

APPLICATIONS

Fast and Accurate GC-MS Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) in Rubber and Plastic using a Zebron™ ZB-PAH-EU GC Column

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil and gas, garbage, or other organic compounds. PAHs can be found in petrochemicals, lubricants, oil, paints, leather and other products. Studies have shown that PAHs are also present in the plasticized and rubber components of consumer products. Although PAHs have no function and therefore RE not intentionally added in products, their presence often comes from the use of plasticizer oils as softeners to rubbers and plastics or from the pigment carbon black contaminated with PAHs. Products that have been found to contain PAHs include: plastic bathing shoes, the rubber handle of bicycles, sports items and tools, and car tires. As PAHs are not chemically bound in plastic or rubber materials, they can be released during contact with other materials and their routes of exposure to humans include skin absorption, ingestion and inhalation. EU REACH Annex XVII has placed a restriction on the use of 8 PAHs in tires and extender oil. Tires will not be allowed to be placed on the EU market if 8 PAHs exceed certain concentration thresholds listed in **Table 1**. The restriction also applies to

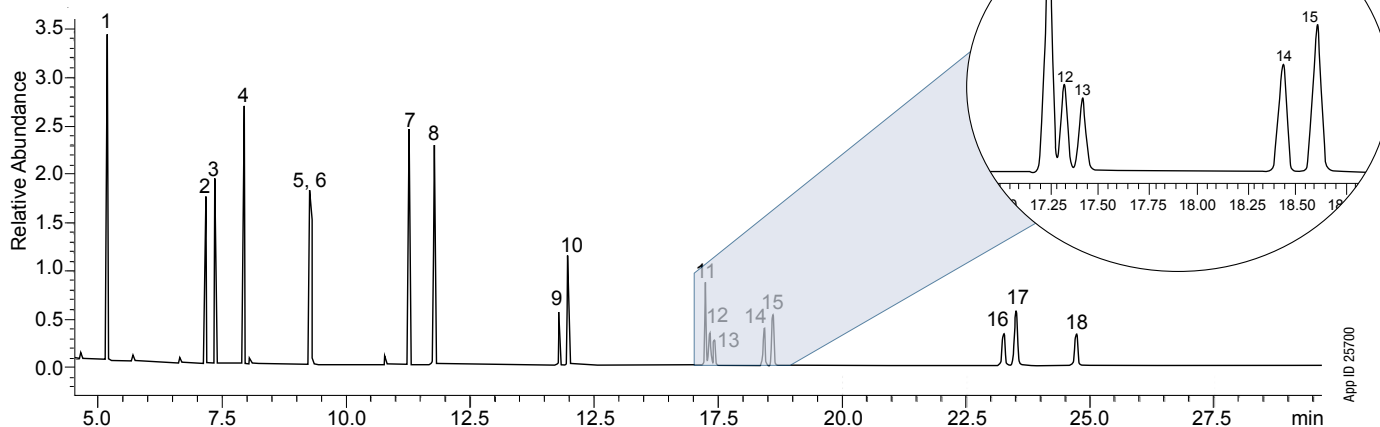
the marketing of tires in EU. In addition to the EU restriction of 8 PAHs in tires and extender oil, the US EPA has restricted 18 PAHs in consumer goods. Restrictions have been extended to also cover consumer products containing rubber or plastic components that come into direct, as well as prolonged or short-term repetitive contact, with human skin or the oral cavity. Products in short and infrequent contact with skin or the oral cavity are outside the restriction scope as the resulting exposure to PAH would be insignificant. A specific time period is provided to give stakeholders to give enough time to make the necessary changes for compliance with these new requirements.

Experimental:

In this study, a Zebron ZB-PAH-EU is used to provide the necessary separation of all 18 PAHs of interest in rubber and plastic, two optimal dimensions 20 meter, 0.18mm, 0.14 μ m and 10 meter, 0.10mm, 0.08 μ m ZB-PAH-EU GC columns were utilized for fast analysis and resolution of all the critical isomers such as the benzo[b,j,k]fluoranthenes.

Figure 1.

Separation of 18 PAH components on a 20 meter ZB-PAH-EU GC column in less than 25 minutes



