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Pyrolysis GC-MS: Identification of Plastics in Toys

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Keywords

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Abstract

Plastics have become a major source of pollution due to their ubiquitous use in a wide array of products. Most plastics are not readily biodegradable and can wind up as litter or are simply disposed of in landfills. It is estimated that only 9% of the plastic in the US is recycled [1]. Plastics discarded into the environment can be ingested by animals, break down into smaller particles which can also be ingested, or leach other compounds into the environment which can potentially cause damage. Leachates can include plasticizers, flame retardants, blowing agents, UV stabilizers, dyes and a host of other compounds added to the polymers.

Inexpensive plastic toys are readily available at many retailers within the US and are often included in children's meals. Unlike plastic containers, these objects rarely contain a recycle code and are most likely discarded in the trash and wind up in a landfill.

This work will show the identification of a variety of plastics in toys purchased at a local discount store. The GERSTEL PYRO Core system in combination with gas chromatography mass spectrometry was used for the analysis.

Introduction

The GERSTEL pyrolizer 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, smart ramped, and fractionated. 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 system has an integrated GERSTEL CIS 4 inlet that can be used to cryofocus analytes in the inlet or be used as a hot split interface for direct transfer to the column. An also integrated GERSTEL MultiPurpose Sampler (MPS) allows for complete automation of the analysis.

This study describes the use of the GERSTEL PYRO Core system for analysis of plastics found in toys from a local discount store.

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Experimental

Instrumentation

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

Analysis Conditions PYRO Core System

PYRO		
	Lead time	0.00 min
	Follow up time	0.50 min
	Initial time	0.00 min
	Temp	300 °C (0 min), 5.0 °C/s to 800 °C (0.0 min)
CIS 4	Split 25:1	
	300 °C isothermal	

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 (1.0 min), 15 °C/min to 320 °C (15 min)

Sample Preparation

Samples included dice, building blocks, hard plastic chips, race track and connectors, and a foam airplane. The plastic packaging associated with the toys was also examined.

Pyrolysis – Approximately one milligram of sample was placed into an open-ended quartz pyrolysis tube 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.

The toy packaging and foam plane were sampled using a 1.2 mm punch (Harris Uni-Core 1.20). The whole punched sample was placed into the quartz pyrolysis tubes.

The race track, building blocks, and race track connector were sampled using a razor knife to slice a small piece of the object. A die was sampled by scraping the edge with a razor. The scrapings were then placed in a quartz pyrolysis tube.

Results and Discussion

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

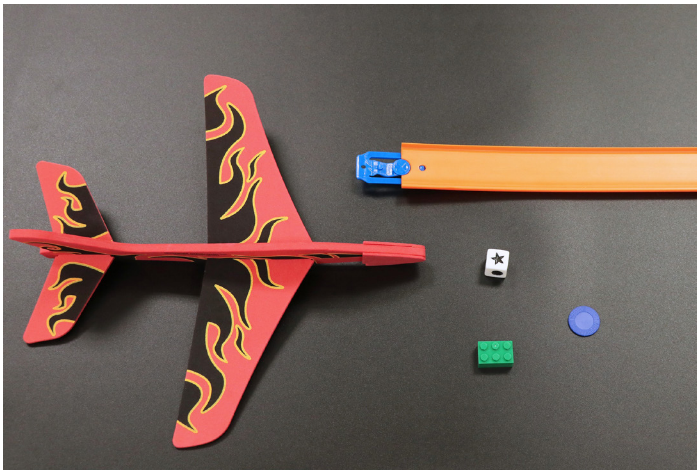

Figure 1: Picture of toys used in this study.

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Figures 2 shows the resulting pyrogram from the analysis of the foam airplane. The pattern shows that the airplane is made from polyethylene.

