

# Application Note: An evaluation of the analysis of polyaromatic hydrocarbons (PAHs) using a gas chromatograph-flame ionisation detector (GC-FID) with generated & cylinder/compressor gases

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## Introduction

PAHs are aromatic hydrocarbons with two or more fused benzene rings. PAHs are colourless WPGCFID-00-EN ss, white and pale yellow solids with low solubilities in water, high melting and boiling points and low vapour pressure. With increases in molecular weight, their solubility in water decreases; melting and boiling point increases and vapour pressure decreases <sup>[1]</sup>. The chemical structures of some commonly studied PAHs, such as those outlined in this application note, are shown in **Figure 1**.

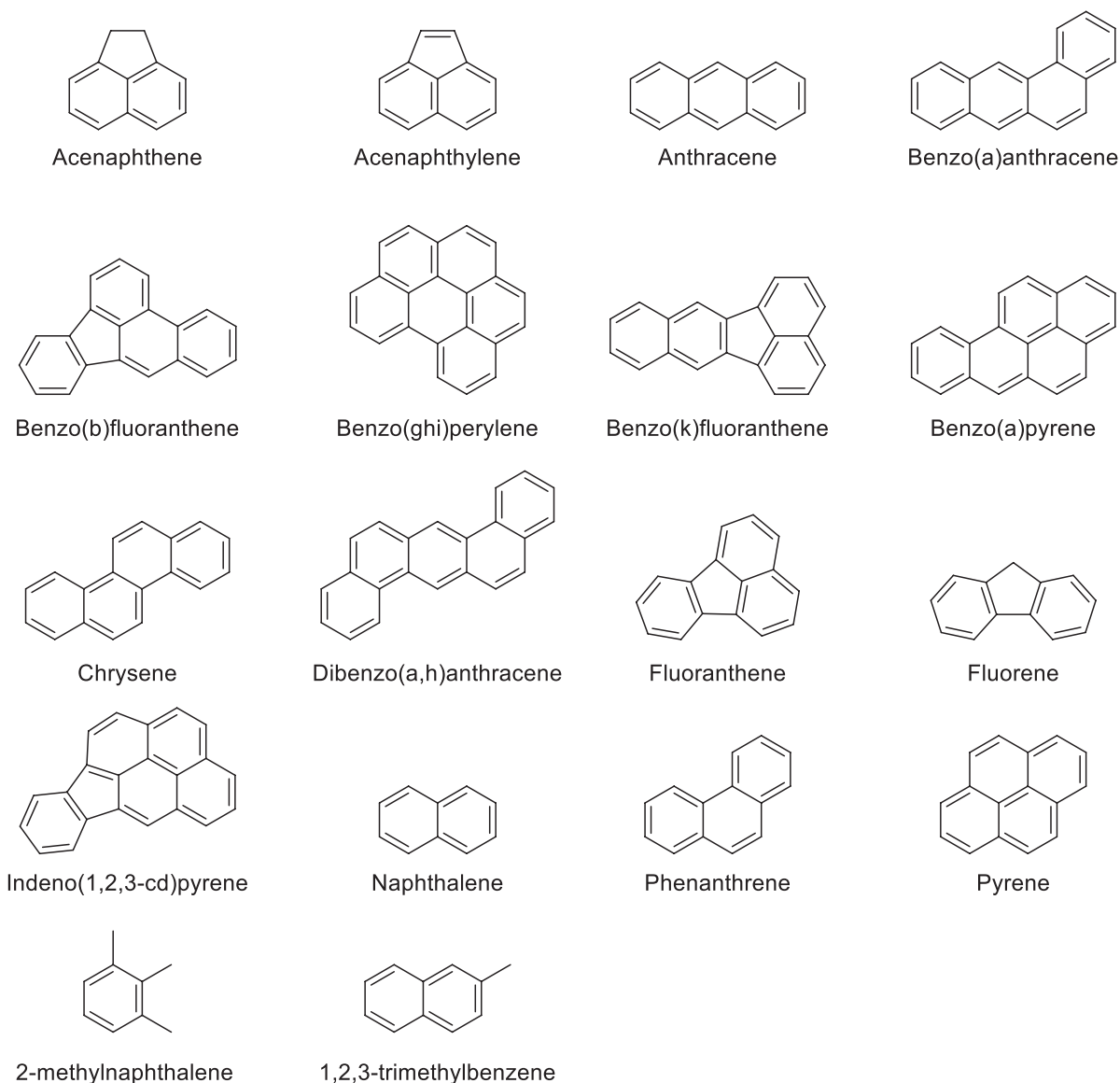
Common sources of PAHs in the environment are both natural and anthropogenic. They are formed during the thermal decomposition of organic molecules and their subsequent recombination. Natural sources include forest fires, oil seeps, volcanic eruptions, coal and wood. Man-made sources of PAHs include the burning of fossil fuel, coal tar, wood, garbage, refuse, used lubricating oil, oil filters, waste incineration, mining or industrial activities such as aluminium, iron and steel production<sup>[2]</sup>.

