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APPLICATIONS

An Improved Test Method for Measuring Polycyclic Aromatic Hydrocarbons in Electronic Components using Zebron™ ZB-PAH by GC-MS

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Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are hazardous for both our human health and the environment. Many PAHs have toxic, mutagenic and/or carcinogenic properties. PAHs are found naturally in the environment and they are also created as environmental pollutants during the incomplete combustion of organic materials. PAHs can be found in consumer products, such as toys, sporting goods, tools, shoes, and electronics. According to the German Federal Institute for Risk Assessment (BFR) "Products for everyday use by consumers and children in particular sometimes displayed very high PAH contents".[11]

PAHs are not easily dissolved in water and they are lipophilic which means they are readily absorbed and distributed in an organisms fatty tissues. In general, the more aromatic rings in the PAH molecule, then the better it accumulates in the body, and in addition PAH can bind to cellular proteins and DNA. It is shown in tests on animals that they can lead to mutations, create both immunosuppressants and birth defects, and in many cases cause cancer. Even worse are the potential nitrogen derivatives of PAH (NPAH) which are even more carcinogenic and mutagenic.

In response to these concerns, the European Union has classified many PAHs as carcinogenic, mutagenic, and reprotoxic (CMR). There are eight PAHs that are included in the REACH Annex XVII restricted substances list. These PAHs are restricted from use in rubber extender oils and articles supplied to the general public, especially to children. The EU Commission Regulation Number 1272/2013, that amends this regulation, lists eight PAH components as classified carcinogenic category 1B. The 8 PAHs included in these regulations are:

1. Benzo[a]pyrene (BaP) CAS No 50-32-8
2. Benzo[e]pyrene (BeP) CAS No 192-97-2
3. Benz[a]anthracene (BaA) CAS No 56-55-3
4. Chrysene (CHR) CAS No 218-01-9
5. Benzo[b]fluoranthene (BbFA) CAS No 205-99-2
6. Benzo[j]fluoranthene (BjFA) CAS No 205-82-3
7. Benzo[k]fluoranthene (BkFA) CAS No 207-08-9
8. Dibenz[a,h]anthracene (DBAhA) CAS No 53-70-3

The EU has created the restriction on commercial articles if they contain more than 1 mg/kg (0.0001 % by weight of this component) of any of the listed PAHs, so that they cannot be placed on the market for supply to the general public, if any of their components come into direct as well as prolonged or short-term repetitive contact with the human skin or the oral cavity while under normal or reasonably foreseeable conditions of use.

In addition, 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 is creating 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).

As of April 2018, the IEC is proposing test method IEC 62321-10 Ed.1.0 with the preliminary title "DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS – Part 10: Polycyclic aromatic hydrocarbons (PAHs) in polymers and electronics by gas chromatography-mass spectrometry (GC-MS)". The proposed method finds PAHs quantitatively by subjecting the electronic component material through an ultrasonic or soxhlet extraction followed by GC-MS, and both qualitatively and quantitatively using selected ion monitoring (SIM). The proposed test procedure creates samples for analysis from the electronic components that are intended to come in human contact, by cryogenically freezing and then grinding off material fine enough to pass through a 500 µm sieve. This fine particle sample will then go through an extraction step, as mentioned above, before it is analyzed.

For the development of the analytical method, the IEC proposes to use a standard solution that is a mix of several suspect PAH chemicals which are the same as those listed in AfPS GS 2014:01 (shown in **Table 1**). Typical analysis run times are 45 to 60 minutes when using test methods that are similar to the proposed IEC 62321-10 Ed.1.0 and the established AfPS GS 2014:01 test procedures.

The following parameters are recommended in the most recent draft of the IEC report:

Column:	5 % phenyl, 95 % methyl polysiloxane or similar
Dimensions:	20 to 30 meters
Injection:	Splitless @ 280 °C, 1 µL
Carrier Gas:	Helium @ 1.0 mL/min (constant flow)
Oven Program:	50 °C to 300 °C @ 10 °C/min
Detector:	MSD @ 280 °C; 50 – 550 amu

Typical run times for the above proposed method are about 45 to 60 minutes, and there is a value for improving the analysis time.