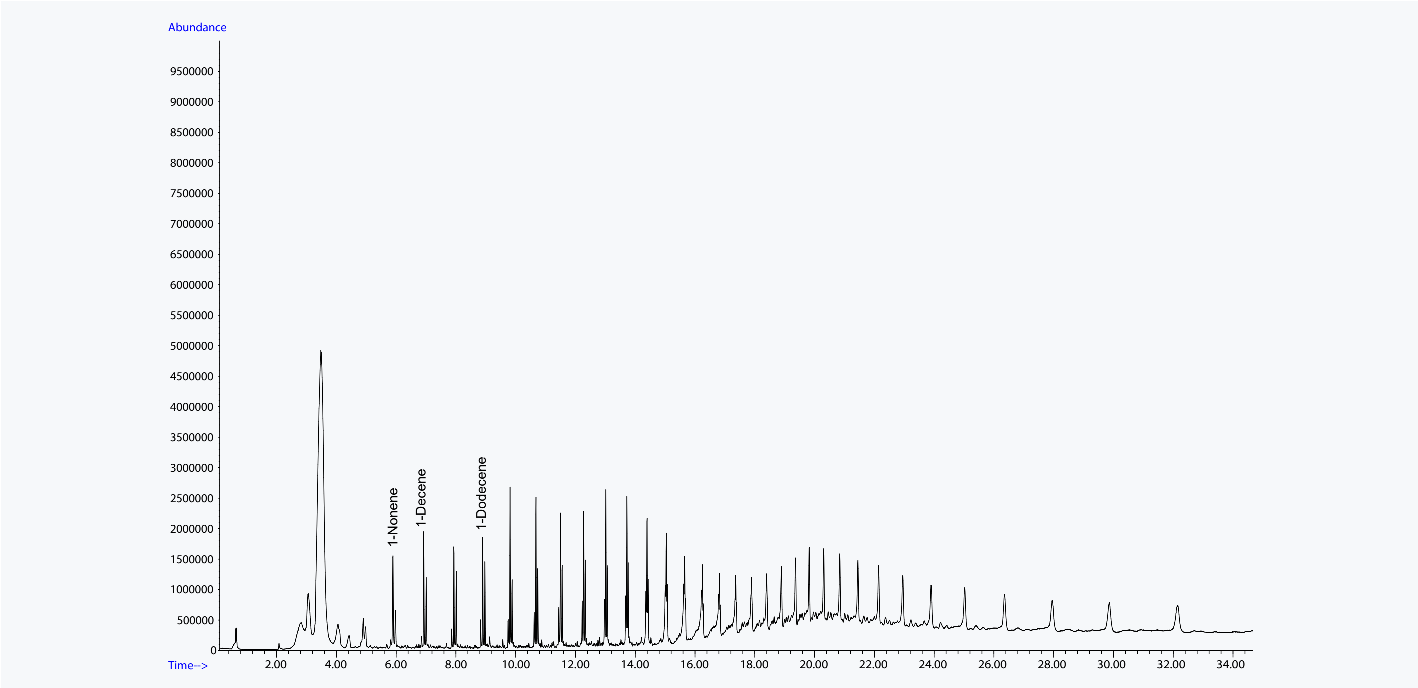

Figure 2: Pyrogram of foam airplane material.

Figure 3 shows a stacked view of pyrograms from the race track (top) and the race track connector (bottom). The race track pyrogram shows the pattern for a polyethylene, the connector shows a distinctive pattern for polypropylene.

