipate polyol and 1,4-butanediol is also present.

GERSTEL AppNote 278

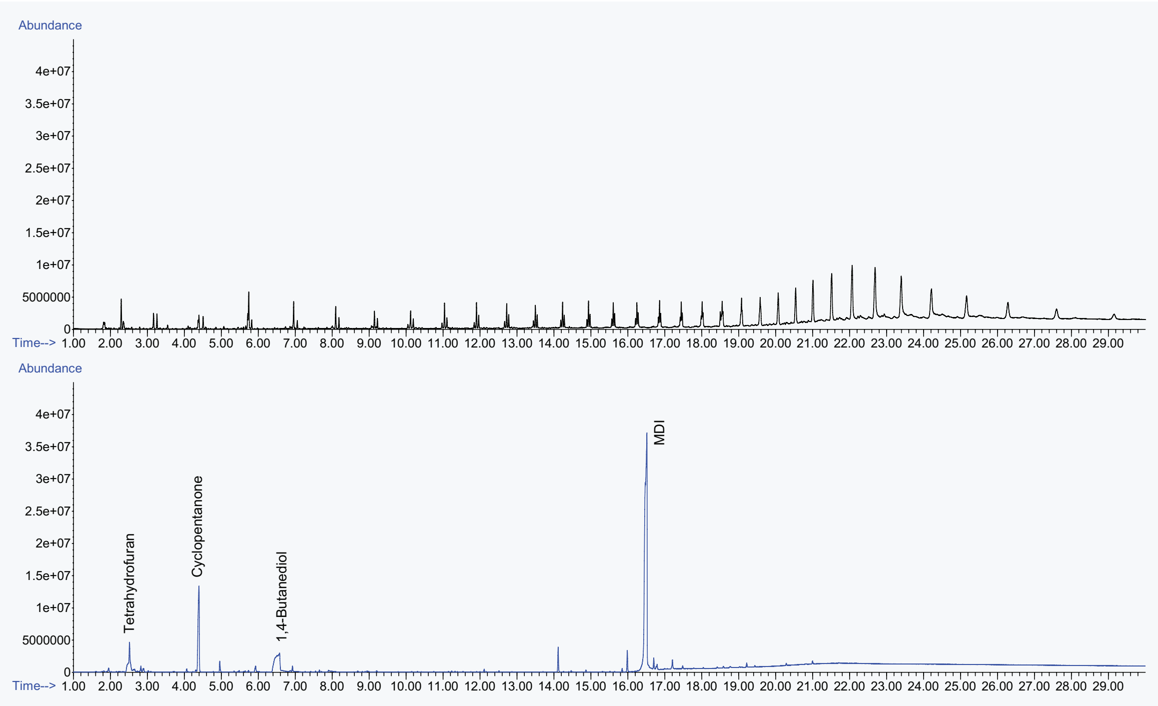

Figure 6: Stacked view of total ion chromatograms for pyrolysis of two discs from the same manufacturer.

In all, twelve discs were analyzed. Five discs were made from polyurethane, five were made from a polypropylene/polystyrene copolymer, one was made from polyester and another from polyethylene.

Conclusion

In this study, Smart Ramped Pyrolysis was used to produce an optimized pyrogram without needing method development for unknown plastics used to make disc golf discs. Several polymer types were identified in the discs including polyester, polystyrene, polyethylene, polypropylene, and polyurethane. Polymer additives, such as UV stabilizers and crosslinkers, can also be identified using pyrolysis GC/MS.

The GERSTEL PYRO Core 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.