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

	Category 1	Category 2		Category 3	
Parameter		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, mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[e]pyrene, mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benz[a]anthracene, mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[b]fluoranthene, mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[j]fluoranthene, mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[k]fluoranthene, mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Chrysene, mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Dibenz[a,h]anthracene, mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Benzo[g,h,i]perylene, mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Indeno[1,2,3-cd]pyrene, mg/kg	< 0.2	< 0.2	< 0.5	< 0.5	< 1
Acenaphthylene, acenaphthene, fluorene, phenanthrene, pyrene, anthracene, fluoranthene, mg/kg	<1 (sum)	<5 (sum)	<10 (sum)	<20 (sum)	<50 (sum)
Naphthalene, mg/kg	< 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 analytical method using the Zebron™ ZB-PAH GC column was developed for comparison to highlight opportunities to save time and improve the quality of the GC-MS results as compared to the proposed IEC method.

GC-MS Method Parameters

Column: Zebron ZB-PAH
Dimensions: 20 meter x 0.18 mm x 0.14 µm
Part No.: 7FD-G038-47 (serial no. 810330)
Injection: Splitless @ 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 @ 280 °C (Shimadzu® GC-MS-QP2010 Ultra)
Sample: see Table 2 for analyte list

The Zebron ZB-PAH 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 GC has great thermal stability with very low column bleed

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

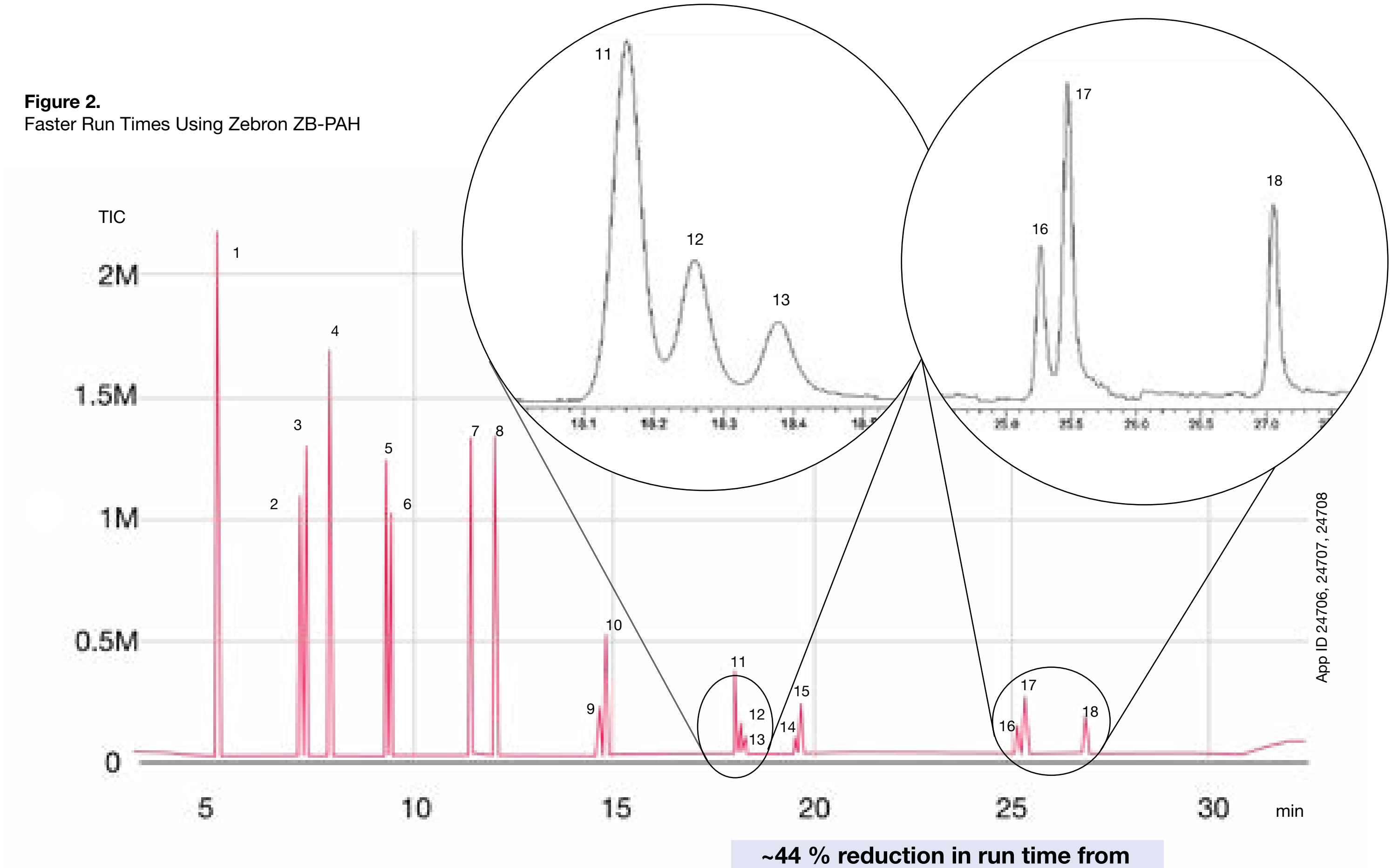
Table 2.
PAH Sample Standard Mix (Part No. AE-00025-10ML, AccuStandard)