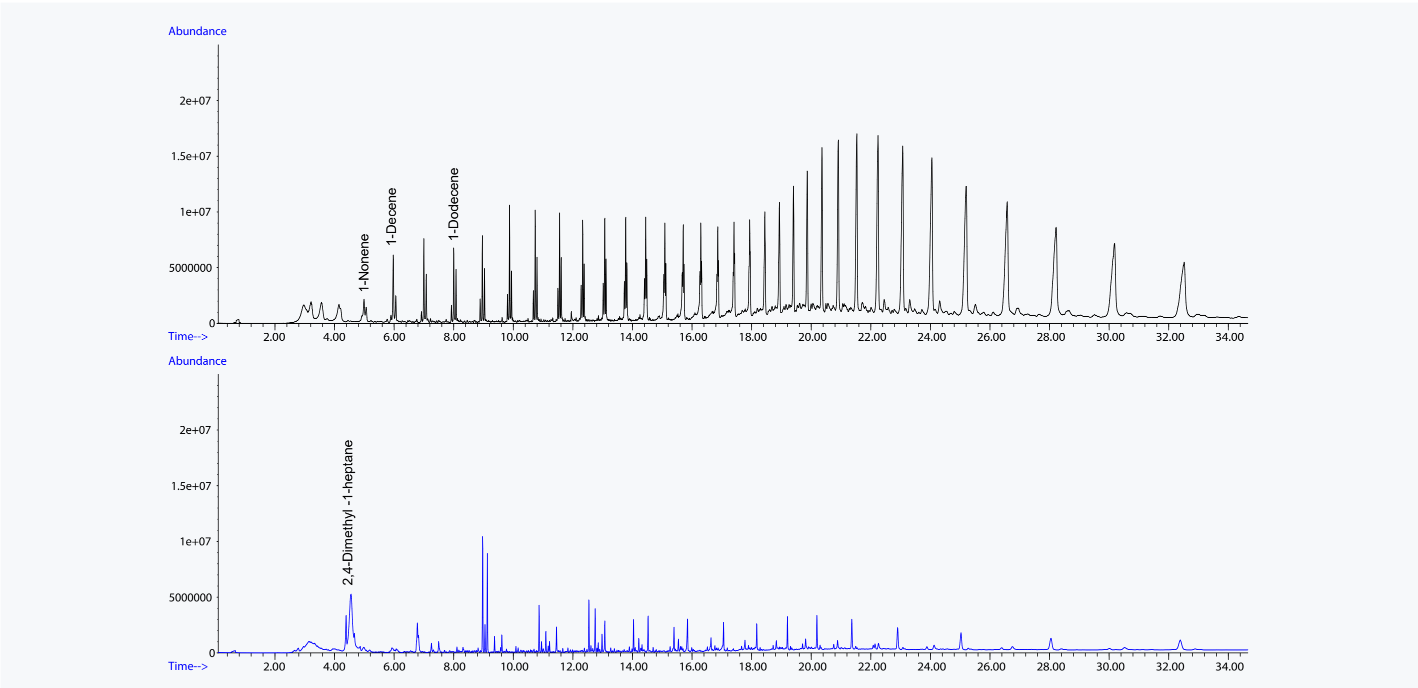

Figure 3: Stacked view of pyrograms of the race track (top) and the race track connector materials (bottom).

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Figure 4 shows a stacked view of the pyrograms from the green building block (top) and the clear packaging for the green building block (bottom). The pyrogram profile for the packaging is clearly polypropylene. The pyrogram from the green building block shows acrylonitrile, styrene, α-methylstyrene, styrene dimer and the styrene trimer. This indicates the building blocks are made from an acrylonitrile/styrene co-polymer. Other peaks in the program are from acrylonitrile/styrene dimers and trimer combinations.

