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Pyrolysis GC-MS: Anatomy of a Golf Ball

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Keywords

Polymers, golf balls, pyrolysis, gas chromatography, mass spectrometry

Abstract

The global golf ball market was estimated to be over one billion dollars in 2017. It is estimated that each year, over 300 million golf balls are lost in the United States, alone. Golf balls are not recyclable or biodegradable, so if not recovered, the balls are left in waterways and woodlands.

Materials used to construct golf balls have evolved over the years. The original golf balls were made of wood. The next generation of balls were made from boiled feathers stuffed in a leather pouch. In the mid 1800's, the "guttie" type ball was introduced and consisted of dried sap which was molded into a sphere. At the beginning of the 20th century, the wound rubber ball covered with balata was invented. In the 1960's, Dupont introduced Surlyn™, an ionomer of ethylene acid, which was quickly adopted as a cover material for golf balls due to its enhanced durability. Polyurethane was also introduced to replace the softer balata covers which were easily cut. These materials and other polymers are used to construct modern golf balls [1].

This work will show the identification of materials used in the construction of modern commercially available golf balls. 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 pyrolysis. In addition, lower temperatures can be used to perform thermal desorption before pyrolysis to remove volatile and semi-volatile compounds and thus leading to a cleaner pyrogram. The unique heating system provides uniform sample heating and unmatched reproducibility. The GERSTEL PYRO Core System also 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. The GERSTEL Multi-Purpose Sampler (MPS) allows for complete automation of the analysis.

This study describes the use of the GERSTEL PYRO Core System for the determination of polymers found in golf balls.

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Experimental

Instrumentation

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

Analysis Conditions PYRO Core System

Thermal Desorption Conditions

PYRO	Splitless
	80 °C (0 min), 300 °C/min to 300 °C (2.17 min)
CIS 4	Split 75:1
	300 °C isothermal

Pyrolysis (Microplastic Samples)

Lead time	0.00 min
Follow up time	0.50 min
Initial time	0.00 min
Initial temp	300 °C (0 min), 5.0 °C/s to 800 °C (0.0 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, Pi = 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

Golf balls were cut in half using a ratcheting PVC pipe cutter. The individual layers were separated using a razor knife. The razor knife was used to cut a small sample from each layer.

Pyrolysis – Approximately one hundred micrograms of sample was 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.

Figure 2 shows a picture of the cross section of the golf balls analyzed. The balls fall into three general categories, two piece (cover and core), three-piece, or five-piece construction.

Figure 2: Photograph of golf balls prepared for analysis.

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Figure 3 shows pyrograms for the cores from a two-piece ball (bottom) and the five-piece ball (top). The cores from all the balls analyzed showed a similar pattern for polybutadiene. Polybutadiene is the material of choice for the core material due to its high resilience. The main peak in all pyrograms is 4-ethenylcyclohexene.

The bottom pyrogram shows a peak for butylated hydroxytoluene which is added as an antioxidant. The core from the five-piece ball is a styrene-butadiene rubber as indicated by the additional styrene and α-methylstyrene peaks.

