APPLICATIONS

An Improved Test Method for Fast Measurement of Polycyclic Aromatic Hydrocarbons (PAHs) in Electronic Components by GC-MS using a Zebron™ ZB-PAH-EU GC Column

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Introduction

There are many Polycyclic Aromatic Hydrocarbons (PAHs) that are hazardous for both our human health and the environment, and some even have toxic, mutagenic and/or carcinogenic properties. PAHs are organic compounds composed of carbon and hydrogen positioned in multiple aromatic rings. They are found naturally in the environment and they are also created as environmental pollutants during the incomplete combustion of organic materials. There are instances where the hazardous PAHs can be found in consumer products, such as toys, sporting goods, tools, shoes, and electronics. As a consequence, The Product Safety Commission (AfPS) in Germany has assigned the requirements of PAH testing in the course of GS mark certification as a specification according to article 21 Product Safety Act (ProdSG) paragraph 1 number 3. There are 18 different PAH chemicals on this list (**Table 1**) which are not to exceed the individual limits of 0.2 to 1 mg/kg (depending on the contact category).

The International Electrotechnical Commission (IEC) is the world's leading organization that prepares and publishes International Standards for all electrical, electronic, and related technologies. The widespread use of electronic products has drawn increased attention to their impact on the environment. Due to the concern on their environmental impact and the associated effects on our health, the IEC has created test series 62321 as an international standard to determine the levels of the concerned substances for daily use. Part 10 in this series is a test for measuring PAHs in polymers and electronics by gas chromatography-mass spectrometry (GC-MS) "DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS – Part 10: Polycyclic aromatic hydrocarbons (PAHs) in polymers and electronics by gas chromatography-mass spectrometry (GC-MS)".

For the development of the analytical method, the IEC used a standard solution that is a mix of several suspect PAH chemicals which are the same as those listed in AfPS GS 2014:01. Typical chromatography analysis run times are 45 to 60 minutes when using test method IEC 62321-10 Ed.1.0 and the established AfPS GS 2014:01 test procedures. Phenomenex has developed a proprietary selectivity to optimize the analysis and resolution of the critical PAH components per the IEC test method.

Table 1.
List of PAH components restricted in AfPS GS 2014:01

	Category 1	Category 2		Category 3	
Parameter (mg/kg)		**Toys in the scope of 2009/48/EC**	**Other products in the scope of ProdSG**	**Toys in the scope of 2009/48/EC**	**Other products in the scope of ProdSG**
Benzo[a]pyrene	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[e]pyrene	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benz[a]anthracene	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[b]fluoranthene	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[k]fluoranthene	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[j]fluoranthene	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Chrysene	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Dibenz[a,h]anthracene	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[g,h,i]perylene	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Indeno[1,2,3-cd]pyrene	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Acenaphthylene, acenaphthene, fluorene, phenanthrene, pyrene, anthracene, fluoranthene	<1 (sum)	<5 (sum)	<10 (sum)	<20 (sum)	<50 (sum)
Naphthalene	< 1	< 2		< 10	
Sum of 18 PAHs, mg/kg	< 1	< 5	< 10	< 20	< 50
Category 1	Materials intended to be put in the mouth, or materials of toys with intended to long-term skin contact (longer than 30 seconds)				
Category 2	Materials not covered by Category 1, with foreseeable skin contact for longer than 30 seconds (long-term skin contact) or repeated short-term skin contact				
Category 3	Materials not covered by category 1 or 2 with foreseeable skin contact up to 30 seconds (short-term skin contact)				

Experimental

An improved fast GC-MS analytical method was developed using the Zebron ZB-PAH-EU GC column to improve the analytical separation and run time as compared to the IEC method. Optimal proprietary selectivity and column dimensions were utilized to get a highly efficient separation and faster throughput analysis. Additionally, a 10 meter column was used to reduce the analysis run time.

The Zebron ZB-PAH-EU GC column was selected because:

- With its special uniquely designed stationary phase it offers enhanced resolution of the PAHs, preventing co-elution of interfering PAHs that can cause false positives and inaccurate results
- The columns are individually tested to provide consistent performance
- The ZB-PAH-EU GC column has great thermal stability with very low column bleed
- In this technical piece a faster run time is also evaluated with a 10 meter column as per the IEC test method

The temperature ramp was modified slightly to improve the peak efficiencies along with a reduction in the run, which was provided by the improved retention properties from the ZB-PAH-EU column.