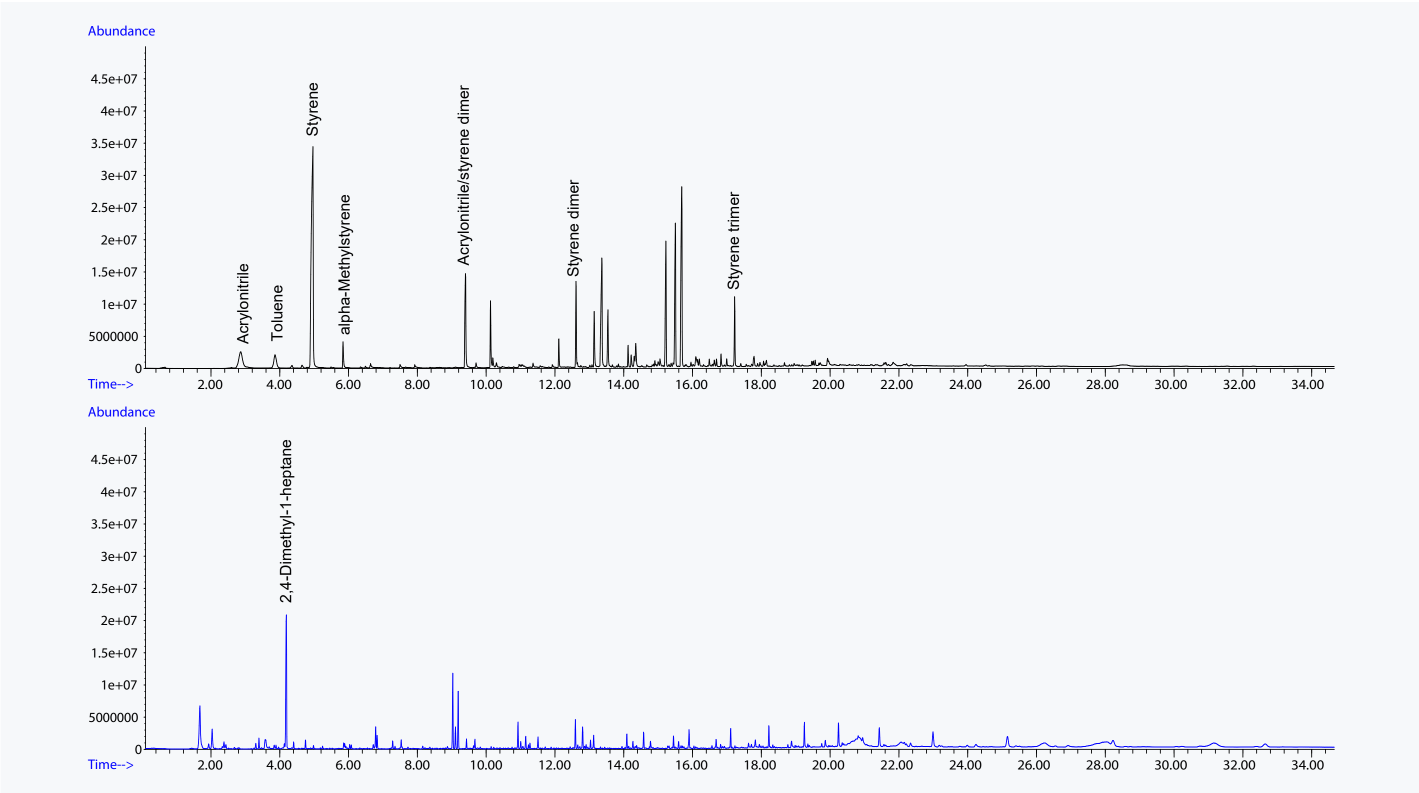

Figure 4: Stacked view of pyrograms of the green building block (top) and green building block packaging materials (bottom).

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Figure 5 shows the resulting pyrogram from the blue chip. The main peaks are styrene, styrene dimer and the styrene trimer indicating the chip is made of polystyrene. This a somewhat surprising result as polystyrene is most often associated with blown cooler associated applications. The CIS was cooled to -120 °C for this pyrogram.

