PAH Analysis: GC Column Selection and Best Practices for Success

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Abstract

Incomplete combustion of organic fuels such as coal, petroleum and wood leads to the formation of polycyclic aromatic hydrocarbons (PAHs) that can then enter the environment or the food supply. Mixtures of these materials can spread widely from an original combustion source in the form of smoke, particulates in the air, or contaminates in soil or water. Some of the components in this chemical class are carcinogenic and need ongoing monitoring to preserve the health of both our food supply and environment worldwide.

European Union (EU) regulation of PAHs focuses on contamination in the food supply while US-Environmental Protection Agency (EPA) regulation has historically focused on PAHs from environmental sources. The regulated lists of PAHs from each authority are distinct with some overlapping compounds. The EU list contains heavier molecular weight PAHs that require higher elution temperatures for GC/MS. Separation of 3 isomers of benzofluoranthene is particularly challenging. A variety of non-polar and moderately polar capillary GC columns have been used for these analytes. Non-polar phases are more effective for the lower boiling US-EPA set, while moderately polar phases are more effective for the EU 15 + 1 set.

Important criterion to consider when selecting a column for a given PAH analysis include the sample set being analyzed, the speed of analysis desired, critical pairs to be separated, potential matrix effects and instrument capabilities. Often the analyst must find an appropriate balance of these factors to achieve optimal results in their laboratory. The focus of this presentation is a discussion of best practices in achieving better PAH analysis results.

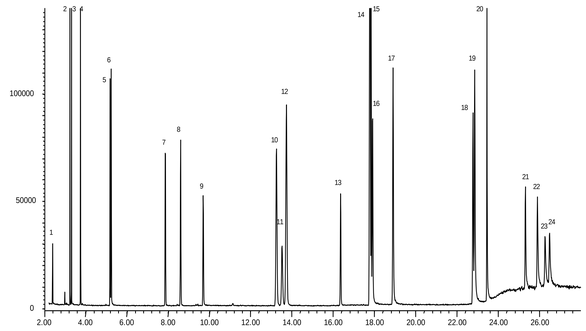
EU 15+1 and US-EPA PAHs

Peak #	Component	CAS #	MW	EU 15+1	EPA
1	Naphthalene	91-20-3	128		x
2	Acenaphthylene	208-96-8	152		x
3	Acenaphthene	83-32-9	154		x
4	Fluorene	86-73-7	166		x
5	Phenanthrene	85-01-8	178		x
6	Anthracene	120-12-7	178		x
7	Fluoranthene	206-44-0	202		x
8	Pyrene	129-00-0	202		x
9	Benzo[c]fluorene	205-12-9	216	x	
10	**Benz[a]anthracene**	56-55-3	228	x	x
11	*Cyclopenta[c,d]pyrene*	27208-37-3	226	x	
12	**Chrysene**	218-01-9	228	x	x
13	*5-Methylchrysene*	3697-24-3	242	x	
14	**Benzo[b]fluoranthene**	205-99-2	252	x	x
15	**Benzo[k]fluoranthene**	207-08-9	252	x	x
16	*Benzo[j]fluoranthene*	205-82-3	252	x	
17	**Benzo[a]pyrene**	50-32-8	252	x	x
18	**Indeno[1,2,3-cd]pyrene**	193-39-5	276	x	x
19	**Dibenz[a,h]anthracene**	53-70-3	278	x	x
20	**Benzo[g,h,i]perylene**	191-24-2	276	x	x
21	*Dibenzo[a,l]pyrene*	191-30-0	302	x	
22	*Dibenzo[a,e]pyrene*	192-65-4	302	x	
23	*Dibenzo[a,i]pyrene*	189-55-9	302	x	
24	*Dibenzo[a,h]pyrene*	189-64-0	302	x	

Table 1. Regulated PAH compounds shown in plain text are included only in the US-EPA set, compounds in *Italic* are included only in the *EU 15+1 list*, and the compounds in **bold** are included in **both the US-EPA and EU 15+1 lists**.

