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Characterization of Rubber using Pyrolysis Gas Chromatography-Mass Spectrometry

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Abstract
Rubber is one of the most ubiquitous materials that each of us come into contact with every day. It is used in footwear, tires, sporting goods, on athletic fields, automobiles and in a myriad of other products. Many types of rubber are used in these products such as natural, styrene-butadiene, nitrile, ethylene propylene diene monomer (EPDM) and other polymeric materials.

Pyrolysis GC-MS is a useful tool for identifying polymers. In this study, the GERSTEL pyrolysis system, in combination with gas chromatography-mass spectrometry, was used for the analysis of products containing different types of rubber.

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 rubber containing proucts 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.

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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, 320 °C (10 min)

Sample Preparation

Sample types included various products made of rubber. A razor knife was used to cut a piece from each sample type. The samples, approximately 100 µg, were placed atop a quartz wool plug in an open-ended quartz pyrolysis tube.

Pyrolysis

The quartz tubes were connected to pyrolysis adapters and placed into a 40-position pyrolysis tray. The samples were analyzed using Smart Ramped Pyrolysis.

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.

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Figure 2 shows the total ion chromatogram (TIC) for the pyrolysis of a latex laboratory glove. The marker compounds for natural rubber, isoprene and isoprene dimer, are seen in the pyrogram. Also found are a series of trimers, tetramers, pentamers and higher molecular weight oligomers.

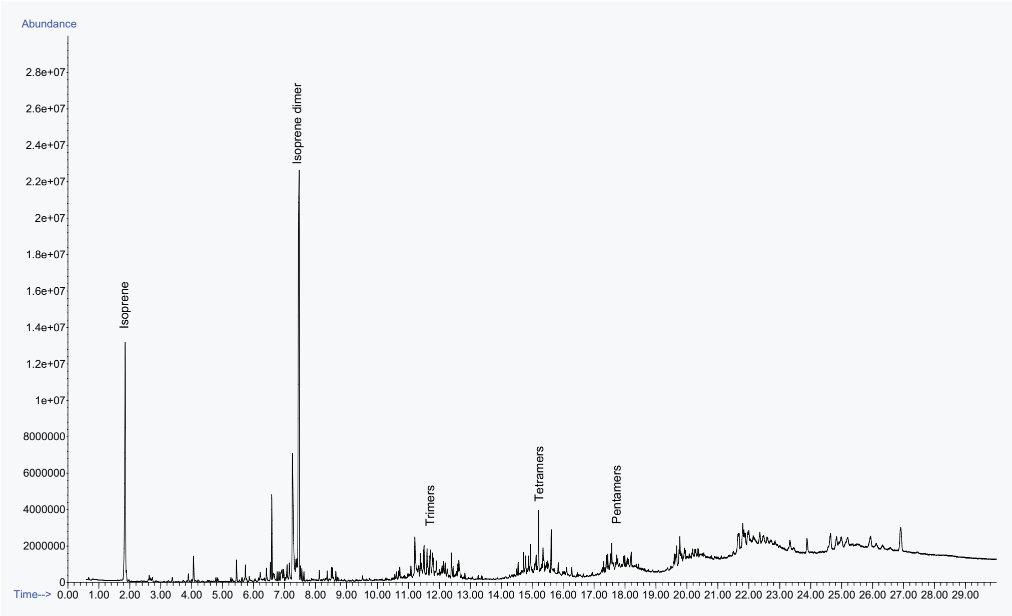

Figure 2: Total ion chromatogram for pyrolysis of a latex laboratory glove.

Figure 3 shows the total ion chromatogram (TIC) for the pyrolysis of a rubber mallet. The marker compounds isoprene and isoprene dimer, are seen in the pyrogram indicating the mallet is made from natural rubber. 2-Mercaptobenzothiazole and its breakdown product benzothiazole are also seen in the pyrogram. 2-Mercaptobenzothiazole is used as a vulcanizer for rubber in order to crosslink the polymer. This adds strength and rigidity to the polymer which is needed for its use in a mallet.