GC-MS Method Parameters

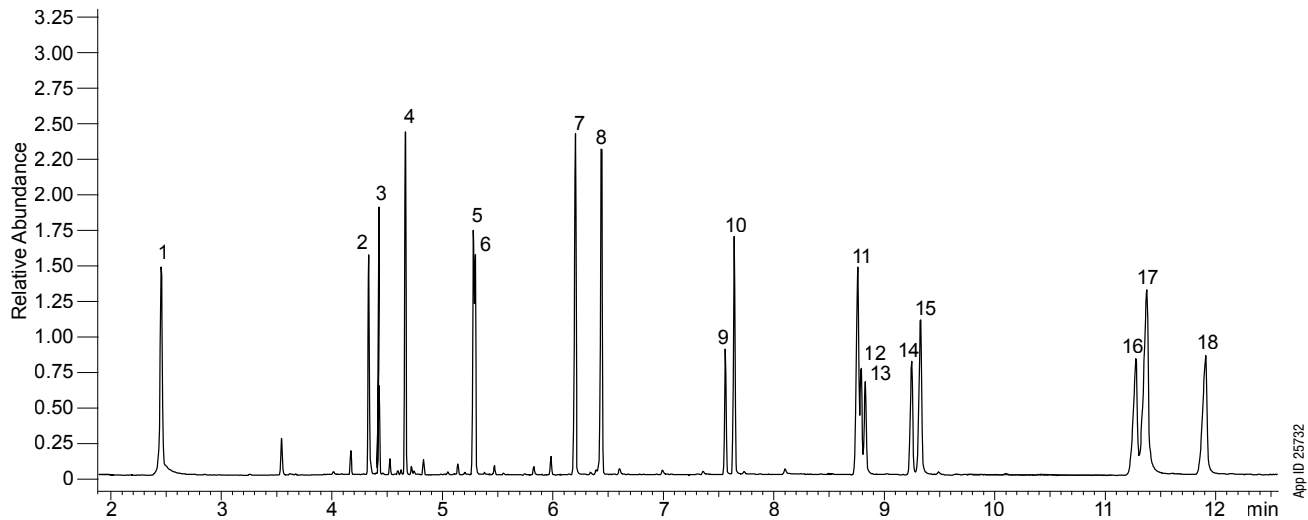
Column: Zebron ZB-PAH-EU
Dimension: 20 meter x 0.18 mm x 0.14 μ m
Part No.: [7FD-G043-47](#)
Injection: Splitless for 1.0 min @ 290 °C, 1.0 μ L
Recommended Liner: Zebron PLUS Single Taper Z- Liner™
Liner Part No.: [AG2-3B03-05](#) (for Shimadzu® 2010 GC System)
Carrier Gas: Helium @ 1.75 mL/min (constant flow)
Oven Program: 50 °C for 1.0 min to 200 °C @ 20°C/min to 260 °C @ 10°C/min for 1.0 min to 290 °C @ 2°C/min for 1.0 min to 330 °C @ 40°C/min for 1 min
Detector: MSD, Scan (50-500 m/z)
Source Temperature: 300 °C
Transfer line Temperature: 300 °C

Sample:

1. Naphthalene	10. Chrysene
2. Acenaphthylene	11. Benzo[b]fluoranthene
3. Acenaphthene	12. Benzo[k]fluoranthene
4. Fluorene	13. Benzo[j]fluoranthene
5. Phenanthrene	14. Benzo[a]pyrene
6. Anthracene	15. Benzo[e]pyrene
7. Fluoranthene	16. Indeno[1,2,3-cd]pyrene
8. Pyrene	17. Dibenz[a,h]anthracene
9. Benz[a]anthracene	18. Benzo[g,h,i]perylene

Figure 2.

Fast Separation of 18 PAH components on a 10 meter ZB-PAH-EU GC column in less than 13 minutes



App ID 25732

GC-MS Method Parameters

Column: Zebron™ ZB-PAH-EU

Dimension: 10 meter x 0.10 mm x 0.08 µm

Part No.: [7CB-G043-59](#)

Injection: Split (5:1) @ 320 °C, 1.0 µL

Recommended Liner: Zebron PLUS Single Taper Z- Liner™

Liner Part No.: [AG2-3B03-05](#) (for Shimadzu® 2010 GC System)

Carrier Gas: Helium @ 0.68 mL/min (constant flow)

Oven Program: 100 °C for 3.0 min to 200 °C @ 60°C/min to 270 °C @ 22°C/min to 300 °C @ 4.5°C/min to 330 °C @ 80°C/min for 0.5 min

Detector: MDS, Scan (50-500 m/z)

Source Temperature: 300 °C

Transfer line Temperature: 330 °C

Sample:

1. Naphthalene	10. Chrysene
2. Acenaphthylene	11. Benzo[b]fluoranthene
3. Acenaphthene	12. Benzo[k]fluoranthene
4. Fluorene	13. Benzo[j]fluoranthene
5. Phenanthrene	14. Benzo[a]pyrene
6. Anthracene	15. Benzo[e]pyrene
7. Fluoranthene	16. Indeno[1,2,3-cd]pyrene
8. Pyrene	17. Dibenzo[a,h]anthracene
9. Benzo[a]anthracene	18. Benzo[g,h,i]perylene

Table 1.