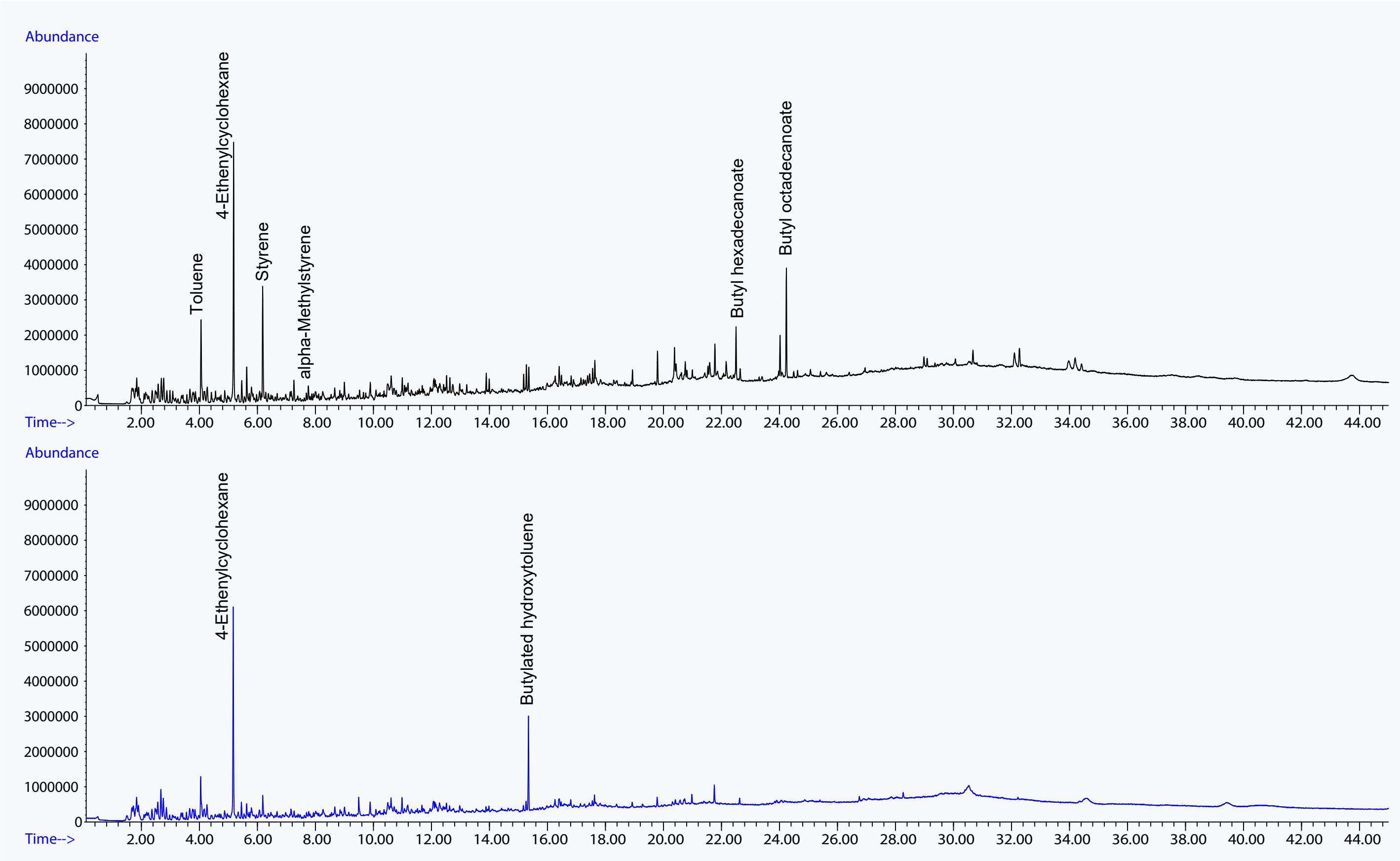

Figure 3: Stacked view of pyrograms for the cores of five-piece ball (top) and the two-piece ball (bottom).

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Figure 4 shows a pyrogram for the outer shell of a two-piece ball. The general pattern suggests polyethylene, but other marker compounds are present indicating a mixed polymer composition for the outer layer for this ball. 2-methylbutanoic acid and 2-methyl-2-propenoic acid suggest a poly(ethylene-co-methacrylic acid) polymer. Styrene, α-methylstyrene and triphenylcyclohexane are indicative of polystyrene. Also present in the pyrogram are 1,6-diisocyanatohexane, isophorone diisocyanate, and tetrahydrofuran which are indicative of a polyurethane. The plasticizer, bis(2-ethylhexyl) phthalate is also seen in the chromatogram.