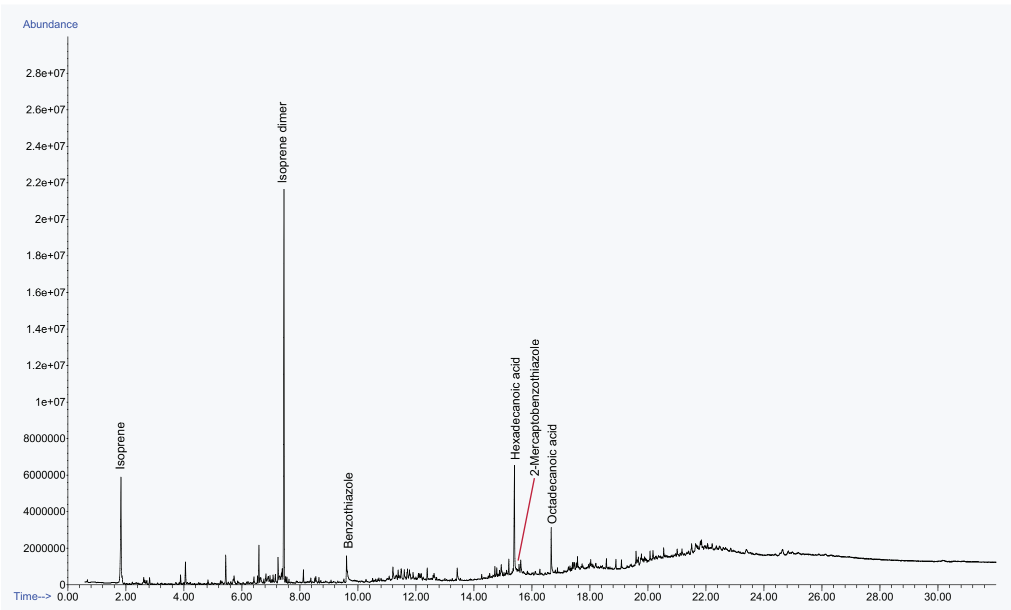

Figure 3: Total ion chromatogram for pyrolysis of a rubber mallet.

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Figure 4 shows the total ion chromatogram (TIC) for the pyrolysis of a rubber eraser. The marker peaks present in the pyrogram include 1,3-butadiene, 4-vinyl cyclohexene, styrene, styrene dimer and styrene trimer indicating the rubber is made from styrene-butadiene.

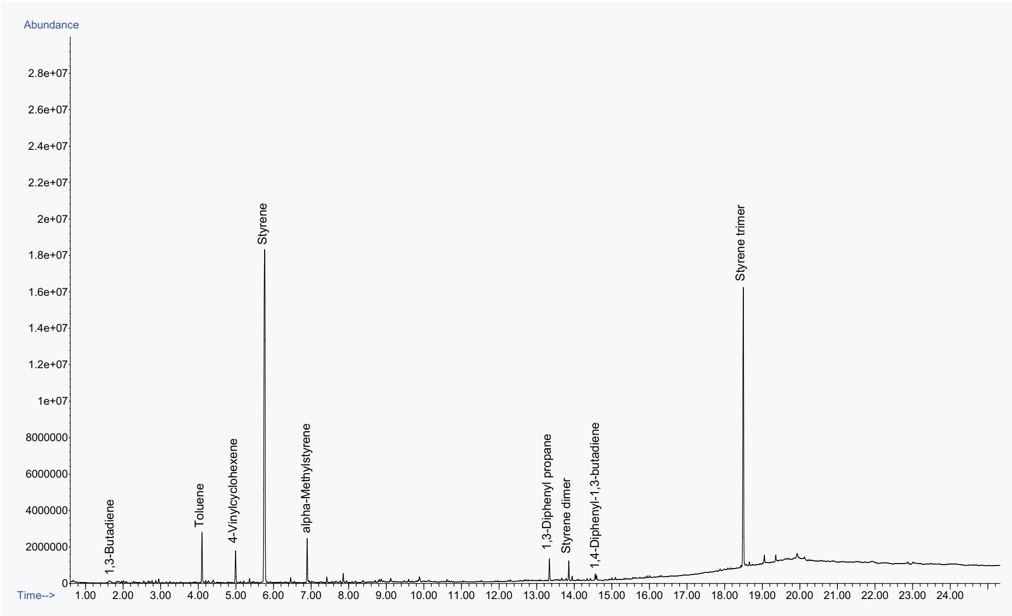

Figure 4: Total ion chromatogram for pyrolysis of a rubber eraser.

