Fast Analysis of Regulated PAHs by GC-MS using Zebron™ ZB-PAH-EU and Zebron ZB-PAH-SeleCT

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Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are organic (highly hydrophobic) compounds that contain multiple aromatic rings (e.g. Naphthalene, Chrysene and Benzo[b]fluoranthene). PAHs often result from the incomplete combustion of organic substances such as wood, coal and oil and are found as contamination in air, water and soil. Furthermore, PAHs enter the food chain via deposition or transfer from air, water and soil or food processing. Amongst the PAHs are some of the most toxic compounds known. Including some that are carcinogenic, mutagenic, and teratogenic. In the United States, the EPA (Environmental Protection Agency) has listed 16 priority PAHs. The European Union (EU) has regulated a series of PAHs found in food matrices. The list of EPA, EU(15+1) PAH and EFSA4 PAH are listed in **Table 1**. In addition, there are various regulations for PAH in plastic, rubber and electronic components. Listed below are common challenges associated with PAH separation.

Separation of Critical PAH	High efficiency and high selectivity for aromatic compounds are essential to provide higher resolution
Long Analysis Time	High efficiency dimension and optimal stationary phase chemistry are necessary for cutting down the run time
Ghost Peaks and Matrix Effects	Higher temperature limits and extensive crosslinking are necessary for high temperature GC bakeout
False Positives	Alternate selectivity and high efficiency dimensions are necessary to avoid false positives

Materials and Methods

In this study, we utilized two unique GC columns: Zebron ZB-PAH-EU and ZB-PAH-SeleCT to resolve PAH components. Various column dimensions were explored to get optimal separation, fast and high-throughput analysis. While both column chemistries provided faster run time compared to other commercially available PAH columns, ZB-PAH-EU offered a maximum temperature of 340/360°C. In addition, it resolved 24 priority PAH components in less than 16 minutes. ZB-PAH-SeleCT offered highest resolution for critical pair Chrysene and Triphenylene, which helps to minimize false positives in PAH analysis.

FIGURE 1.
Zebron ZB-PAH-EU & ZB-PAH-SeleCT Benefits

ZB-PAH-EU
- Up to 70% Faster PAH Analysis
- Elevated Temperature Stability (340/360 °C)

ZB-PAH-SeleCT
- Enhanced Resolution for Chrysene and Triphenylene (PAH Interferences)
- Increased Benzo[b,k]fluoranthene Separation

TABLE 1.
PAH Isomers Listed in Various Regulations

PAHs	EPA PAH	EFSA PAH 15+1	EFSA PAH 4
Naphthalene	x		
Acenaphthylene	x		
Acenaphthene	x		
Fluorene	x		
Phenanthrene	x		
Anthracene	x		
Fluoranthene	x		
Pyrene			
Benzo[c]fluorene	x	x	
Cyclopenta[cd]pyrene	x	x	
Benz[a]anthracene		x	x
Chrysene		x	x

PAHs (continued)	EPA PAH	EFSA PAH 15+1	EFSA PAH 4
5-Methylchrysene		x	
Benzo[b]fluoranthene	x	x	x
Benzo[k]fluoranthene	x	x	
Benzo[j]fluoranthene		x	
Benzo[a]pyrene	x	x	x
Indeno[1,2,3-cd]pyrene	x	x	
Benzo[g,h,i]perylene	x	x	
Dibenz[a,h]anthracene	x	x	
Dibenzo[a,l]pyrene		x	
Dibenzo[a,i]pyrene		x	
Dibenzo[a,e]pyrene		x	
Dibenzo[a,h]pyrene		x	

FIGURE 2.
Complete Separation of EU(15+1) Isomers on Zebron ZB-PAH-EU GC Column

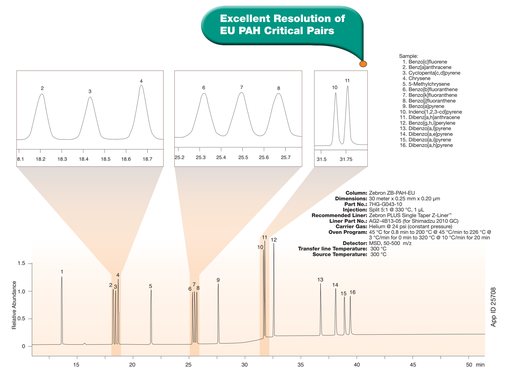
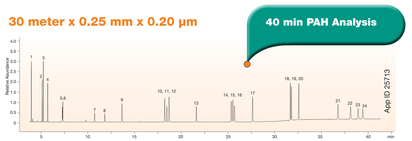