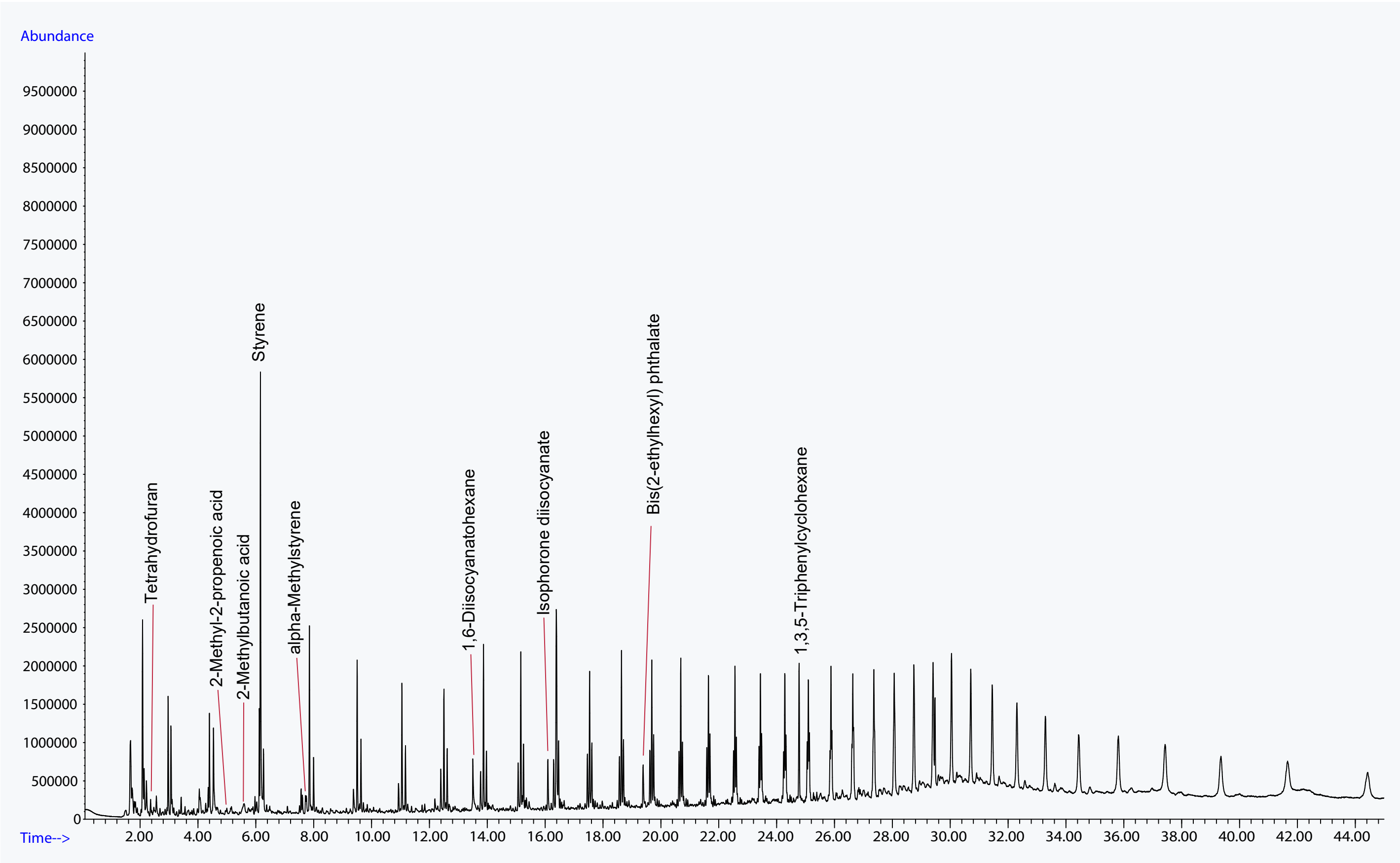

Figure 4: Pyrogram for outer shell of two-piece ball.

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Figure 5 shows an overlay of pyrograms from the inner (top) and outer (bottom) shells of a three-piece ball. The interior core, polybutadiene, is not shown. The two pyrograms are similar. Both include marker peaks; methyl methacrylate, 2-methylbutanoic acid, 2-methyl-2-propenoic acid and an ethylene pattern. These suggest they are both a poly(ethylene-co-methacrylic acid) polymer along with polymethyl methacrylate. The outer shell pyrogram also contains a peak for 1,6-diisocyanatohexane indicating it has a polyurethane component to the outer shell, but not the inner shell.

