

# 采用安捷伦 J&W DB-EUPAH GC 色谱柱分析橡胶和塑料制品中的 低含量多环芳烃 (PAH)

## Application Note

Gas Chromatography/Mass Spectrometry

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### Abstract

安捷伦 J&W DB-EUPAH GC 色谱柱经专业设计，可用于分析欧盟重点管制的 PAH。本应用介绍了一种 GC/MS 方法，使用此类色谱柱测定橡胶和塑料中的 20 种 PAH，包括 16 种 EPA 重点管制的 PAH 以及 4 种受到普通监控的 PAH（包括苯并[*j*]荧蒽、苯并[*e*]芘、2-甲基萘和 1-甲基萘）。为了确保结果的准确性，在定量时使用了五种同位素标记的 PAH（氘代萘、氘代蒽、氘代菲、氘代屈和氘代芘）作为内标，并采用氘代三联苯作为替代标准品。所有 26 种化合物都能够通过 DB-EUPAH 色谱柱很好地实现分离。结果具有良好的线性和样品回收率，证明本应用摘要中描述的方法在针对复杂样品基质中的目标 PAH 进行痕量检测和确认时具有较高的选择性。



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## Introduction

Polycyclic aromatic hydrocarbons (PAHs), containing two to eight aromatic rings [1], are identified as some of the most persistent organic pollutants (POPs). Due to their well known carcinogenic and mutagenic properties, some PAHs are classified as priority pollutants by both the U.S. EPA and the European Commission. The U.S. EPA designated 16 PAH compounds as priority pollutants, including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene. The 16 EPA priority PAHs are often targeted for measurement in environmental samples.

PAHs may be present in oil, coal, rubber, and plastics. Some rubber products such as tires are produced using extender oils that may unintentionally contain various levels of PAHs. These extender oils along with the PAHs are incorporated into the rubber matrix and remain locked in the final products. In 2005, the European Commission adopted a Directive [2] restricting the marketing and use of certain PAHs in extender oils for tire production. All tires produced after 1 January 2010 are required to comply with the new Directive.

In the Directive, extender oils may not be used for the production of tires if they contain more than 1 mg/kg benzo(a)pyrene (BaP), or more than 10 mg/kg of the sum of the eight PAHs of concern including benzo(a)pyrene (BaP), benzo(e)pyren (BeP), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbFA), benzo(j)fluoranthene (BjFA), benzo(k)fluoranthene (BkFA) and dibenzo(a, h)anthracene (DBaHA). BeP and BjFA were not included in 16 EPA-regulated priority PAHs.

Five percent phenyl methylpolysiloxane stationary phase was the most commonly-cited GC column for the analysis of the 16 EPA-regulated PAHs, [3,4]. The resolution of the Benzo(b,k,j)fluoranthenes isomers were not easily obtained using this GC column.

In this application note, a DB-EUPAH column was chosen to provide the necessary separation for all 20 PAHs of interest in rubber and plastic articles. This includes the resolution of all the critical isomers such as the benzo(b,k,j)fluoranthenes. With its exceptional thermal stability, low column bleed at elevated temperatures, and consistent column inertness, the Agilent J&W DB-EUPAH column delivers fast, reliable results while meeting demanding regulatory requirements.

## Experimental

The experiments were performed on one Agilent 7890 gas chromatograph equipped with an Agilent 5975C series GC/MSD, and an Agilent 7683 Automatic Liquid Sampler (ALS). The instrument conditions are listed in Table 1.

### Chemicals and Standards

All standards in the experiment were purchased from Sigma-Aldrich (St. Louis, MO, USA). The CAS numbers and nominal molecular mass are provided in Table 2.

### Surrogate Spiking Solution

p-Terphenyl-d14 was used as a surrogate standard in this experiment. The surrogate spiking solution was prepared from aliquots of pure compound diluted with toluene to a concentration of 10 µg/mL, and served as a stock solution. Surrogate solution was added to all samples and all quality control samples prior to extraction.