Figure 1a.
Separation of Polycyclic Aromatic Hydrocarbons in Electronic Components by GC-MS on ZB-PAH-EU

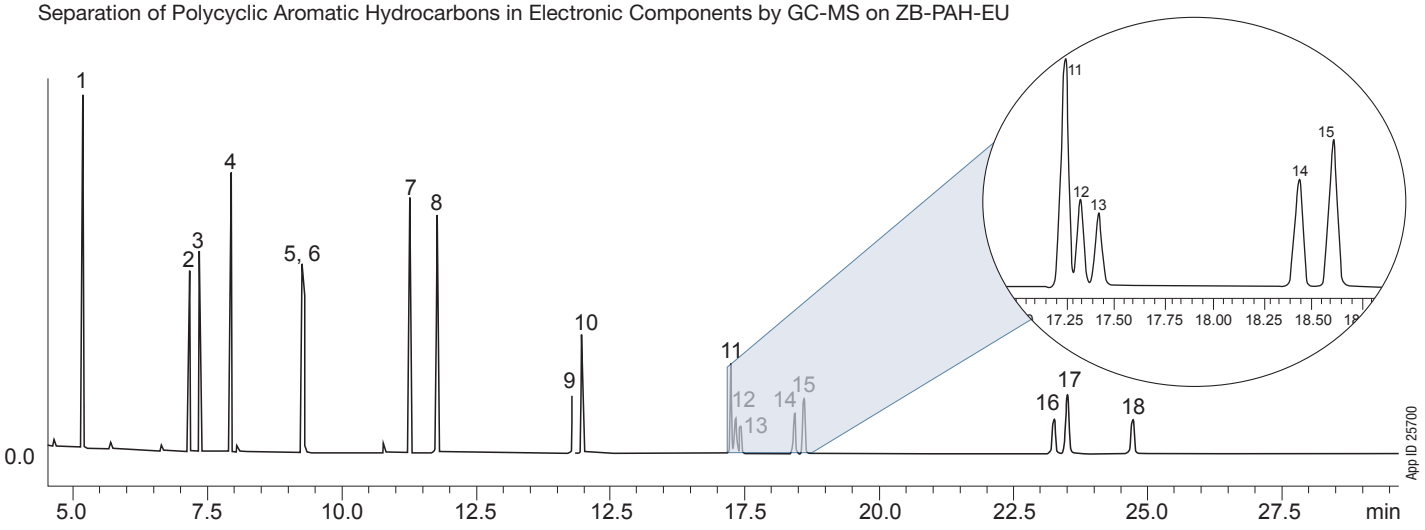
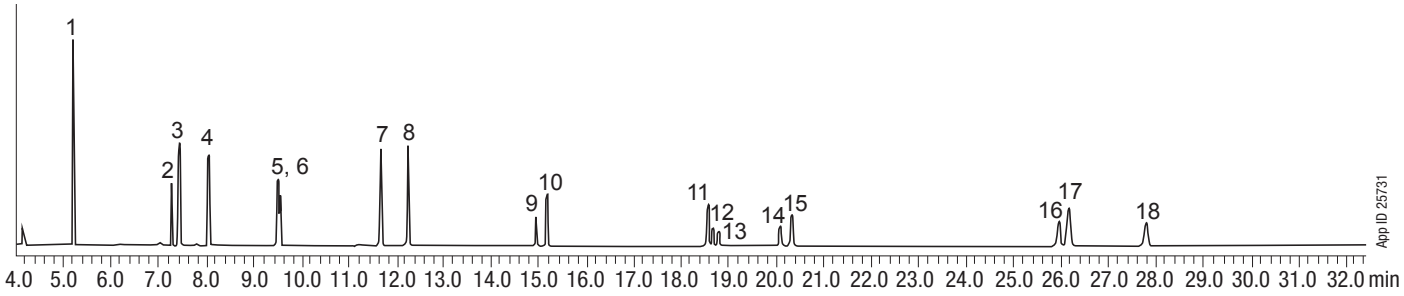


Figure 1b.
Separation of Polycyclic Aromatic Hydrocarbons in Electronic Components by GC-MS on Popular Brand A