Example Chromatograms

European Union 15+1 and US-EPA PAH Separation
Agilent J&W DB-EUPAH 20m x 0.18mm x 0.14µm



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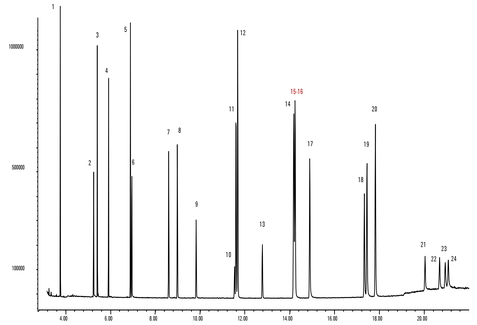
17	Benzo[a]pyrene
18	Indeno[1,2,3-cd]pyrene
19	Dibenz[a,h]anthracene
20	Benzo[g,h,i]perylene
21	Dibenzo[a,l]pyrene
22	Dibenzo[a,e]pyrene
23	Dibenzo[a,i]pyrene
24	Dibenzo[a,h]pyrene

7890/5975C GC/MSD Conditions

Sample: 0.5 µl 1-2 ug/ml EU+ EPA PAHs
Column: Agilent J&W DB-EUPAH 20 m x 0.18 mm x 0.14 µm (Agilent part # 121-9627)
Carrier: He, 60 cm/sec 1.8 ml/min constant flow
Oven: 70 °C (0.8 min) to 180 °C (70 °C/min) ,7 °C/min to 230 °C (6 min hold) , to 280 °C (40 °C/min, 5 min hold), to 335 °C (25 °C/min, 5 min hold)
Inlet: splitless 300 °C, switched purge flow 100 ml/min at 0.25 min,
MSD: Sim/Scan mode 50-400 AMU, transfer line 340 °C, source 340 °C, quad 150 °C

European Union 15+1 and US-EPA PAH Separation
Agilent J&W DB-5ms 20m x 0.18mm x0.18µm



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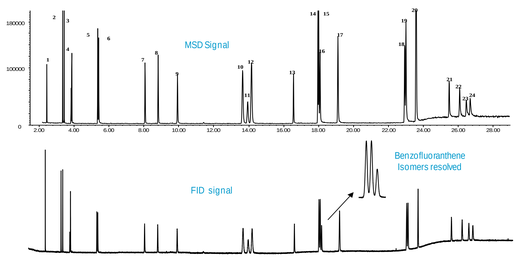
23	Dibenzo[a,i]pyrene
24	Dibenzo[a,h]pyrene

7890/5975C GC/MSD Conditions

Sample: 0.5 µL 1-2 µg/mL EU + EPA PAHs
Column: Agilent J&W DB-5ms 20 m x 0.18 mm x 0.18 µm (Agilent part # 121-5522)
Carrier: He, 60 cm/sec 1.8 ml/min constant flow
Oven: 55 C (0.4 min) to 200 C (25 C/min), 8 C /min to 280 C, 10 C/min to 320 C (2 min)
Inlet: splitless 300 C purge flow 50 ml/min at 0.35 min, switched septum purge 6 ml/min
MSD: transfer line 340 C, source 340 C, quad 180 C (TAD)

European Union 15+1 and US-EPA PAH Separation
Agilent J&W DB-EUPAH 20m x 0.18mm x0.18µm with back-flush



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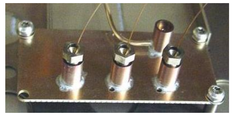
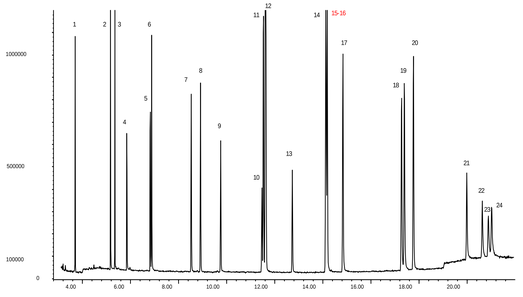
7890/5975C GC/MSD Conditions