Table 1. Gas Chromatograph and Mass Spectrometer Conditions

<b>GC Conditions</b>	
Column:	Agilent J&W DB-EUPAH, 20 m × 0.18 mm × 0.14 µm (Agilent p/n 121-9627)
Inlet temperature:	290 °C
Carrier gas:	Helium, constant flow mode, 52 cm/s
Injection mode:	Splitless, purge flow 50 mL/min at 0.75 min
Injection volume:	1 µL
Oven:	120 °C (1 min), 8 °C/min to 200 °C (0.5 min), 11 °C/min to 270 °C, 2 °C/min to 300 °C,
Post run:	320 °C (4 min)
<b>MS Conditions</b>	
Solvent delay:	2.8 min
MS temp:	250 °C (Source); 180 °C (Quad)
Transfer line:	290 °C
MS:	EI, SIM/Scan
Scan mode:	Mass range (50-450 amu)
For other parameters, see Table 2	
<b>Miscellaneous Parts</b>	
Septa:	Long-lifetime septa (Agilent p/n 5183-4761)
Liner:	Splitless deactivated dual taper direct connect liner (Agilent p/n G1544-80700).
Syringe	5 µL syringe (Agilent p/n 5181-1273)

Table 2. Polycyclic Aromatic Hydrocarbons, CAS Number, Nominal Molecular Mass and Corresponding Ions

Compound	CAS No.	Nominal molecular mass	Corresponding ions
Naphthalene-d8*	1146-65-2	136	<b>136</b> , 108, 68
Acenaphthene-d10*	15067-26-2	164	<b>164</b> , 160
Phenanthrene-d10*	1719-06-8	188	<b>188</b>
Chrysene-d12*	1719-03-5	240	<b>240</b> , 236, 120
p-Terphenyl-d14**	1718-51-0	244	<b>244</b> , 122, 212
Perylene-d12*	1520-96-3	264	<b>264</b> , 265, 260
Naphthalene	91-20-3	128	<b>128</b> , 127, 129
2-methylnaphthalene	91-57-6	142	<b>142</b> , 141, 115
1-methylnaphthalene	90-12-0	142	<b>142</b> , 141, 115
Acenaphthylene	208-96-8	152	<b>152</b> , 153, 151
Acenaphthene	83-32-9	154	<b>153</b> , 154, 152
Fluorene	86-73-7	166	<b>166</b> , 165, 167
Phenanthrene	85-01-8	178	<b>178</b> , 176, 179
Anthracene	120-12-7	178	<b>178</b> , 176, 179
Fluoranthene	206-44-0	202	<b>202</b> , 200, 101
Pyrene	129-00-0	202	<b>202</b> , 200, 101
Benzo(a)anthracene	56-55-3	228	<b>228</b> , 226, 229
Chrysene	218-01-9	228	<b>228</b> , 226, 229
Benzo(b)fluoranthene	505-99-2	252	<b>252</b> , 253, 126
Benzo(j)fluoranthene	205-82-3	252	<b>252</b> , 253, 126
Benzo(k)fluoranthene	207-08-9	252	<b>252</b> , 253, 126
Benzo(e)pyrene	192-97-2	252	<b>252</b> , 253, 126
Benzo(a)pyrene	50-32-8	252	<b>252</b> , 253, 126
Indeno(1,2,3-cd)pyrene	193-39-5	276	<b>276</b> , 138, 277
Dibenzo(a,h)anthracen	53-70-3	278	<b>278</b> , 139, 279
Benzo(g,h,i)perylene	191-24-2	276	<b>276</b> , 138, 277

1. \* Internal standard

2. \*\* surrogate standard

3. Suggested quantitative ions are in bold.

## Internal Standard Solution

The internal standard solution included naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12. The internal standard solution was made from aliquots of pure compounds, diluted with toluene to a concentration of 10 µg/mL, and served as a stock solution.

## Calibration Solution

Calibrations solutions were prepared in five different concentrations ranging from 5 to 500 ppb by diluting commercially available certified solutions containing analytes of interest. Each standard solution contained 500 µg/L of internal standards (ISTDs).

## Sample Preparation

According to ZLS standard ZEK 01.2-08 to prepare samples, rubber and plastic articles were cut into pieces no larger than 2–3 mm in size. Five hundred milligrams of cut pieces were extracted by 20 mL of toluene and mixed with internal standards for 1 hour in the ultrasonic bath at a temperature of 60 °C. After cooling to room temperature, an aliquot was taken from the extract for analysis.

One rubber sample and one plastic sample spiked with PAHs of interest at the 100 ppb level respectively were treated according to the procedure described above.