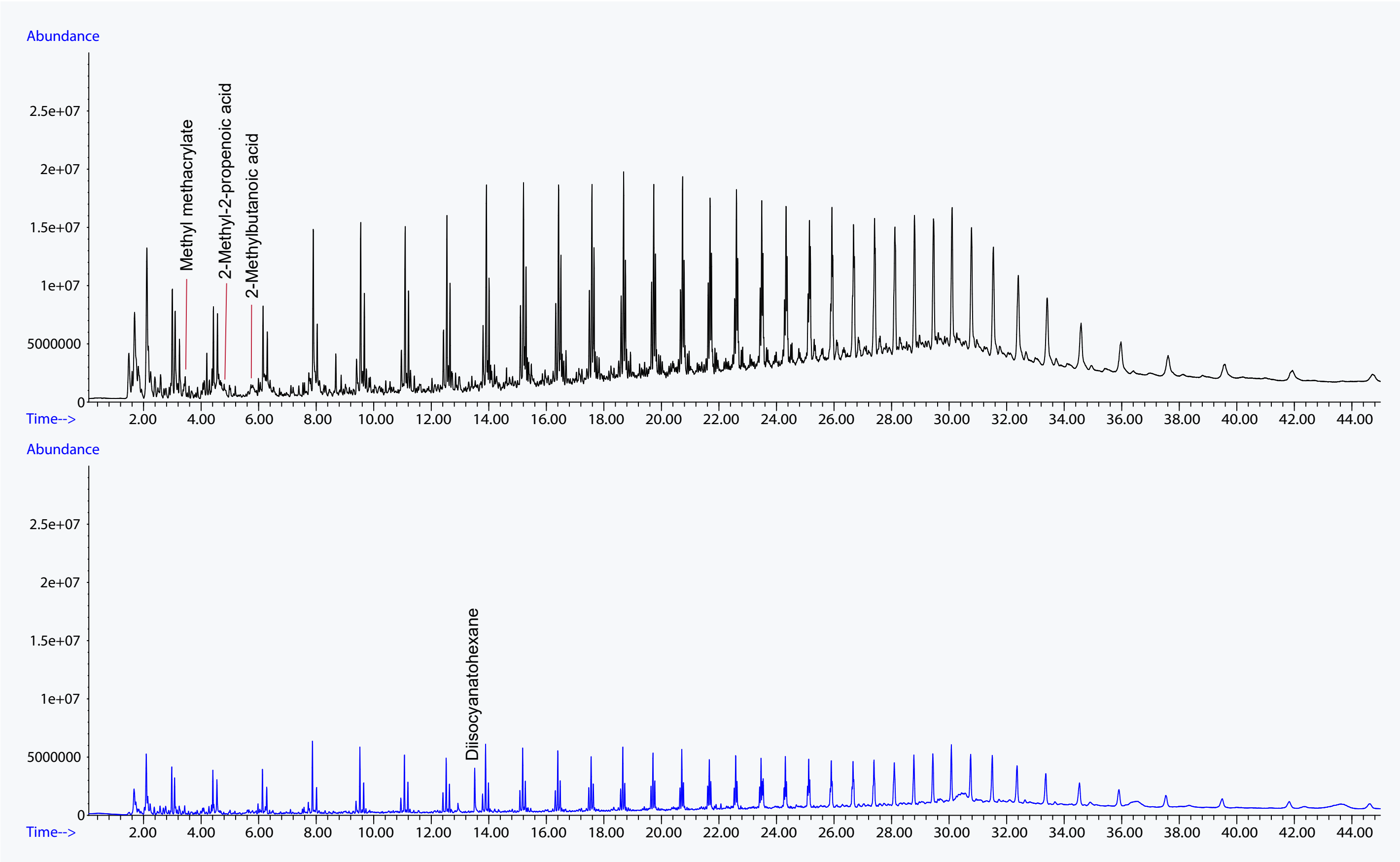

Figure 5: Pyrograms for inner (top) and outer (bottom) shell of three-piece ball.

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Figure 6 shows the resulting pyrograms from the shells from the five-piece ball. The core was polybutadiene and is not shown in the figure. The top pyrogram, A, is from the shell closest to the core. Pyrogram B is the next layer. Pyrogram C is the fourth layer and pyrogram D is the cover. Table 1 lists specific compound identification and retention times.