Analyte details for 18 component PAHs analysis

Peak No	Analyte Name	Concentration (ppm)	Retention Time on a 20 m column (Figure 1) (min)	Retention Time on a 10 m column (Figure 2) (min)
1	Naphthalene	20	5.15	2.50
2	Acenaphthylene	10	7.15	4.32
3	Acenaphthene	10	7.35	4.43
4	Fluorene	16	7.95	4.69
5	Phenanthrene	12	9.25	5.29
6	Anthracene	10	9.32	5.32
7	Fluoranthene	16	11.25	6.20
8	Pyrene	16	11.75	6.45
9	Benzo[a]anthracene	4	14.25	7.57
10	Chrysene	8	14.50	7.65
11	Benzo[b]fluoranthene	10	17.25	8.80
12	Benzo[k]fluoranthene	5	17.35	8.83
13	Benzo[j]fluoranthene	4	17.40	8.87
14	Benzo[a]pyrene	8	18.42	9.27
15	Benzo[e]pyrene	5	18.60	9.35
16	Indeno[1,2,3-cd]pyrene	10	23.25	11.25
17	Dibenzo[a,h]anthracene	16	23.50	11.35
18	Benzo[g,h,i]perylene	10	24.75	11.90

Table 2.
List of PAH Components and Concentration Limits in Rubber or Plastic

Substance	Scope and Limits
Benzo[a]pyrene (BaP) Benzo[e]pyrene (BeP) Benzo[a]anthracene (BaA) Chrysene (CHR) Benzo[b]fluoranthene (BbFA) Benzo[k]fluoranthene (BkFA) Benzo[j]fluoranthene (BkFA) Dibenz[a,h]anthracene (BBAhA)	<p>Consumer articles containing rubber or plastic components that come into direct as well as prolonged or short-term repetitive contact with the human skin or the oral cavity, under normal or reasonably foreseeable conditions of use.</p> <p>There are two different limits, depending on the product type:</p> <ul style="list-style-type: none"> • Limit: 1 mg/kg (0.0001%). <p>Products include (among others):</p> <ul style="list-style-type: none"> • Sport equipment such as bicycles, golf clubs, racquets. • House-hold utensils, trolleys /carts, baby walkers. • Tools for domestic use. • Clothing, footwear, gloves and sportswear. • Watch-straps, wrist-bands, masks, head-bands. <p>• Limit: 0.5 mg/kg (0.00005%).</p> <p>Products include:</p> <ul style="list-style-type: none"> • Toys (including activity toys). • Childcare articles. <p>The limits are calculated by weight of the component.</p>

Results and Discussion

Separation of PAH components with reasonable runtime is very important for evaluating them in articles made of plastic and rubber. The Zebron™ ZB-PAH-EU GC column offers a selective stationary phase that effectively separates the critical 18 PAH isomers. Represented in **Figure 1** is the separation of 18 component PAH on a 20 meter x 0.18 mm x 0.14 µm ZB-PAH-EU GC column. The high selectivity and efficiency of the stationary phase provides excellent recognition of PAH components in less than 25 min. In addition, the column is equipped with Engineered Self Cross-Linking (ESC™) that provides an upper temperature limit of 340/360°C. Such high temperature limits are extremely helpful for elution of higher boiling point PAHs as well as to bake out matrix contaminants that can otherwise cause ghost peaks. For faster analysis, the same test mix was optimized on a 10 meter x 0.01 mm x 0.08 µm GC column. The optimized method separated 18 PAH components in less than 12 minutes as demonstrated in **Figure 2**. Such fast separation is possible because of the proprietary selectivity and optimal dimensions of ZB-PAH-EU GC column. Thus, ZB-PAH-EU GC column not only presents high resolution of critical pairs, but also provides fast GC-MS separation for high-throughput PAH analysis.

Conclusion

The Zebron ZB-PAH-EU GC column can effectively separate the 18 PAH isomers, resolving all the critical and difficult to separate pairs while providing 340/360°C thermal stability, low column bleed at elevated temperatures, and consistent column inertness. This application shows a highly sensitive and selective method for PAH analysis in rubber and plastic products using the Zebron ZB-PAH-EU GC column that provides fast and reliable PAH analysis.

APPLICATIONS

Ordering Information

Zebtron™ ZB-PAH-EU GC Column

Length (meter)	ID (mm)	df (µm)	Temp. Limits °C	Part No.
10	0.10	0.08	40 to 340/360	7CB-G043-59
20	0.18	0.14	40 to 340/360	7FD-G043-47
30	0.25	0.20	40 to 340/360	7HG-G043-10
60	0.25	0.20	40 to 340/360	7KG-G043-10

Zebtron™ ZB-PAH-CT GC column

Length (meter)	ID (mm)	df (µm)	Temp. Limits °C	Part No.
20	0.18	0.14	40 to 320/340	7FD-G044-47
30	0.25	0.20	40 to 320/340	7HG-G044-10
40	0.18	0.14	40 to 320/340	7PD-G044-47

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