## Results and Discussion

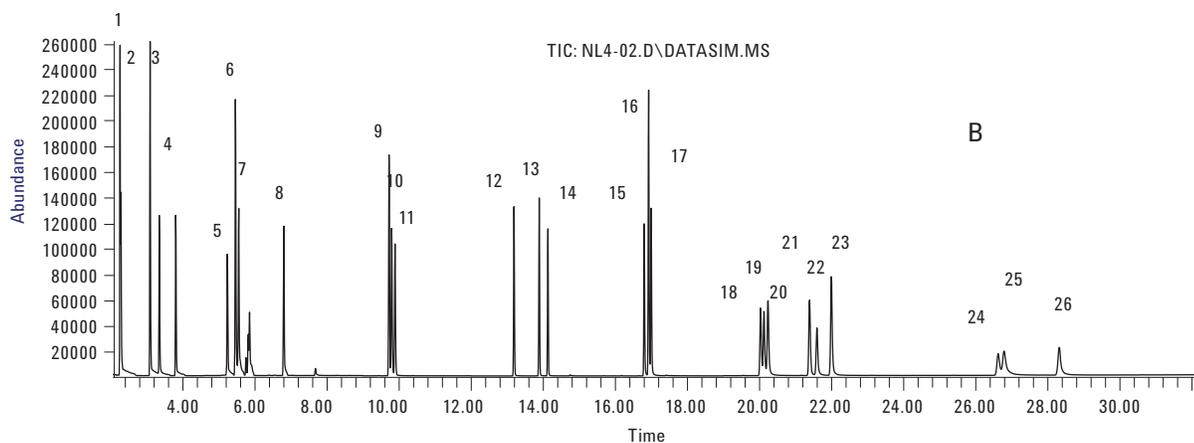
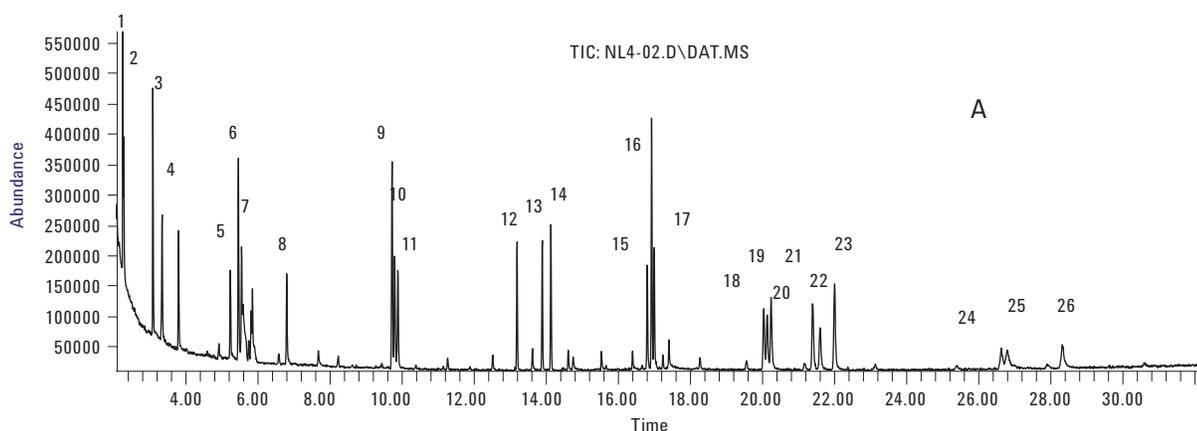
Figure 1 shows the GC/MS total ion chromatograms for the compounds of interest. Due to the presence of isomers, some compounds listed in Table 2 with the same quantitation ions could be eluting quite closely. Therefore good resolution is very important for these isomers to achieve accurate quantitative results. As shown in Figure 1, all 20 targeted PAH compounds were well-resolved with the DB-EUPAH column.

Figure 2 exhibits the baseline resolution of some critical PAH pairs of interest, including phenanthrene and anthracene ( $m/z$  178), fluoranthene and pyrene ( $m/z$  202), benzo[a]anthracene and chrysene ( $m/z$  228), with excellent peak shapes using the DB-EUPAH column.

Benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(e)pyrene and benzo(a)pyrene are isomers with the same quantitation ion ( $m/z$  252). According to 2005/ 69/ EC Directive, the content of benzo(a)pyrene was restricted to be less than 1 mg/kg. Figure 2 shows that benzo(a)pyrene can be separated well, and the resolution of benzo(a)pyrene and benzo(e)pyrene is 2.82 with the DB-EUPAH column. Benzo(b, k, j)fluoranthenes are difficult-to-chromatograph isomers. Benzo(b)fluoranthene (BbFA) and benzo(j)fluoranthene (BjFA) often show coelution on the commonly used 5% phenyl methylpolysiloxane stationary phase GC column. The resolution of benzo(b, j, k)fluoranthene is 1.41

and 1.63 respectively, meeting the requirement of analysis. The three benzo(b,k,j)fluoranthene isomers could be baseline separated, however, with the compromise of a extra 10-min run time. Therefore, it is a trade-off between speed and resolution. The described method in this application note was chosen to provide a reasonable sample run time when meeting the regulatory requirements.

Calibration curves were constructed from the data obtained by the 1- $\mu$ L injections of standards at 5, 50, 100, 250, 500 ppb. Each standard solution contained 500 ppb of internal standards (ISTDs). All the PAHs have excellent linearity with calibration coefficients greater than 0.998 as shown in Table 3.



- |                        |                     |                          |                            |
|------------------------|---------------------|--------------------------|----------------------------|
| 1. Naphthalene-d8      | 8. Fluorene         | 15. Benzo(a)anthracene   | 22. Benzo(a)pyrene         |
| 2. Naphthalene         | 9. Phenanthrene-d10 | 16. Chrysene-d12         | 23. Perylene-d12           |
| 3. 2-methylnaphthalene | 10. Phenanthrene    | 17. Chrysene             | 24. Indeno(1,2,3-cd)pyrene |
| 4. 1-methylnaphthalene | 11. Anthracene      | 18. Benzo(b)fluoranthene | 25. Dibenzo(a,h)anthracene |
| 5. Acenaphthylene      | 12. Fluoranthene    | 19. Benzo(k)fluoranthene | 26. Benzo(g,h,i)perylene   |
| 6. Acenaphthene-d10    | 13. Pyrene          | 20. Benzo(j)fluoranthene |                            |
| 7. Acenaphthene        | 14. p-Terphenyl-d14 | 21. Benzo(e)pyrene       |                            |

Figure 1. Twenty PAHs at 250 ppb each with ISTDs at 500 ppb each and surrogate at 250 ppb, using synchronous SIM/SCAN mode, A: SCAN mode B: SIM mode.