PAHs are ubiquitously present and are toxic, mutagenic and carcinogenic <sup>[2,3]</sup>. They have attracted concern because of their presence in all components of the environment, their resistance towards biodegradation under natural conditions, their potential to bio-accumulate and their carcinogenic activity <sup>[2]</sup>.

Due to these concerns, PAHs are a class of compounds that are regulated by the US Environmental Protection Agency (USEPA) and the European Union (EU)<sup>[4]</sup>. Within this class, 16 are marked as priority pollutants and these range from the two-ringed naphthalene to multi-ring structures such as benzo[a]pyrene. Analysis is typically performed by HPLC, GC-FID or GC-MS techniques. Detection limits vary depending upon the medium used and the analytical technique employed <sup>[4]</sup>.

USEPA Method 610 provides guidance for the analysis of 16 PAHs in wastewater <sup>[4][5]</sup> detailing HPLC and GC-FID approaches. This application note uses GC-FID to evaluate the analysis of 16 USEPA Method 610 PAHs and 2 additional compounds. The study compares the use of on-site generated FID detector gases, supplied by a Parker domnick hunter 110H-MD hydrogen generator and a Parker UHP-75 ZA-S zero air generator, to gases obtained from a hydrogen cylinder and an air compressor. Since the GC-FID detection technique relies upon retention time alone for identification purposes, GC-MS was also employed to confirm the identity of each analyte.





**Figure 1:** USEPA Method 610 PAHs and 2 additional compounds (2-Methyl naphthalene & 1,2,3-Trimethyl benzene) analysed by GC-FID & GC-MS.

USEPA Method 610 was modified to permit the use of capillary columns, in order to improve the speed of analysis and the chromatographic separation of these species. Analytical parameters of USEPA Method 610 and this application note are reported in **Table 1** for comparison.

	USEPA Method 610	Application Note
<b>Columns</b>	Packed column Chromosorb W-AW-DCMS (100/120 mesh) coated with 3% OV-17 1.8 m x 2.0 mm i.d. glass	Capillary column J&W HP5-MS IU 30 m x 0.25 mm i.d. x 0.25 µm
<b>Carrier Gas</b>	Nitrogen	Helium
<b>Carrier Gas flow</b>	40 ml/min	1.4 ml/min
<b>Detector</b>	HPLC/GC-FID	GC-FID & GC-MS

**Table 1:** Comparison of the column and carrier gases of the USEPA Method 610 and those used in this method.

## Experimental

The polyaromatic hydrocarbon standard mix (1000 µg/ml,) was obtained from Thames Restek UK (Catalogue # 31469) and prepared in hexane at six different concentrations (0.05, 0.1, 0.3, 0.5 & 0.75 µg/ml). With a 1 µl splitless injection these concentrations were the equivalent to 0.05 - 0.75 ng on-column injections.