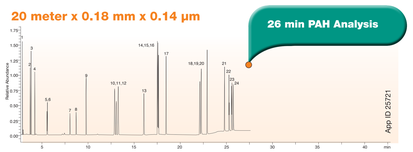
FIGURE 3.
Fast PAH Analysis with Optimal Dimension on Zebron ZB-PAH-EU GC Columns

30 meter x 0.25 mm x 0.20 µm



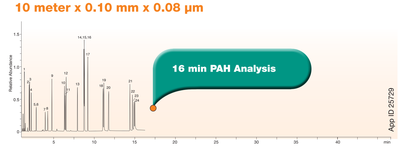
Dimensions: 30 meter x 0.25 mm x 0.20 µm
Part No.: 7HG-G043-10
Injection: Split 5:1 @ 330 °C, 1 µL
Recommended Liner: Zebron PLUS Single Taper Z-Liner
Liner Part No.: AG2-4B13-05 (for Shimadzu 2010 GC)
Carrier Gas: Helium @ 24 psi (constant pressure)
Oven Program: 45 °C for 0.8 min to 200 °C @ 45 °C/min to 226 °C @ 3 °C/min for 0 min to 320 °C @ 10 °C/min for 20 min
Detector: MSD, 50-500 m/z
Transfer line Temperature: 300 °C
Source Temperature: 300 °C

20 meter x 0.18 mm x 0.14 µm



Dimensions: 20 meter x 0.18 mm x 0.14 µm
Part No.: 7FD-G043-47
Injection: Split 5:1 @ 330 °C, 1 µL
Recommended Liner: Zebron PLUS Single Taper Z-Liner
Liner Part No.: AG2-4B13-05 (for Shimadzu 2010 GC)
Carrier Gas: Helium @ 1.75 mL/min (constant flow)
Oven Program: 70 °C for 0.8 min to 180 °C @ 70 °C/min to 230 °C @ 7 °C/min for 6 min to 280 °C @ 40 °C/min for 5 min to 335 °C @ 25 °C/min for 5 min
Detector: MSD, 100-500 m/z
Transfer line Temperature: 300 °C
Source Temperature: 300 °C

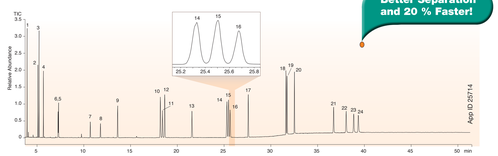
10 meter x 0.10 mm x 0.08 µm



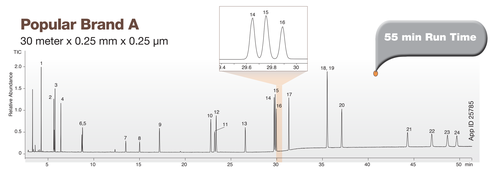
Dimension: 10 meter x 0.10 mm x 0.08 µm
Part No.: 7CB-G043-59
Injection: Split 10:1 @ 320 °C, 1 µL
Recommended Liner: Zebron PLUS Single Taper Z-Liner
Liner Part No.: AG2-4B13-05 (for Shimadzu 2010 GC)
Carrier Gas: Helium @ 0.88 mL/min (constant flow)
Oven Program: 70 °C for 0.4 min to 180 °C @ 140 °C/min to 230 °C @ 14 °C/min for 3 min to 280 °C @ 85 °C/min for 5 min to 330 °C @ 40 °C/min for 5 min
Detector: MSD, 100 to 500 m/z
Transfer line Temperature: 300 °C
Source Temperature: 300 °C

FIGURE 4.
Comparison of Resolution and Speed of Analysis on PAH GC Columns

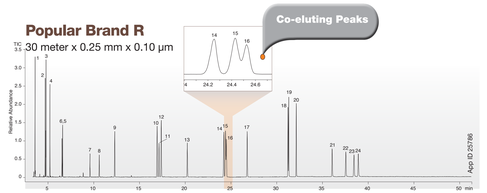
Zebron ZB-PAH-EU
30 meter x 0.25 mm x 0.20 µm