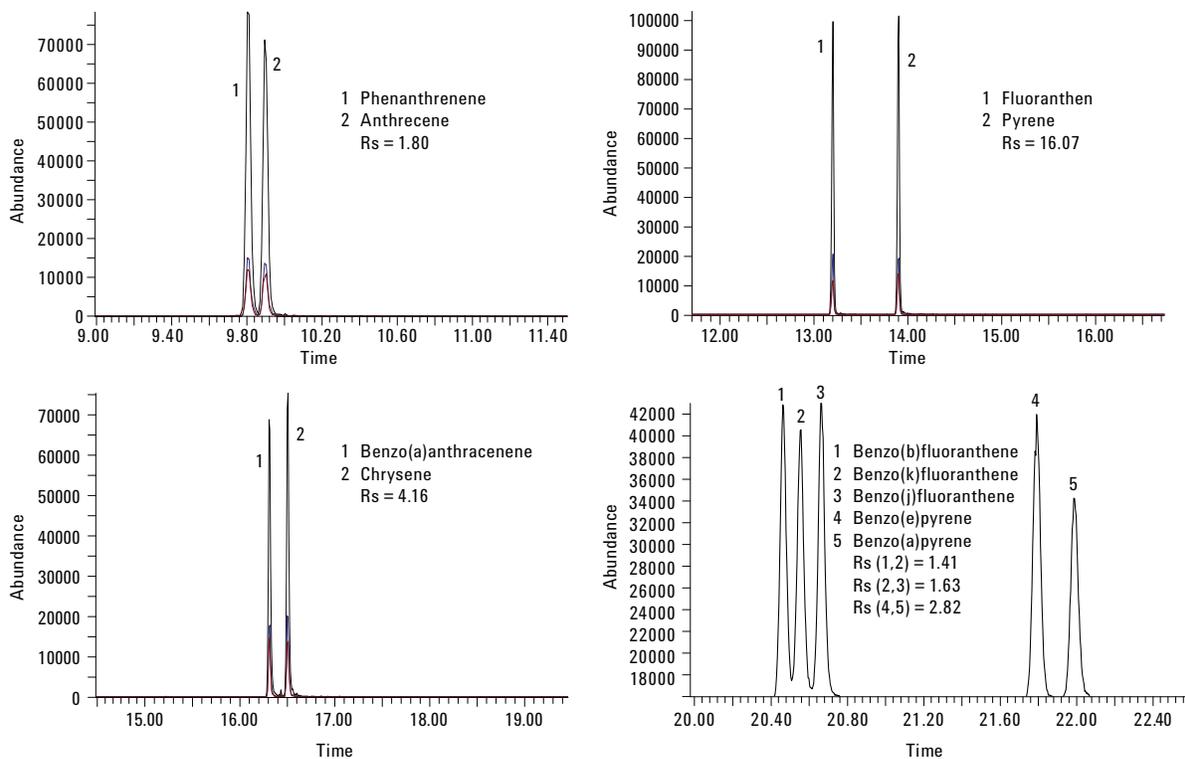


Figure 2. Resolution of Critical isomer Pairs with the DB-EUPAH column, 20 m × 0.18 mm × 0.14 μm (Agilent p/n 121-9627).

The GC/MS TIC for matrix spiked extract is illustrated in Figure 3. The spiked samples were treated according to the procedure described in the sample preparation. The recovery data for the spiked samples are listed in Table 4. All data were based on three replicates of matrix spikes with the 20 targeted PAHs at the 100 ppb level. Good recoveries were achieved for all the compounds, ranging from 73.5% to 119.4%, satisfying both the US-EPA and EU regulatory requirements.

## Conclusion

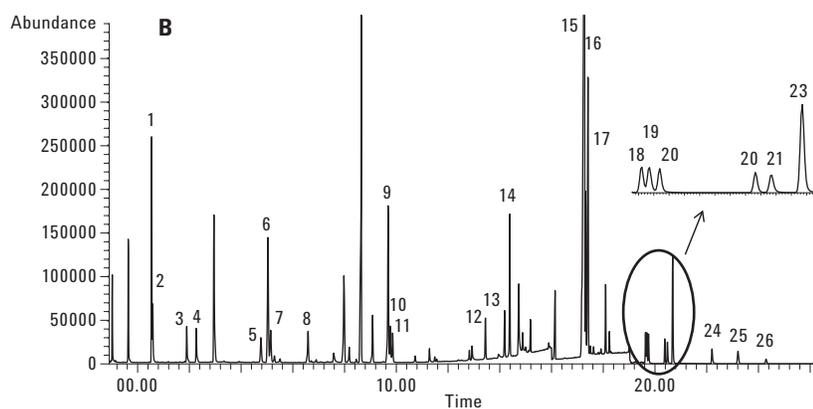
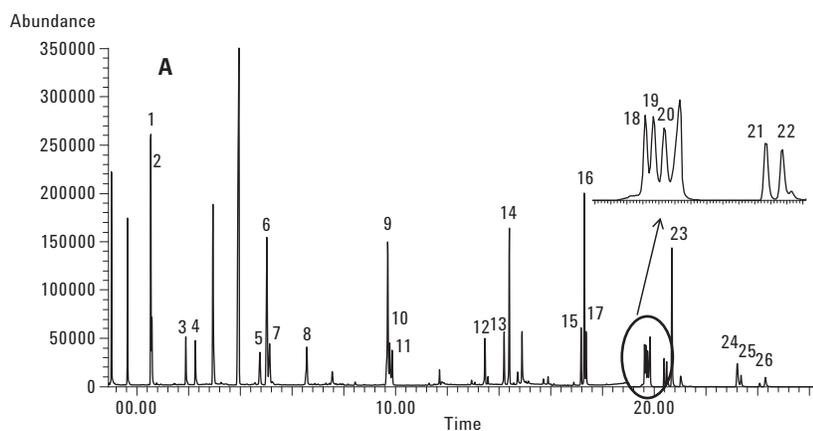
This application demonstrates a highly sensitive and selective GC/MS method for PAH analysis in rubber and plastic products using an Agilent J&W DB-EUPAH GC column. The DB-EUPAH column can effectively separate the 20 PAHs of interest, resolving all the critical, difficult-to-separate pairs. The system allows for trace-level detection of the PAHs in rubber and plastic articles. Good linearity and recoveries were achieved for all targeted compounds. The Agilent J&W DB-EUPAH column delivers fast, reliable results while meeting the requirements of both EPA and EU regulatory methods.