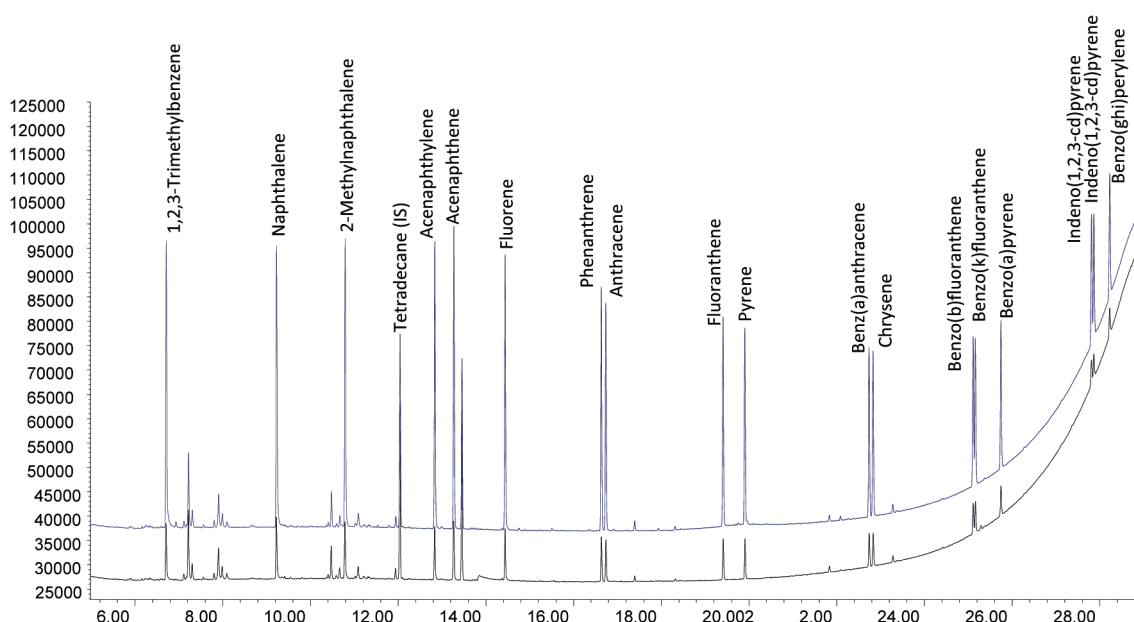
Standard solutions each contained: Acenaphthene, Acenaphthylene, Anthracene, Benz(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(ghi)perylene, Chrysene, Dibenz(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, 2-Methylnaphthalene, Naphthalene, Phenanthrene, Pyrene and 1,2,3-Trimethylbenzene. Tetradecane (0.3 µg/ml) was used as an internal standard in all standard solutions.

Analyses were performed using an Agilent 6890 GC fitted with an OPTIC3 PTV inlet (GLSciences, Eindhoven, The Netherlands) an Agilent FID & Agilent 5973N (inert) MSD ([www.agilent.com](http://www.agilent.com)). Helium carrier gas was supplied from a cylinder (Air Products, CP grade). Hydrogen, as the FID fuel gas, was supplied from a Parker domnick hunter 110H-MD hydrogen generator and a zero-grade hydrogen cylinder (99.995%). The hydrogen cylinder and compressor were located outside the laboratory and supplied via copper tubing to the instrument. Air, the FID oxidising gas, was produced via an air compressor and was used directly and purified by the Parker UHP-75 ZA-S zero air generator. Both gas generators were installed in the laboratory and the instruments were supplied via copper tubing. No additional gas purification traps were installed in the system.

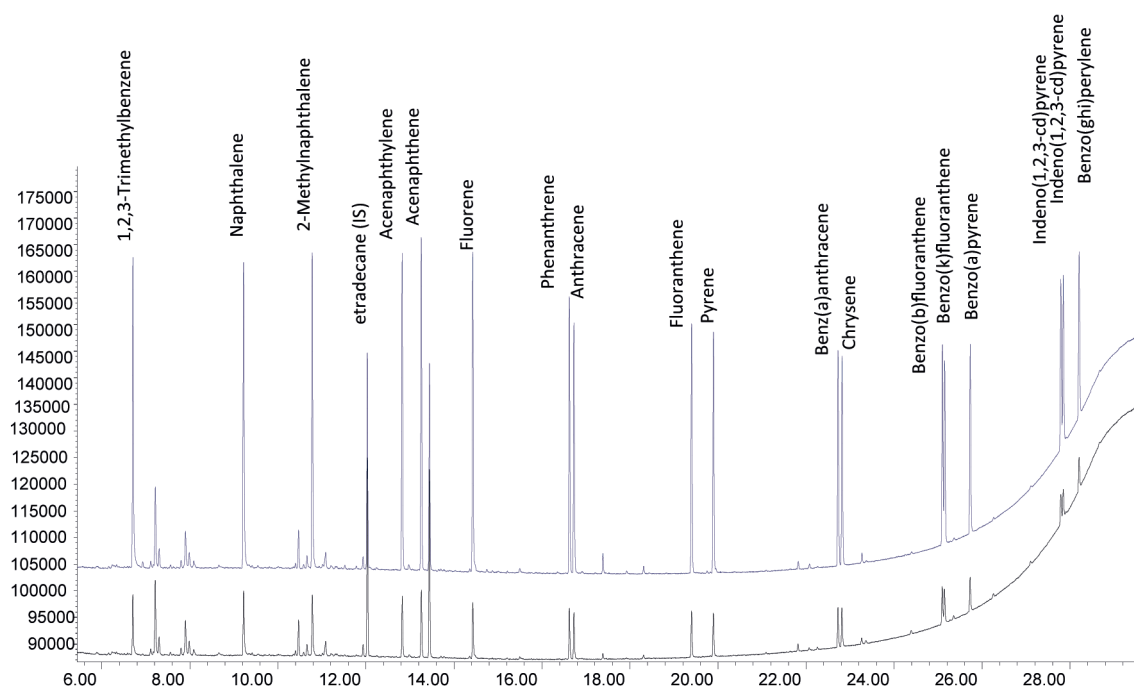
An injection volume of 1 µl was introduced via a 7683 series autosampler. The inlet temperature held at 48°C for 5 seconds followed by heating at a rate of 12 °C/s to 325 °C. A deactivated focus liner (3.4 mm i.d., split/splitless, tapered) was used in the inlet and the analytes were transferred to the column in splitless mode. A pressure pulse injection at 30 psi was held for 1 minute, followed by a constant carrier flow rate of 1.4 ml/min for the separation. Separation was performed on a J&W HP5-MS IU column (30 m x 0.25 mm i.d. x 0.25 µm). The initial GC oven temperature was set at 50 °C and held for 1 minute, following which was raised at a rate of 10 °C/min to 325 °C and held for 5 mins. The FID temperature was set at 325 °C. Hydrogen and air gases flowed through the detector at 30 and 300 ml/min respectively. The data acquisition rate was 10 Hz.