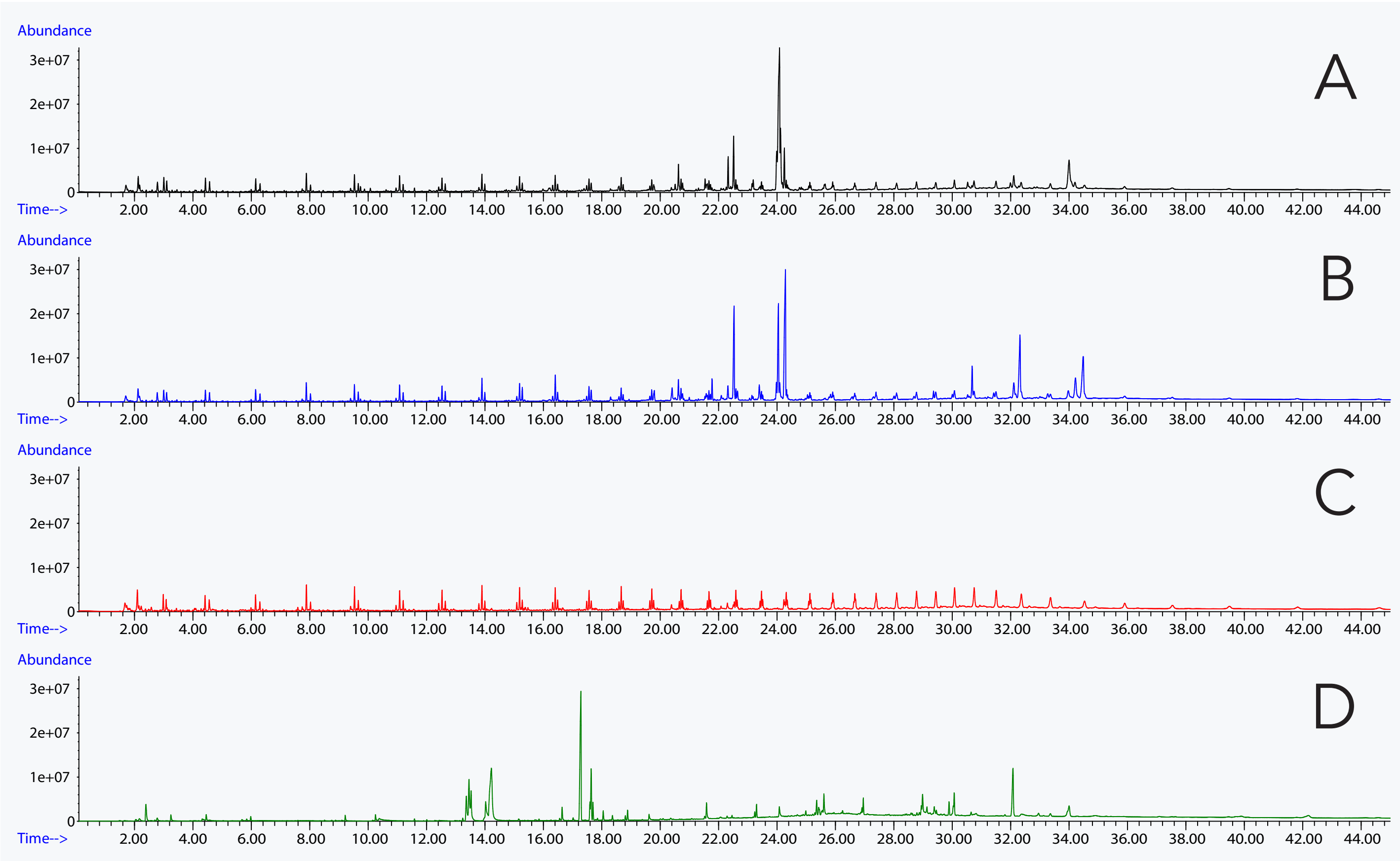

Figure 6: Pyrograms for five-piece ball; (A) shell next to core, (B) second shell, (C) third shell, (D) cover material.

