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Pyrolysis of Compostable and Biodegradable Materials

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Abstract
Compostable products have gained popularity due to their green environmental claims. However, most of these materials are not strictly plant-based nor are they disposed of at the proper industrial composting sites. In this study, the GERSTEL PYRO Core system enables efficient automation of the thermal extraction and pyrolysis of three compostable and/or biodegradable materials and two natural sources.

Introduction
Plastic waste production is a pressing global concern, with the USA leading in per capita plastic waste generation. In 2023 alone, the USA generated an alarming 42 million tons of plastic waste, equating to approximately 130 kg per person [1]. Addressing this issue requires a shift towards using compostable and biodegradable products crafted from plant-based materials. However, most use "compostable" and "biodegradable" as interchangeable terms when they are not. While biodegradability signifies natural breakdown, the time required can vary. On the other hand, compostable materials decompose under specific conditions within defined timeframes, ensuring a more sustainable end-of-life cycle.

Despite many retail stores promoting items labeled as "compostable," a significant portion of these single-use products ends up in landfills or incinerators, where the necessary conditions for composting are absent. Additionally, the marketing claims that the products are made from plant-based materials such as starch, wood, or polylactic acid are not always accurate, and specific product composition is often not disclosed on the packaging [2]. Furthermore, to make plant-based materials structurally sound, they must undergo chemical modifications to increase their stability and structure in the final product. For instance, starches can be cross-linked, pyro-converted, and acetylated to name a few [3]. While these products are designed to safely decompose in industrial composters, their presence in landfills and incinerators can be just as detrimental as conventional plastics [4]. This means that compostable plastics will persist in the environment as microplastics, causing health concerns for animals and humans. Therefore, marketing claims surrounding biodegradable and compostable materials as plant-based or renewable may be deceiving to the average consumer.

The GERSTEL PYRO Core system operates in various pyrolysis modes, ensuring uniform sample heating and unparalleled reproducibility. Integrated with the CIS 4 inlet, the system allows cryofocusing of analytes or serves as a hot split interface for direct transfer to the analytical column. The GERSTEL PYRO Core autosampler adds another layer of efficiency, enabling complete automation of the analysis. In this study, smart ramped pyrolysis (SRP) was employed to analyze fragmentation patterns of a russet potato, wood, a compostable straw, fork, and sandwich bag to provide insight on natural or synthetic composition and potential chemical modifications. SRP mode eliminates the need for pyrolysis temperature optimization thus greatly shortening the time needed to obtain results, especially when determining unknown constituents.

Experimental

Instrumentation

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

Analysis Conditions PYRO CORE System

Lead time	0.00 min
Follow-up time	0.25 min
Initial time	0.00 min
Temperature	300 °C (0 min), 5.0 °C /s to 800 °C (0 min)
PYRO Body	Splitless 40 °C (0 min), 300 °C/min to 300 °C (2.17 min)
CIS 4	Split 30:1 -120 °C (0 min); 12 °C/s; 325 °C (5 min)

Analysis Conditions Agilent 8890 GC

Column	30 m Rxi-5Sil MS (Restek) 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 min), 10 °C /min to 325 °C (7 min)

Analysis Conditions Agilent 5977C Inert Plus MSD

Full Scan	25 – 550 amu

Sample Preparation

Samples include a russet potato, a wooden stick, a compostable straw, fork, and sandwich bag. All samples were purchased online, from a local grocery store, or obtained outside.

A razor knife was used to slice small pieces of each sample. The samples were placed into conditioned, open-ended quartz pyrolysis tubes with quartz wool. The quartz tubes were connected to pyrolysis transport adapters and placed into individually sealed sample positions in a 40-position PYRO tray on the MPS robotic.

Results and Discussion

A russet potato and wooden stick were chosen for this analysis as they are made from starch, lignin, and cellulose, which are some of the building blocks to compostable and biodegradable materials. The resulting pyrograms of the potato and wood provided insight on their natural decomposition profiles. By comparing the natural material to a compostable or biodegradable product, variations in thermal decomposition were compared.