Table 3. The Regression Equations and Correlation Coefficient of PAHs

Compound	Range of linearity (ng)	Correlation coefficient (R <sup>2</sup> )
Naphthalene	0.005-0.5	0.9997
2-Methylnaphthalene	0.005-0.5	0.9999
1-Methylnaphthalene	0.005-0.5	0.9998
Acenaphthylene	0.005-0.5	0.9996
Acenaphthene	0.005-0.5	0.9999
Fluorene	0.005-0.5	0.9994
Phenanthrene	0.005-0.5	0.9999
Anthracene	0.005-0.5	0.9992
Fluoranthene	0.005-0.5	0.9990
Pyrene	0.005-0.5	0.9996
Benzo[a]anthracene	0.005-0.5	0.9985
Chrysene	0.005-0.5	0.9998
Benzo[b]fluoranthene	0.005-0.5	0.9998
Benzo[j]fluoranthene	0.005-0.5	0.9983
Benzo[k]fluoranthene	0.005-0.5	0.9990
Benzo[e]pyrene	0.005-0.5	0.9992
Benzo[a]pyrene	0.005-0.5	0.9997
Indeno[1,2,3-c,d]pyrene	0.005-0.5	0.9989
Dibenzo[a,h]anthracene	0.005-0.5	0.9989
Benzo[g,h,i]perylene	0.005-0.5	0.9993

Table 4. Recoveries of PAHs in Substantial Plastic Sample and Rubble Sample

Compounds	Spiked (ppb)	Recovery (%) plastic sample	Recovery (%) rubber sample
Naphthalene	100	101.99	106.7
2-Methylnaphthalene	100	93.3	95.7
1-Methylnaphthalene	100	91.22	92.6
Acenaphthylene	100	111.32	120.8
Acenaphthene	100	98.45	109.0
Fluorene	100	107.66	114.6
Phenanthrene	100	92.54	109.1
Anthracene	100	106	110.8
Fluoranthene	100	110.52	119.4
Pyrene	100	111.62	104.0
Benzo[a]anthracene	100	102.61	118.5
Chrysene	100	107.67	95.9
Benzo[b]fluoranthene	100	103.18	114.6
Benzo[j]fluoranthene	100	103.02	118.9
Benzo[k]fluoranthene	100	91.13	88.8
Benzo[e]pyrene	100	90.8	92.3
Benzo[a]pyrene	100	106.58	119.2
Indeno(1,2,3-cd)pyrene	100	75.36	79.9
Dibenzo(a,h)anthracen	100	80.47	89.9
Benzo(g,h,i)perylene	100	76.45	73.5



- |                        |                     |                          |                            |
|------------------------|---------------------|--------------------------|----------------------------|
| 1. Naphthalene-d8      | 8. Fluorene         | 15. Benzo(a)anthracene   | 22. Benzo(a)pyrene         |
| 2. Naphthalene         | 9. Phenanthrene-d10 | 16. Chrysene-d12         | 23. Perylene-d12           |
| 3. 2-methylnaphthalene | 10. Phenanthrene    | 17. Chrysene             | 24. Indeno(1,2,3-cd)pyrene |
| 4. 1-methylnaphthalene | 11. Anthracene      | 18. Benzo(b)fluoranthene | 25. Dibenzo(a,h)anthracen  |
| 5. Acenaphthylene      | 12. Fluoranthene    | 19. Benzo(k)fluoranthene | 26. Benzo(g,h,i)perylene   |
| 6. Acenaphthene-d10    | 13. Pyrene          | 20. Benzo(j)fluoranthene |                            |
| 7. Acenaphthene        | 14. p-Terphenyl-d14 | 21. Benzo(e)pyrene       |                            |

Figure 3. TIC of matrix spiked extract using Agilent GC/MS system and Agilent J&W DB-EUPAH 20 m × 0.18 mm, 0.14 μm column (Agilent p/n 121-9627) A: plastic, B: rubber.

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