Pyrogram A shows the typical pattern for a polyethylene. The presence of additional substituted alkenes in the pyrogram suggests a low-density polyethylene. Several butyl esters are also present in the pyrogram including butyl hexadecanoate, butyl -9-octadecanoate and butyl octadecenoate and butyl 9,12-octadecadienoate. These are used as plasticizers and add softness to the polymer.

Pyrogram B shows a similar pattern as Pyrogram A, suggesting a low density polyethylene. The same butyl esters are present at lower levels, possibly to increase the hardness of this layer. In addition to these plasticizers, several long chain alkyl ketones, such as 18-pentatriacontanone are seen. These are anti-slip/blocking agents, which provide a microscopic rough barrier that minimizes the contact between adjacent plastic surfaces.

Pyrogram C shows a general pattern that suggests polyethylene, but other marker compounds are present indicating a mixed polymer composition for this layer. 2-Methylbutanoic acid and 2-methyl-2-propenoic acid suggest a poly(ethylene-co-methacrylic acid) polymer.

Pyrogram D shows the outer cover for this golf ball. The marker compounds, tetrahydrofuran, 1,6-hexanediol, 1,3-diisocyanato-2-methylbenzene, 2,4-diisocyanato-1-methylbenzene and 1,6-diisocyanatohexane indicate the cover material contains polyurethane. Methyl methacrylate and 2-ethylhexyl acrylate are present indicating the presence of polyacrylate in the cover. The rest of the peaks in the pyrogram consist of plasticizers, light stabilizers, antioxidants, and other polymer additives.

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Table 1: Compound identification for figure 6.

Pyrogram	Compound	RT	Comment
6A	n-Butyl hexadecanoate	22.5	Plasticizer
6A	n-Butyl 9,12-octadecadienoate	23.9	Plasticizer
6A	n-Butyl-9-octadecanoate	24.0	Plasticizer
6B	n-Butyl octadecanoate	24.3	Plasticizer
6B	Hentriacontanone	30.7	Anti-slip/blocking agent
6B	Tritriacontanone	32.2	Anti-slip/blocking agent
6B	18-Pentatricontanone	34.4	Anti-slip/blocking agent
6C	2-Methyl-2-propenoic acid	4.58	Polymer marker
6C	2-Methyl butanoic acid	5.55	Polymer marker
6D	Tetrahydrofuran	2.38	Polymer marker
6D	Methyl methacrylate	3.24	Polymer marker
6D	1,6-Hexanediol	10.4	Polymer marker
6D	1,3-Diisocyanato-2-methyl benzene	13.3	Polymer marker
6D	2,4-Diisocyanato-1-methyl benzene	13.5	Polymer marker
6D	1,6-Diisocyanatohexane	13.6	Polymer marker
6D	5-Methyl-1,3-dihydro-2H-benzimidazol-2-one	14.2	Antioxidant
6D	4-(6-Methoxy-3-methyl-2-benzofuranyl)-3-buten-2-one	17.3	Antioxidant
6D	Bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate	32.1	Light stabilizer
6D	3,5-Bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid, octadecyl ester	33.4	Antioxidant

Conclusion

Several makes and models of golf balls were surveyed in this study. The results for three types are discussed in detail above. In general, the core for all the balls studied was found to be made of polybutadiene with various plasticizers added. The covers for the balls fell into two general categories: Polyurethane or poly(ethylene-co-methacrylic acid) polymers. Some of the polyurethane covers contained co-polymers such as poly methyl methacrylate or polystyrene. A variety of polymer additives were found including plasticizers, antioxidants, UV adsorbers, blocking agents and light stabilizers.

Smart Ramped Pyrolysis combines a slow heating rate with a quick transport rate to apply a broad temperature range to a sample without overheating its components. This results in an optimized pyrogram for a sample without having to compromise overt pulsed pyrolysis temperature. This is especially important for unknown samples, polymer mixtures, or whenever the amount of sample is limited. It was applied in this study. 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 the analysis of polymers and polymer additives.

References

[1] "Golf Ball" en.wikipedia.org/wiki/golf_ball