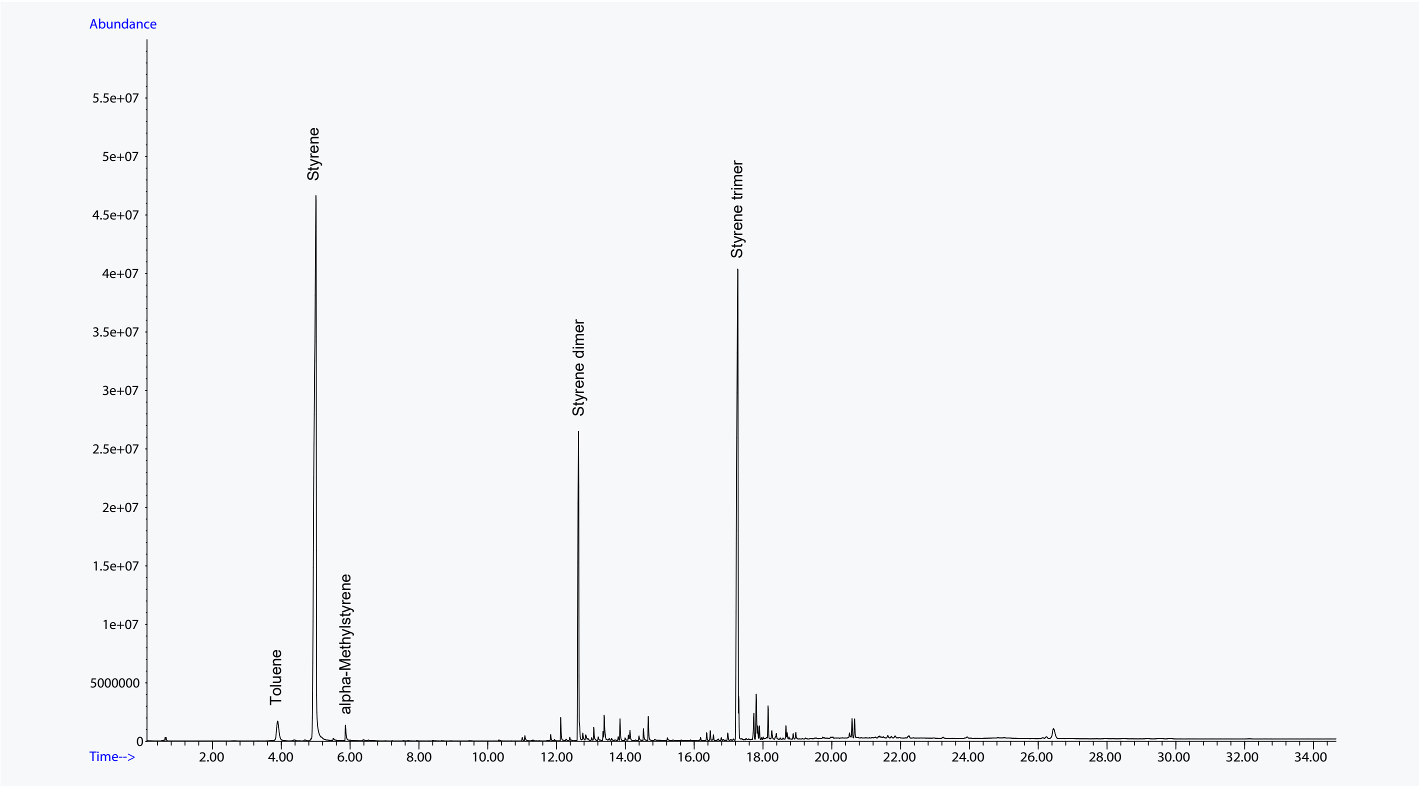

Figure 5: Pyrogram of the blue chip material.

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Figure 6 shows the resulting pyrogram from the die scrapings. Cryocooling the CIS at -120 °C was used for this run to help with resolution of early eluting peaks. Many of the compounds resulting from the pyrolysis of the dice are highly polar and would benefit from separation on a wax phase column. The compounds in the pyrogram include; triazine, urea, methyl urea, N,N-dimethyl urea, N,N-dimethylamine, isocyanatomethane, 2-propenenitrile, as well as other nitrogen containing compounds, and furans. These compounds are indicative of a melamine-urea-formaldehyde (MUF) resin. These resins fall into the category of thermoset plastics which are generally hard, abrasion resistant plastics and would be highly suitable in this application as material for dice.