Figure 5 shows the total ion chromatogram (TIC) for the pyrolysis of a rubber ball. The marker peaks present in the pyrogram include 1,3-butadiene, 4-vinyl cyclohexene, trimers and tetramers indicating the ball is made from butyl rubber.

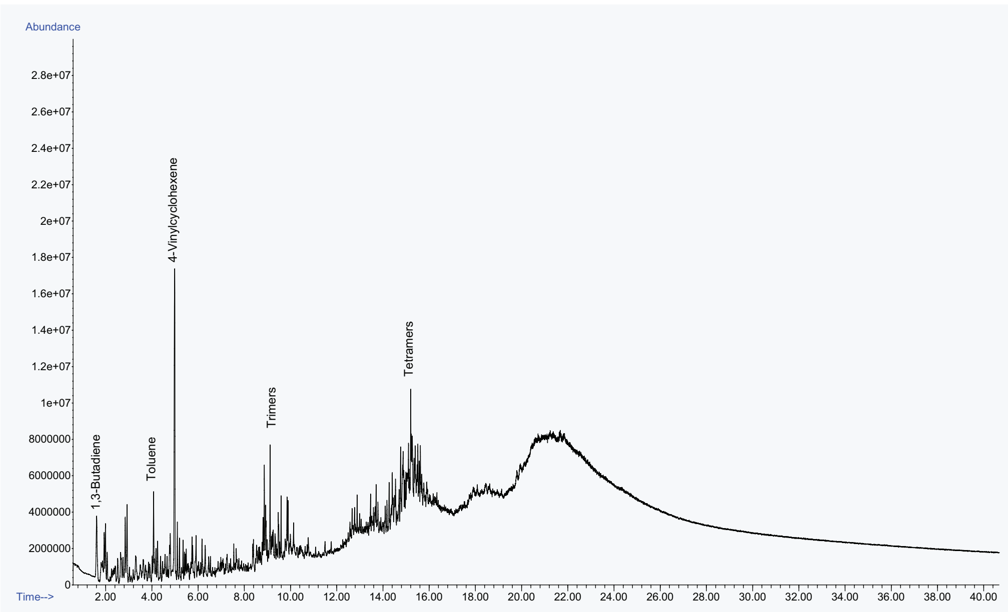

Figure 5: Total ion chromatogram for pyrolysis of a rubber ball.

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Figure 6 shows the total ion chromatogram (TIC) for the pyrolysis of a sample from the sole of a shoe. The marker peaks present in the pyrogram include 1,3-butadiene, isoprene, 4-vinyl cyclohexene, styrene, alpha-methylstyrene, isoprene dimer and styrene trimer. These compounds indicate the shoe bottom is composed of natural and styrene-butadiene rubbers. 2-Mercaptobenzothiazole and benzothiazole are indicative of crosslinking in the rubber. The plasticizer bis (2-ethylhexyl) phthalate is seen in the chromatogram. Three peaks are labeled as Naugard® Q Extra. These peaks arise from this compound, which is added to rubber as an antioxidant [1].