Peak Number	Retention Time (minutes)	Analyte	Final Sample Concentration (µg/mL)
1	5.09	Naphthalene	20
2	7.17	Acenaphthylene	10
3	7.34	Acenaphthene	10
4	7.95	Fluorene	16
5	9.32	Phenanthrene	12
6	9.41	Anthracene	10
7	11.51	Fluoranthene	16
8	12.07	Pyrene	16
9	14.72	Benz[a]anthracene	4
10	14.92	Chrysene	8
11	18.16	Benzo[b]fluoranthene	10
12	18.25	Benzo[j]fluoranthene	5
13	18.38	Benzo[k]fluoranthene	4
14	19.62	Benzo[a]pyrene	8
15	19.84	Benzo[e]pyrene	5
16	25.27	Indeno[1,2,3-cd]pyrene	10
17	25.47	Dibenz[a,h]anthracene	16
18	27.05	Benzo[g,h,i]perylene	10

Results

- A 44% faster run time resulted from our new improved method using the Zebron™ ZB-PAH GC column (**Figure 2**)
- The improved method provided greater resolution of critical pairs (resolution value) (**Figure 2**)
- The ZB-PAH offers enhanced resolution of the PAHs, preventing co-elution of interfering PAHs that can cause false positives and inaccurate results
- The improved method successfully separates the three troublesome Benzo Fluoranthenes (b,j,k) with a resolution of 1.1 and 1.3 (**Figure 2**)
- Baseline separation was achieved for Indeno[1,2,3-cd]pyrene and Dibenz[a,h]anthracene with a resolution of 1.56 (**Figure 2**)

Figure 2.
Faster Run Times Using Zebron ZB-PAH



Sample:

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

Conclusion

Run time was significantly reduced by ~ 44 % as compared to the proposed IEC method for PAH analysis. Run times using the ZB-PAH method are ~ 27 minutes as compared to 48 minutes for the proposed IEC method. Efficiency and separation were also improved as we could successfully separate the three Benzo Fluoranthenes (b,j,k) with a resolution of 1.1 and 1.3 and achieved baseline separation for Indeno[1,2,3-cd]pyrene and Dibenz[a,h]anthracene with a resolution of 1.56. In addition to method improvements, the ZB-PAH performs exceptionally with great thermal stability with very low column bleed, making it an excellent candidate for PAH analysis by GC-MS for our commercial electronic's environmental testing compliance.

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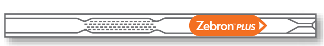
APPLICATIONS

Ordering Information

Zebron PLUS GC Inlet Liners

	Description	Application	Dimensions ID x L (mm)	Unit	Part No.
For Agilent® or Thermo Scientific® GC Systems					
	Single Taper Z-Liner™	Semi-volatiles, dirty samples	4 x 78.5	5/pk	AG2-0A13-05
				25/pk	AG2-0A13-25
	Single Taper with Wool	Semi-volatiles	4 x 78.5	5/pk	AG2-0A11-05
				25/pk	AG2-0A11-25

Zebron™ GC Columns

Phase	ID (mm)	df (µm)	Length (m)	Part No.
ZB-PAH	0.18	0.14	20	7FD-G038-47
ZB-PAH	0.25	0.25	30	7HG-G038-11
ZB-PAH	0.25	0.25	60	7KG-G038-11

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