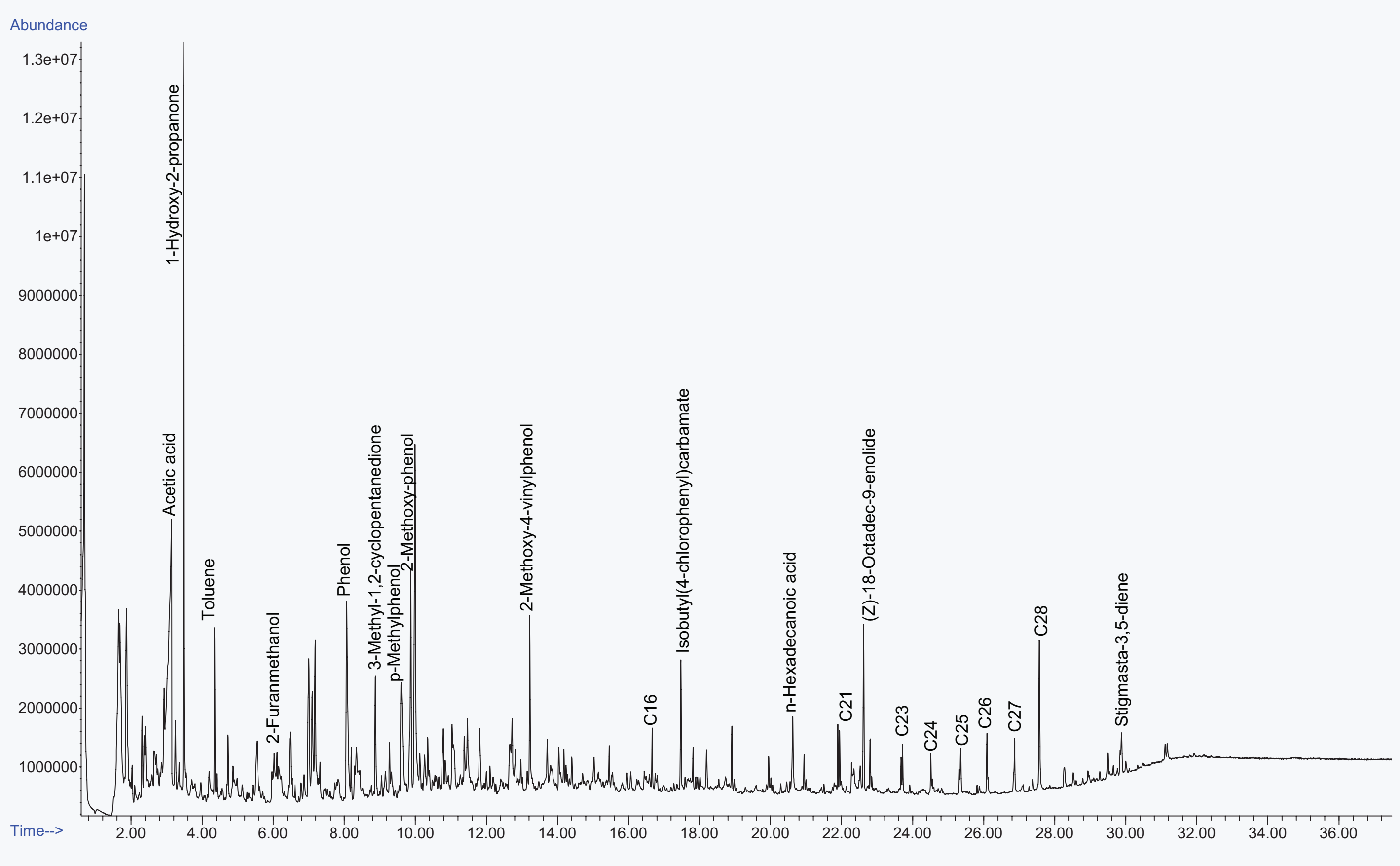

Figure 1: Pyrogram of a russet potato.