GC-MS Method Parameters

Column: Zebron™ ZB-PAH-EU (Figure 1a)
Dimensions: 20 meter x 0.18 mm x 0.14 µm
Part No.: 7FD-G043-47
Column: Popular Brand (Figure 1b)
Dimensions: 20 meter x 0.18 mm x 0.14 µm
Inlet Liner: Zebron PLUS Straight Z-Liner™ AG2-3B03-05
Injection: Splitless 0.5 minutes @ 290 °C, 1 µL
Carrier Gas: Helium @ 1.75 mL/min (constant flow)
Oven Program: 50 °C for 1 min to 200 °C @ 20 °C/min to 260 °C @ 10 °C/ min to 290 °C @ 2 °C/min (hold 1 min) to 330 °C @ 40 °C/min (hold 1 min)
Detector: MSD (Shimadzu® GC-MS-QP2010 Ultra)
Source Temperature: 300 °C
Transfer-line Temperature: 300 °C
Sample: PAH Sample Standard Mix (Part No. AE-00025-10ML, AccuStandard®)

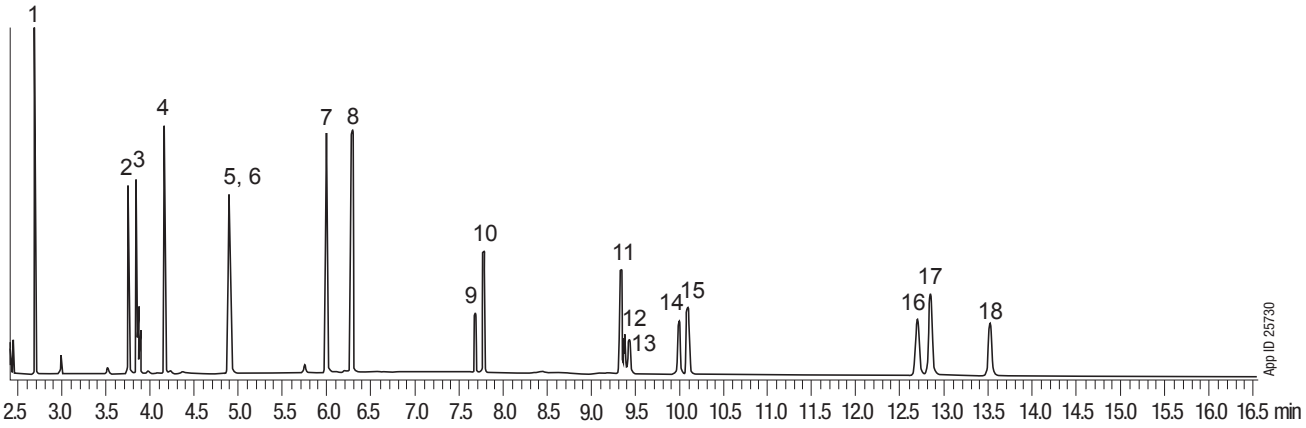
	Figure 1a.	Figure 1b
Analyte Name	**RT (min)**	**RT (min)**
Naphthalene	5.15	5.20
Acenaphthylene	7.15	7.27
Acenaphthene	7.35	7.45
Fluorene	7.95	12.25
Phenanthrene	9.25	9.50
Anthracene	9.32	9.55
Fluoranthene	11.25	11.70
Pyrene	11.75	12.25
Benz[a]anthracene	14.25	14.95
Chrysene	14.5	15.17
Benzo[b]fluoranthene	17.25	18.55
Benzok]fluoranthene	17.35	18.65
Benzo[j]fluoranthene	17.4	18.80
Benzo[a]pyrene	18.42	20.10
Benzo[e]pyrene	18.6	20.35
Indeno[1,2,3-cd]pyrene	23.25	20.95
Dibenz[a,h]anthracene	23.5	26.15
Benzo[g,h,i]perylene	24.75	27.80

The Zebron ZB-PAH-EU and Popular Brand A have similar resolution and separation; however, the ZB-PAH-EU had a run time that is 11 % faster.

* Comparative separations may not be representative for all applications

For further improvement in the run time a 10 meter column was evaluated with some modification to accommodate for the shorter column.