Popular Brand A
30 meter x 0.25 mm x 0.25 µm



Popular Brand R
30 meter x 0.25 mm x 0.10 µm

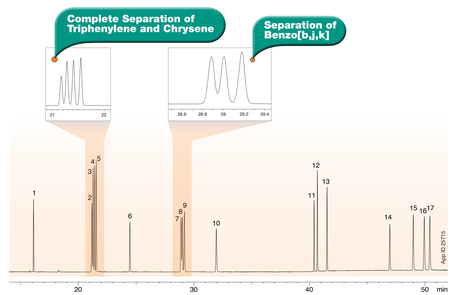


Column: As Indicated
Dimension: As Indicated
Injection: Split 5:1 @ 330 °C, 1 µL
Recommended Liner: Zebron PLUS Single Taper Z- Liner™
Liner Part No.: AG2-4B13-05 (for Shimadzu 2010 GC)
Carrier Gas: Helium @ 24 psi (constant pressure)
Oven Program: 45 °C for 0.8 min to 200 °C @ 45 °C/ min to 226 °C @ 3 °C/min for 0 min to 320 °C @ 10 °C/min for 20 min
Detector: MSD, 50-500 m/z
Transfer line Temperature: 300 °C
Source Temperature: 300 °C

Sample:
1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo[c]fluorene
10. Benz[a]anthracene
11. Cyclopenta[c,d]pyrene
12. Chrysene
13. 5-Methylchrysene
14. Benzo[b]fluoranthene
15. Benzo[k]fluoranthene
16. Benzo[j]fluoranthene
17. Benzo[a]pyrene
18. Indeno[1,2,3-cd]pyrene
19. Dibenz[a,h]anthracene
20. Benzo[g,h,i]perylene
21. Dibenzo[a,l]pyrene
22. Dibenzo[a,i]pyrene
23. Dibenzo[a,e]pyrene
24. Dibenzo[a,h]pyrene

Comparative separations may not be representative of all applications.

FIGURE 5.
Unique Selectivity to Resolve Chrysene and Triphenylene along with other EU(15+1) Isomers

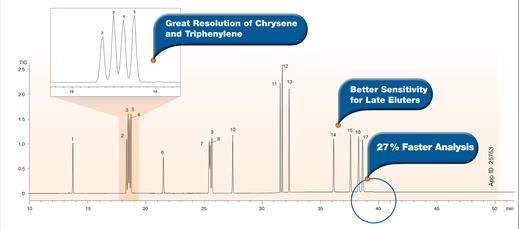


Column: Zebron ZB-PAH-SeleCT
Dimensions: 40 meter x 0.18 mm x 0.14 µm
Part No.: 7FD-G044-47
Liner Part No.: AG2-4B13-05 (for Shimadzu 2010 GC)
Injection: Split 15:1 @ 320 °C, 1 µL
Carrier Gas: Helium @ 78 psi (constant pressure)
Oven Program: 45 °C for 0.8 min to 200 °C @ 45 °C/min to 265 °C @ 3 °C/ min for 5 min to 270 °C @ 1 °C/min to 320 °C @ 10 °C/min for 15 min
Detector: MSD (Shimadzu® QC-MS-QP2010 Ultra)
Mode: SIM
SIM Ions: 216, 226, 228, 242, 252, 276, 278, 302 m/z
Transfer line Temperature: 300 °C
Source Temperature: 300 °C

Sample
1. Benzo[c]fluorene
2. Cyclopenta[c,d]pyrene
3. Benz[a]anthracene
4. Triphenylene
5. Chrysene
6. 5-Methylchrysene
7. Benzo[b]fluoranthene
8. Benzo[j]fluoranthene
9. Benzo[k]fluoranthene
10. Benzo[a]pyrene
11. Indeno[1,2,3-c,d]pyrene
12. Dibenz[a,h]anthracene
13. Benzo[g,h,i]perylene
14. Dibenzo[a,l]pyrene
15. Dibenzo[a,e]pyrene
16. Dibenzo[a,i]pyrene
17. Dibenzo[a,h]pyrene

FIGURE 6.
Short Run Time and Better Sensitivity on ZB-PAH-SeleCT

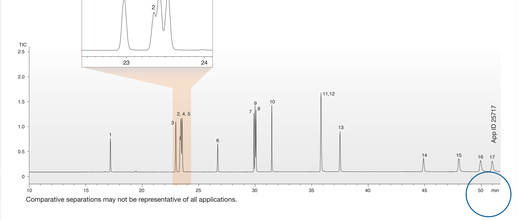
Zebron ZB-PAH-SeleCT
30 meter x 0.25 mm x 0.20 µm