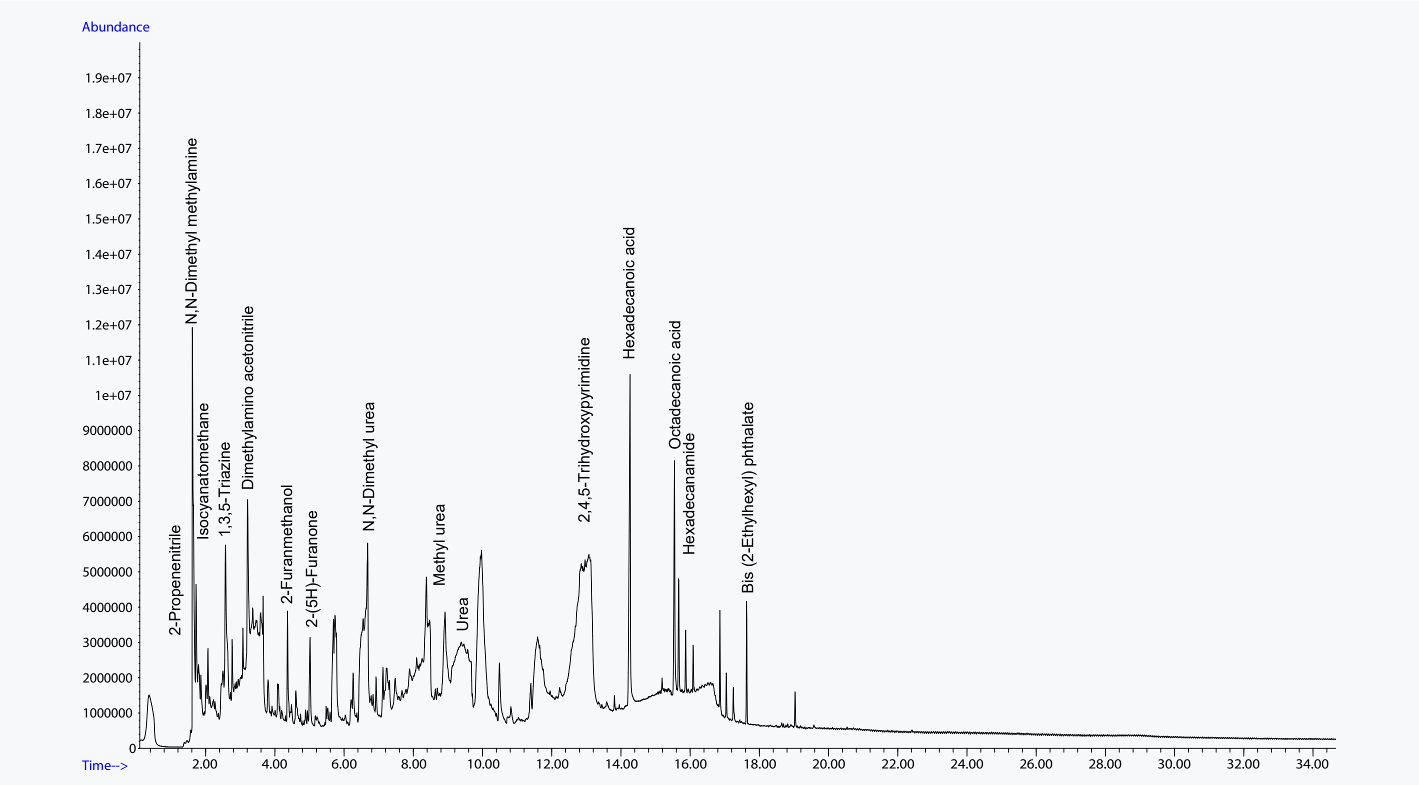

Figure 6: Pyrogram of the die material.

Conclusion

Using the GERSTEL PYRO Core system for pyrolysis of plastic toys from a local discount store showed several types of plastics present including polyethylene, polypropylene, polystyrene, acrylonitrile/styrene, and a melamine-urea-formaldehyde resin. These types of polymers are not easily biodegradable which means if disposed of in a landfill, they will reside in the landfill for a long time potentially leaching other compounds, such as plasticizers into the environment. Biodegradable or non-fossil fuel based polymers, such as polylactic acid, polyhydroxy alkanoate or polyethyl furanoate, are alternatives to conventional plastics, which could be used in the area of plastic toys.

References

[1] *A Whopping 91 Percent of Plastic Isn't Recycled*, https://www.nationalgeographic.org/article/whopping-91-percent-plas