Figure 1 shows the pyrogram of a russet potato. The compounds in the pyrogram include 2-furanmethanol, phenol, p-methylphenol, 2-methoxy-phenol, 2-methoxy-4-vinylphenol, hydrocarbons, and acids. Phenolic compounds are typically more concentrated in potato skins to protect the plant from bacteria and serve as a natural insecticide. The presence of long chain hydrocarbons is likely due to the pyrolysis of fatty acids found in the potato. Potato starch is comprised of numerous glucose monosaccharides, and when the starch pyrolyzes, furans, cyclopentanediones, and phenols will form as shown in the resulting pyrogram. Moreover, the latter compounds are indicative of decomposition products from the natural organic polymer.

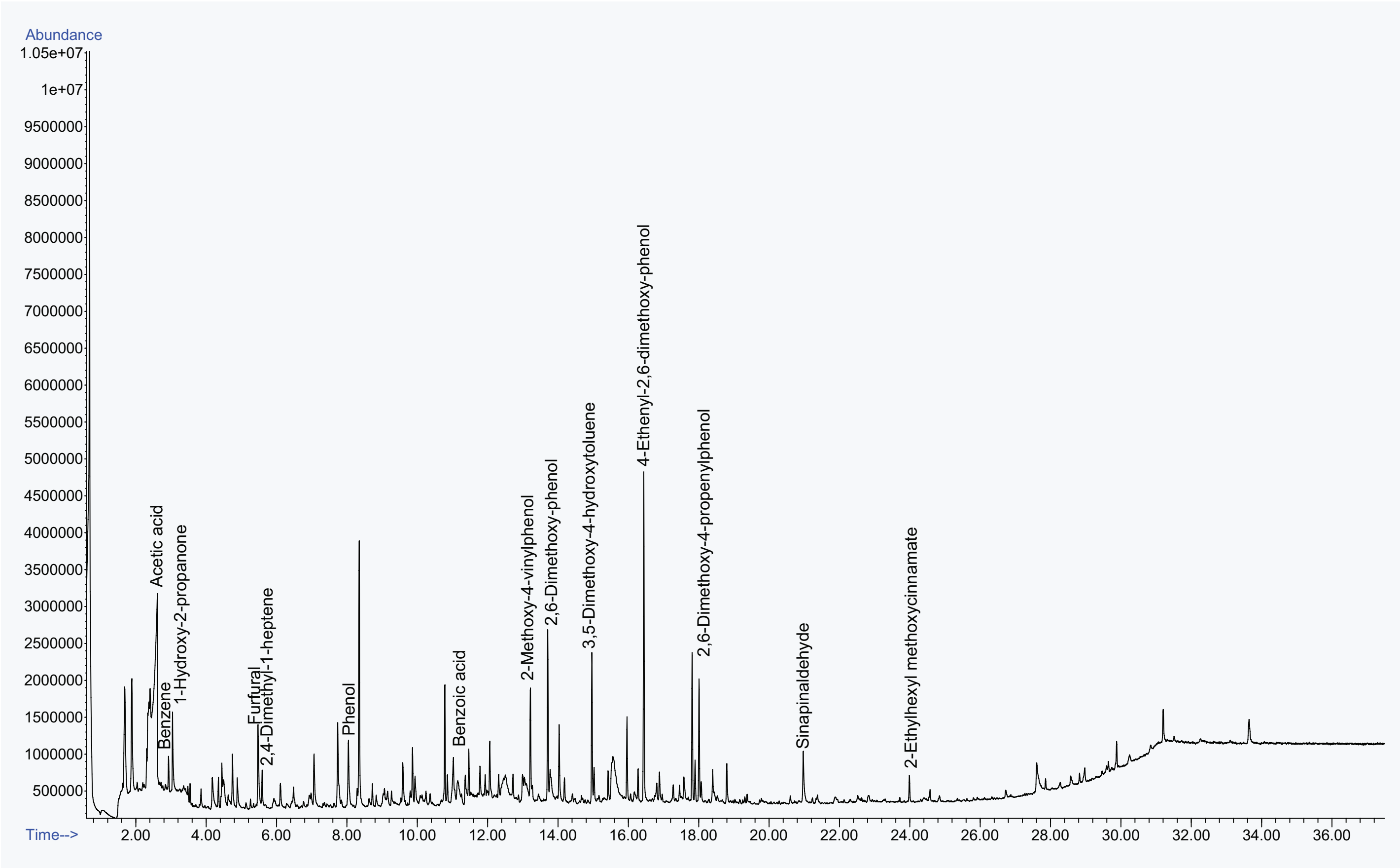