Sample: 0.5 µl 1-2 ug/ml EU+ EPA PAHs
Column: 1) Agilent J&W DB-EUPAH 20 m x 0.18 mm x 0.14 µm (Agilent part # 121-9627)
2) 0.8m x 0.15mm ID flow restrictor (EPC to FID)
3) 1.1 m x 15mm ID flow restrictor (EPC to MSD)
Carrier: He, 52 cm/sec 1.8 ml/min constant flow, AUX EPC 3.8 PSI constant pressure during run
Back-flush: Post run 4 minutes inlet pressure 2 PSI AUX EPC 72 PSI
Oven: 70 °C (0.8 min) to 180 °C (70 °C/min) ,7 °C/min to 230 °C (6 min hold) , to 280 °C (40 °C/min, 5 min hold), to 335 °C (25 °C/min, 5 min hold)
Inlet: splitless 300 °C, switched purge flow 100 ml/min at 0.25 min,
MSD: Sim/Scan mode 50-400 AMU, transfer line 340 °C, source 340 °C, quad 150 °C

2-way Purged Splitter Agilent Part # G3180B



European Union 15+1 and US-EPA PAH Separation
Agilent J&W DB-5ms 20m x 0.18mm x 0.18µm with back-flush



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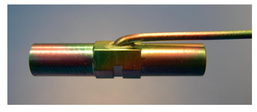
24	Dibenzo[a,h]pyrene

7890/5975C GC/MSD Conditions

Sample: 0.5 µl 1-2 µg/mL EU + EPA PAHs
Column: 1) 2 m x 0.25 mm high temp deactivated tubing (Agilent Part # 160-2845-5)
2) Agilent J&W DB-5ms 20 m x 0.18 mm x 0.18 µm (Agilent Part # 121-5522)
Carrier: He, column 1, 58.3 cm/sec constant flow 1.7 ml/min
Back-flush: Post run 0.25 minutes, inlet pressure 2 PSI, PCM pressure 60 PSI
Oven: 55 C (0.3 min) to 200 C (25 C/min), 8 C /min to 280 C,10 C/min to 310 C (2 min)
Inlet: splitless 300 C purge flow 50 ml/min at 0.2 min, switched septum purge 6 ml/min
MSD: transfer line 340 C, source 340 C, quad 150 C (TAD)

Purged Universal Union Agilent Part # G3186A-60580



Results Summary

- DB-EUPAH column resolves combined EU and US-EPA regulated PAHs in under 28 minutes
- DB-5ms column resolves 23 of 24 EU and US-EPA regulated PAHs in under 22 minutes
- Back-flush is available with either approach to minimize deleterious matrix effects

Factors to Consider in Optimizing PAH Analyses

- When benzo[b,j,k]fluoranthene resolution is required choose a DB-EUPAH column.
- When benzo [b,j,k] fluoranthene isomers can be summed choose a DB-5ms column for 27% faster analysis.
- Consider the use of retention gaps and inlet back-flushing to reduce cycle time
- Achieve faster analysis times with no loss of resolution using 0.18 mm ID High Efficiency GC columns.
- Optimize injection volume, temperature, purge time, and solvent focusing on each instrument.
- Minimize inlet and system dwell time with high linear velocities.
- Keep heated zones hot to avoid cold spots

For More Information

To learn more about Agilent J&W GC/MS and Ultra Inert columns – or Agilent products and services – visit us online at www.agilent.com/chem/myGCcolumns

For the specifics on the applications cited here enter the Agilent Publication (XXXX-XXXXEN) number in the part number field for free display or download of the application note

Pertinent References

Polycyclic Aromatic Hydrocarbon (PAH) Analysis Using an Agilent J&W DB-5ms Ultra Inert Capillary GC Column, Kenneth Lynam and Doris Smith, 5989-9181EN

GC/MS Analysis of European Union (EU) Priority Polycyclic Aromatic Hydrocarbons (PAHs) Using an Agilent J&W DB-EUPAH GC Column with a Column Performance Comparison, Doris Smith and Ken Lynam 5990-4883EN

PAH Analyses with High Efficiency GC Columns: Column Selection and Best Practices, Ken Lynam 5990-5872EN