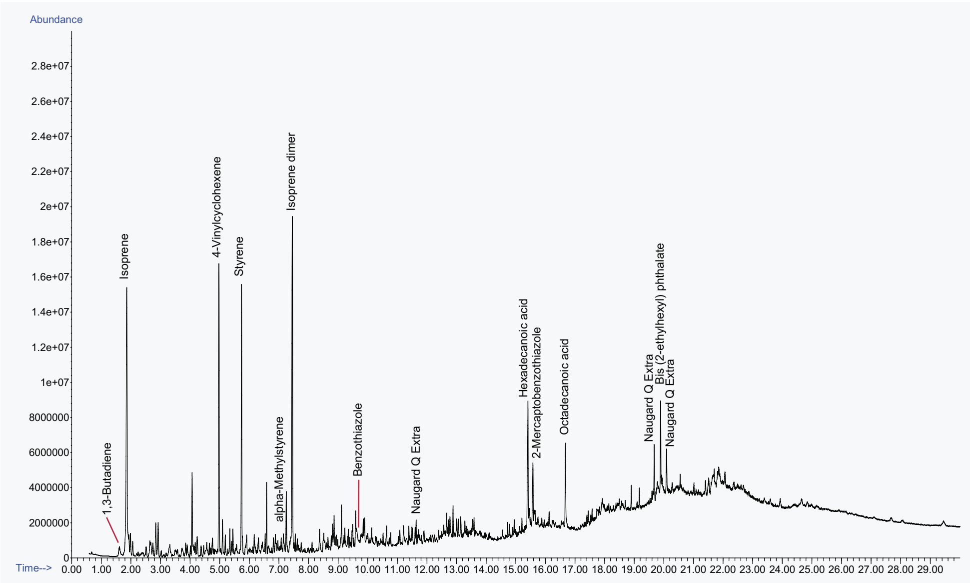

Figure 6: Total ion chromatogram for pyrolysis of sole of a shoe.

Figure 7 shows the total ion chromatogram for a car tire sample. The marker peaks present in the pyrogram include 1,3-butadiene, isoprene, 4-vinyl cyclohexene, styrene, alpha-methylstyrene, isoprene dimer. These compounds indicate the tire is composed of natural and styrene-butadiene rubbers. N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), an anti-aging compound, was identified in the chromatogram. 6PPD reacts with ozone in the air to form 6PPD-quinone. 6-PPD-quinone has been shown to be toxic to fish and has adversely affected salmon populations on the West Coast.

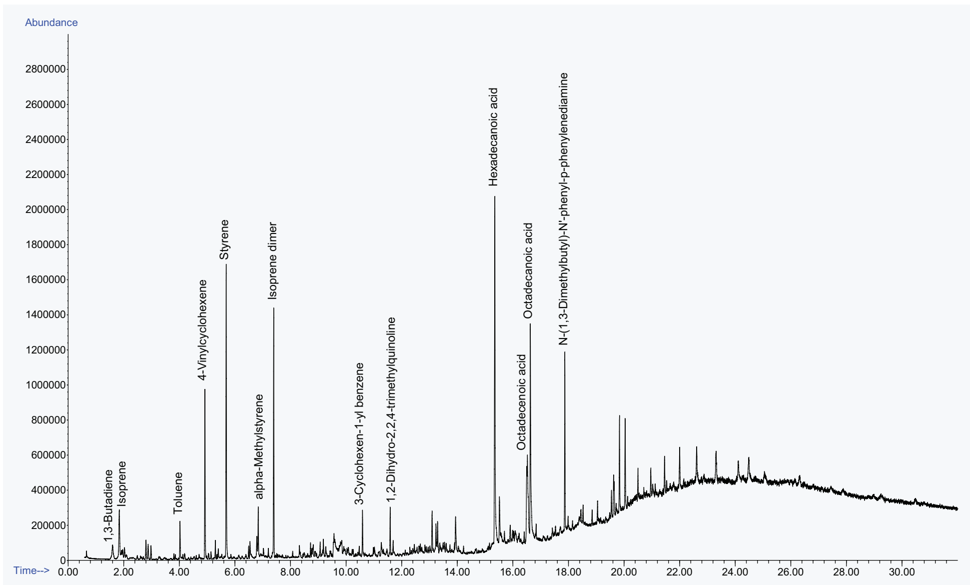

Figure 7: Total ion chromatogram for pyrolysis of a car tire sample.

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Conclusion

In this study, Smart Ramped Pyrolysis was used to produce an optimized pyrogram without the need for method development. The results showed that pyrolysis GC-MS can be a useful tool for determining the type of rubber used in a product. Pyrolysis GC-MS can also be useful for identifying polymer additives used in a product, some of which may be harmful to the environment.

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.

References

[1] Handbook for the Chemical Analysis of Plastic and Polymer Analysis, M. Bolgar, J. Hubball, J. Groeger and S. Meronek, CRC Press **2008**, pp 144-147.