Figure 2: Pyrogram of a wooden stick.

Figure 2 shows the pyrogram of a wooden stick. The compounds in the pyrogram include acetic acid, benzene, 1-hydroxy-2-propanone, furfural, phenols, sinapaldehyde, and 2-ethylhexyl methoxycinnamate. 1-Hydroxy-2-pronanol and furfural are a product of cellulose pyrolysis, and the phenols are a product of lignin pyrolysis. Other compounds like carbon dioxide, water, and acetic acid all likely off-gassed at the lowest temperature of the smart ramped pyrolysis process. Additionally, sinapaldehyde and 2-ethylhexyl methoxycinnamate are intermediate compounds that form lignol, which is a lignin precursor [3,7].

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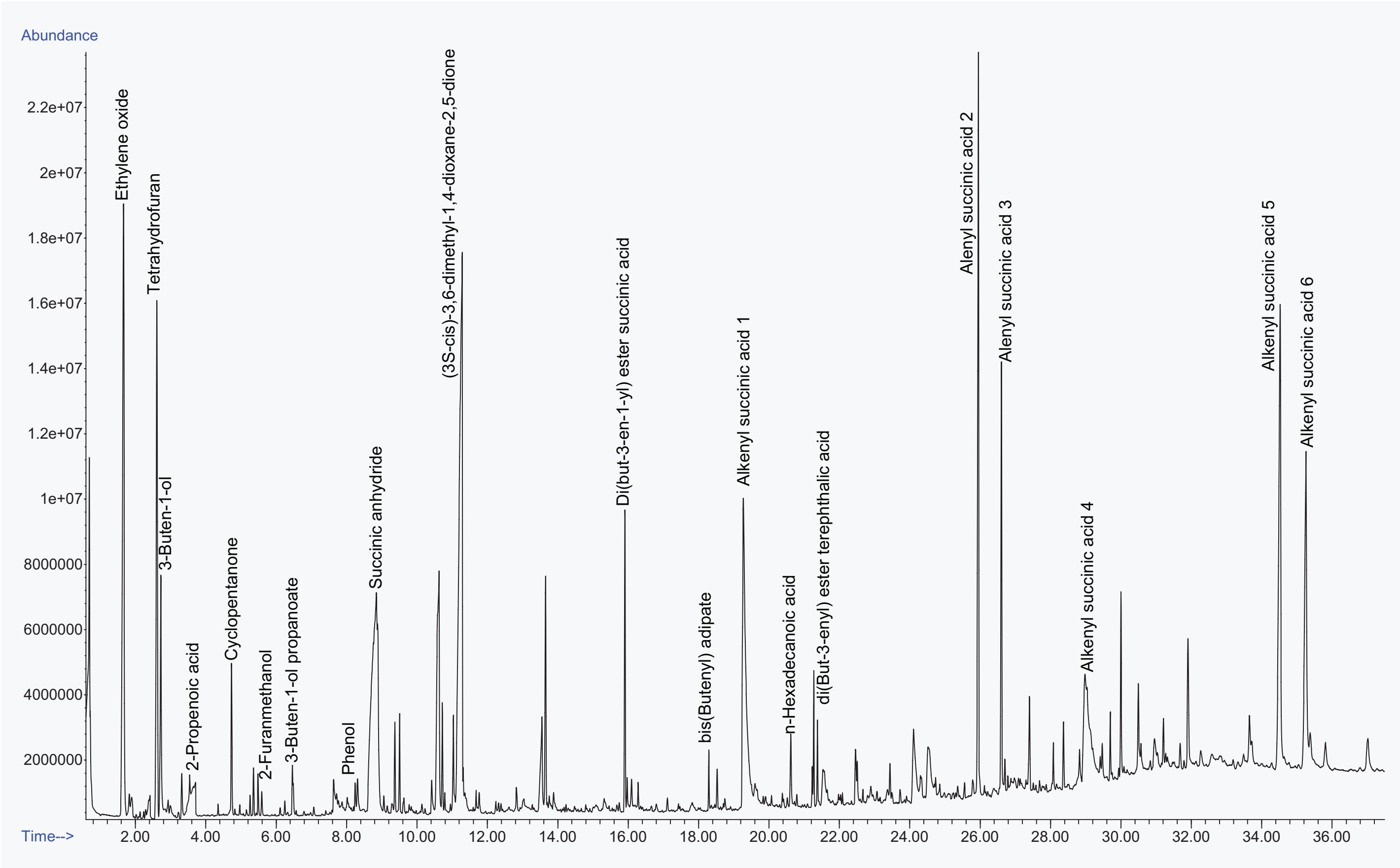