Figure 2.
Fast Separation of Polycyclic Aromatic Hydrocarbons in Electronic Components by GC-MS on a 10 meter Zebron™ ZB-PAH-EU



GC-MS Method Parameters

Column: Zebron ZB-PAH-EU
Dimensions: 10 meter x 0.10 mm x 0.08 µm
Part No.: 7CB-G043-59
Inlet Liner: Zebron PLUS Straight Z-Liner™ AG2-3B03-05
Injection: Splitless 0.5 minutes @ 290 °C, 0.5 µL
Carrier Gas: Helium @ 0.8 mL/min (constant flow)
Oven Program: 50 °C for 0.5 min to 200 °C @ 38 °C/min to 260 °C @ 18 °C/ min to 290 °C @ 3 °C/min (hold 0.5 min) to 330 °C @ 80 °C/min (hold 0.5 min)
Detector: MSD (Shimadzu® GC-MS-QP2010 Ultra)
Source Temperature: 300 °C
Transfer-line Temperature: 300 °C
Sample: PAH Sample Standard Mix (Part No. AE-00025-10ML, AccuStandard®)

Analyte Name	RT (min)
Naphthalene	2.69
Acenaphthylene	3.74
Acenaphthene	3.85
Fluorene	4.15
Phenanthrene	4.88
Anthracene	4.92
Fluoranthene	6.00
Pyrene	6.28
Benz[a]anthracene	7.68
Chrysene	7.78
Benzo[b]fluoranthene	9.33
Benzo[k]fluoranthene	9.38
Benzo[j]fluoranthene	9.43
Benzo[a]pyrene	9.99
Benzo[e]pyrene	10.10
Indeno[1,2,3-cd]pyrene	12.70
Dibenz[a,h]anthracene	12.85
Benzo[g,h,i]perylene	13.52

Results

- Separation and good resolution of 18 PAH analytes in 25 minutes using the ZB-PAH-EU 30 meter column (**Figure 1a**)
    - o The Zebron ZB-PAH-EU GC column had a 48 % improvement from the IEC method PAH analysis (down from 45 minutes)
    - o There was an 11 % faster run time versus the competitive 30 meter product (**Figure 1b**)
    - o Another 45 % improvement was then generated by going to the 10 meter Zebron ZB-PAH-EU GC colum which provided a 13.5 minute run time (**Figure 2**)
- The efficiency and separation were also improved for the Benzo[b,j,k] fluoranthenes with a resolution of 1.1 and 1.4
- There was an achieved baseline separation for Indeno[1,2,3-cd] pyrene and Dibenz[a,h]anthracene with a 2.2 resolution value.

Discussion

In order to optimize the GC-MS analysis run time, it is important to choose the best GC column selectivity and dimensions. The Zebron ZB-PAH-EU GC column was chosen for this analysis because its proprietary stationary phase is optimized for separation and retention of polycyclic aromatic compounds. In addition, the unique, highly efficient column is available in an improved dimension format to further optimize the method.

The ZB-PAH-EU stationary phase undergoes rigorous Engineered Cross Linking (ESC™) to provide a low bleed stationary phase suitable for GC-MS analysis. This also provides a higher upper temperature limit of 340/360 °C which helps in eluting higher boiling PAH analytes, in addition to offering a seamless bake out of matrix contamination. Every column is individually QC tested to provide consistent performance. The ZB-PAH-EU offers enhanced resolution of the PAHs, preventing co-elution of interfering PAHs that can cause false positives and inaccurate results

Conclusion

Zebron ZB-PAH-EU offers proprietary selectivity to resolve critical components. The run time of IEC 62321-10 Ed. 1.0 test method can be significantly expedited by multiple factors of 1.9 to 3.4. The Zebron ZB-PAH-EU successfully separates the three Benzo Fluoranthenes (b,j,k) with a resolution of 1.1 and 1.4 and also an achieved baseline separation for Indeno[1,2,3-cd]pyrene and Dibenz[a,h]anthracene with a resolution of 2.2. In addition to method improvements, the ZB-PAH-EU performs exceptional with great thermal stability and with very low column bleed, making it an excellent candidate for PAH analysis by GC-MS for the European commercial electronics' environmental testing compliance.

Zebron™ ZB-PAH-EU GC Column Ordering Information

Length (m)	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

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