Conditions for both applications:
Column: As Indicated
Dimensions: As Indicated
Part No.: 7HG-G044-10 (Zebron ZB-PAH-SeleCT)
Recommended Liner: Zebron PLUS Single Taper Z-Liner
Liner Part No.: AG2-4B13-05
Injection: Split 15:1 @ 320 °C, 1 µL
Carrier Gas: Helium @ 23.7 psi (constant pressure)
Oven Program: 45 °C for 0.8 min to 200 °C @ 45 °C/min to 265 °C @ 3 °C/ min for 0 min to 320 °C @ 10 °C/min for 20 min
Detector: MSD (Shimadzu® QC-MS-QP2010 Ultra)
Mode: SIM
SIM Ions: 216, 226, 228, 242, 252, 276, 278, 302 m/z
Transfer line Temperature: 300 °C
Source Temperature: 300 °C

Samples:
1. Benzo[c]fluorene
2. Cyclopenta[c,d]pyrene
3. Benz[a]anthracene
4. Triphenylene
5. Chrysene
6. 5-Methylchrysene
7. Benzo[b]fluoranthene
8. Benzo[j]fluoranthene
9. Benzo[k]fluoranthene
10. Benzo[a]pyrene
11. Indeno[1,2,3-c,d]pyrene
12. Dibenz[a,h]anthracene
13. Benzo[g,h,i]perylene
14. Dibenzo[a,l]pyrene
15. Dibenzo[a,e]pyrene
16. Dibenzo[a,i]pyrene
17. Dibenzo[a,h]pyrene

Popular Brand A
30 meter x 0.25 mm x 0.15 µm



Comparative separations may not be representative of all applications.

Results and Discussion

Analysis of PAH components is challenging considering the structural similarities of the components. In addition, it is a time intensive separation and there is a need for fast GC separation. Presented in this study are two GC solutions for fast separation of PAHs. **Table 1** lists the PAH components mandated in various regulations for environmental and food testing. **Figure 2** represents the complete separation of EU(15+1) isomers on a ZB-PAH-EU GC column.

To further optimize run time 30, 20, and 10 meter ZB-PAH-EU GC columns with comparable phase ratio were evaluated as shown in **Figure 3**. With shorter column length and high efficiency dimension like 10 meter x 0.10 mm x 0.08 µm, a run time as short as 16 min was achieved. Such a short run time is extremely useful for high-throughput analysis. In addition, ZB-PAH-EU 30 meter GC column was compared with other commercially available PAH GC columns in the market under identical conditions. ZB-PAH-EU provided fast analysis as well as good separation of EU 15+1 and EPA Method 610 PAH compounds as illustrated in **Figure 4**.

For alternate selectivity and to resolve critical PAHs, like Chrysene and Triphenylene, a ZB-PAH-SeleCT GC column was employed. The test mix had EU(15+1) PAH and Triphenylene in it. As shown in **Figure 5**, ZB-PAH-SeleCT was able to completely separate Chrysene from Triphenylene in addition to other critical pairs. Due to the unique selectivity, this column can provide a selectivity change. For example, the peak order for Benzofluoranthene are Benzo[b]fluoranthene peak 7, Benzo[j]fluoranthene peak 8 and Benzo[k]fluoranthene peak 9 unlike traditional PAH selectivity. This peak order change helps to eliminate false positives and provides the highest resolution between Benzo[b]fluoranthene and Benzo[k]fluoranthene. **Figure 6** shows short run time and better sensitivity on ZB-PAH-SeleCT compared to a popular GC column.

Conclusion

High efficiency column dimensions are absolutely essential for separation of PAH components. In addition, short run time, higher temperature limits, and unique selectivity are essential for high-throughput applications and challenging matrices. ZB-PAH-EU and ZB-PAH-SeleCT provided fast PAH analysis. While ZB-PAH-EU provided shorter analysis time, it also offers a higher temperature limit of 340/360 °C to elute higher PAH and to bake out matrix contaminants. ZB-PAH-SeleCT offered alternate selectivity that can resolve Chrysene from Triphenylene completely, thereby avoiding false positives.

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