Figure 3: Pyrogram of a compostable straw.

Figure 3 shows the pyrogram of a compostable straw. The packaging advertised the straws as "100% compostable". Several compounds were identified including tetrahydrofuran, 2-furanmethanol, phenol, succinic anhydride, and alkenyl succinic acid derivatives. The identification of tetrahydrofuran, 2-furanmethanol, and phenol also indicates that the straw was formulated with a plant starch and/or cellulose, as seen with the russet potato and wood examples. Succinic anhydride and alkenyl succinic acid are commonly used as sizing agents to aid in hydrophobicity and are known starch modifiers in food and pharmaceutical applications [3,6].

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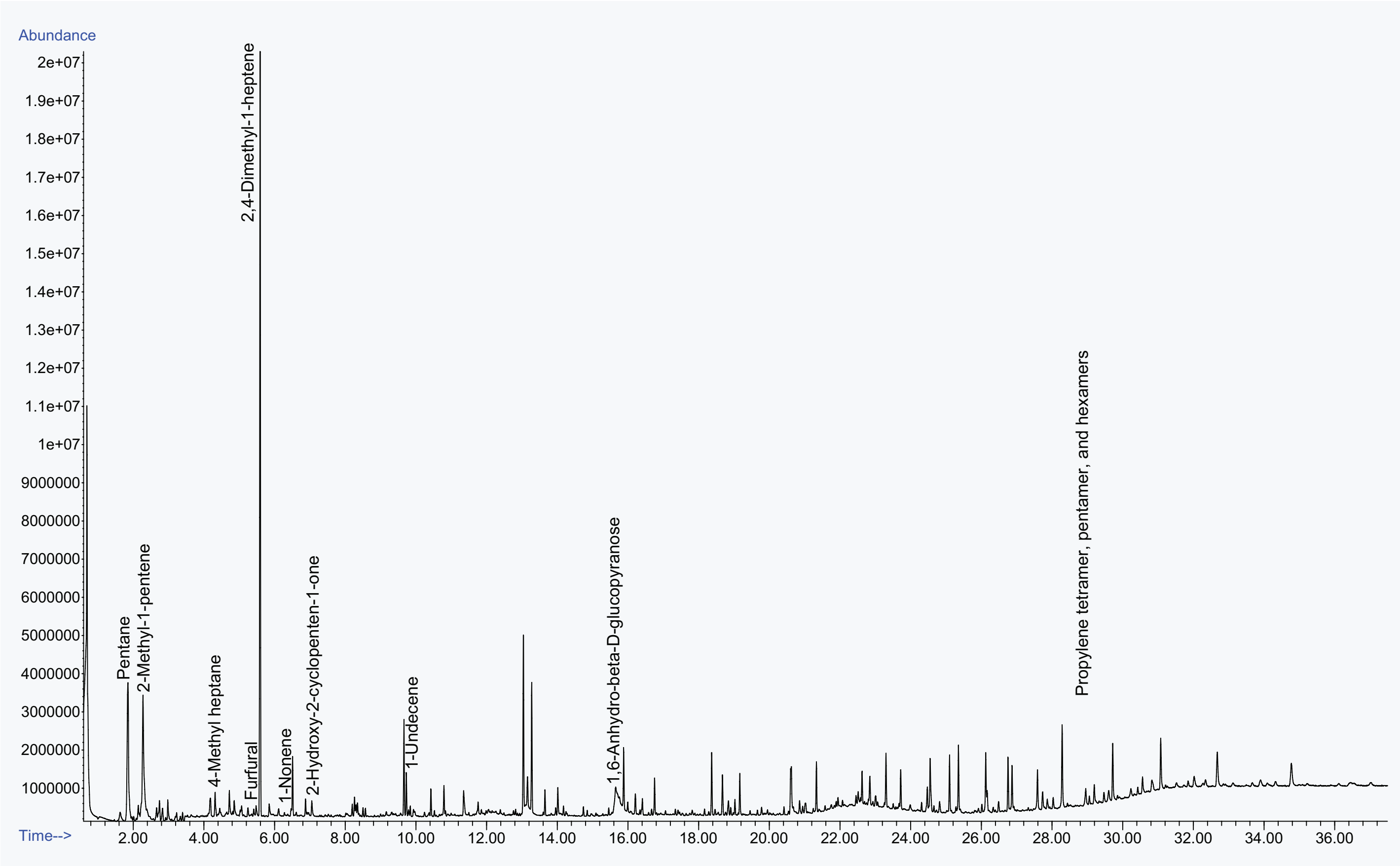

Figure 4: Pyrogram of a compostable fork.

Figure 4 shows the pyrogram of a compostable fork. The packaging advertised the forks as "cornstarch-based" and "made from 70% renewable materials". The compounds identified in the pyrogram included several alkanes, alkenes, furfural, 1,6-anhydro-beta-D-glucopyranose, and propylene decomposition products. Although polypropylene is considered a synthetic polymer, sources have indicated that changing its carbonyl groups will shorten the time it needs to decompose thus making it a biodegradable plastic [5,6]. 2,4-Dimethyl-1-heptene, 2-methyl-1-pentene, and 1-undecene are a few of the main polypropylene decomposition products. However, other compounds known to be derived from a natural source, like furfural and 1,6-anhydro-beta-d-glucopyranose, were identified as well.

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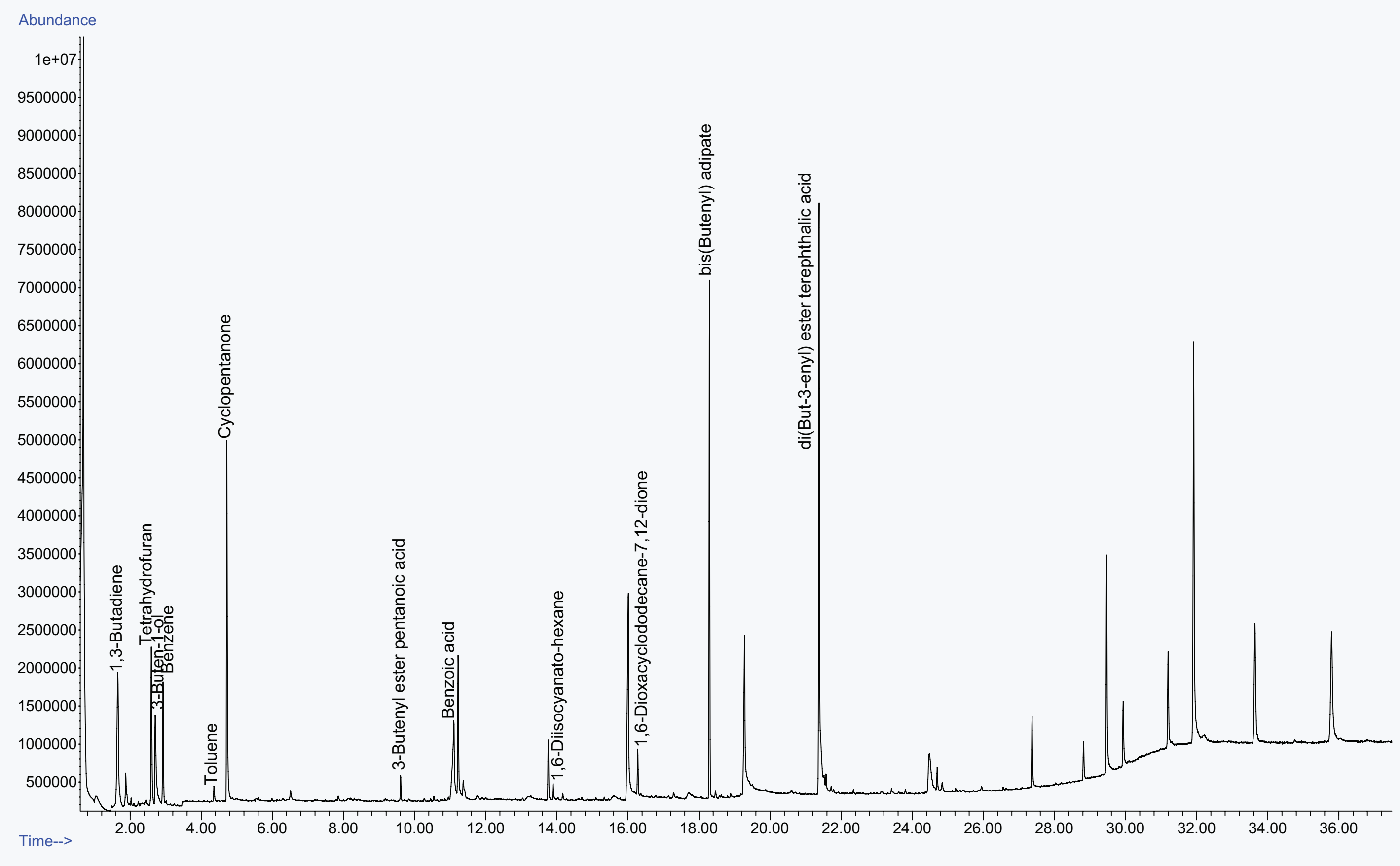

Figure 5: Pyrogram of a compostable sandwich bag.

Figure 5 shows the pyrogram of a compostable sandwich bag. The packaging advertised the bags as "plant-based" and "compostable after use" with no indication of the plant source. The compounds identified in the pyrogram included 1,3-butadiene, tetrahydrofuran, 3-buten-1-ol, benzene, and a few acid esters. Many of these compounds are predetermined decomposition products of lignins and plant cellulose. Terephthalic acid esters, pentanoic acid esters, and bis(butenyl) adipate are likely degradation products of the copolymer polybutylene adipate terephthalate (PBAT). PBAT, also known as the brand name ecoflex®, is known as the first biodegradable and certified compostable plastic and is an alternative to polyethylene [7]. This confirms that not all compostable and biodegradable materials are made entirely from plant-based sources, rather some synthetic materials can be modified to be compostable under certain conditions.

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Conclusion

The GERSTEL PYRO Core system in combination with GC-MS can be used for the determination of organic polymer composition. It provides insight into whether natural or synthetic materials were used and the chemical modifications that took place to produce a final compostable product. Although a product may be marketed as compostable or biodegradable, it does not reveal its true composition. Pyrolysis is an important instrumental technique for unknown polymers analysis, especially when a product's constituents are not specified. Additionally, SRP mode can be conveniently used to simplify method development when such compositions are unknown.

References

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