## Results

The chromatograms obtained at concentrations of 0.1 & 0.5 µg/ml, analysed by GC-FID using cylinder/compressor and generated detector gases, are shown in Figures 2 and 3 respectively.



**Figure 2:** Offset chromatograms of the standard mix analysed with a GC-FID using gas supplied by Parker domnick hunter generators at concentrations of 0.1 & 0.5 µg/ml. Each of the 18 species and IS are labelled.

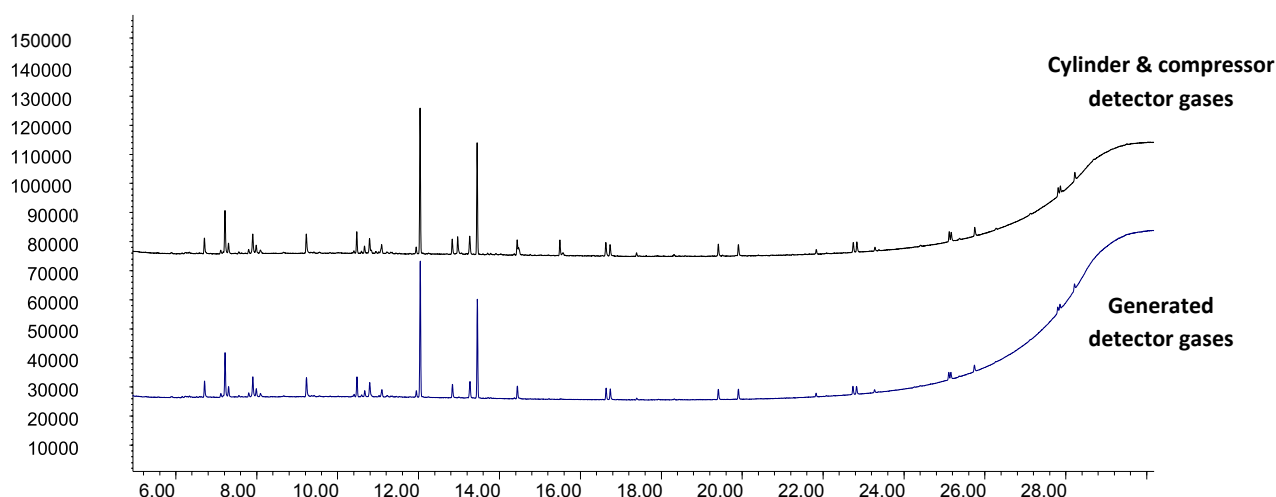


**Figure 3:** Offset chromatograms of the standard mix analysed with a GC-FID at concentrations of 0.1 & 0.5 µg/ml using gas supplied from a cylinder (H<sub>2</sub>) and a compressor (Air). Each of the 18 species and IS are labelled.

It can be seen from the chromatograms that all 18 peaks and the internal standard, tetradecane, were separated and identified.

The peak areas measured for six replicates of 0.05 µg/ml (0.05 ng on-column) were used to calculate Limits of Detection (LODs). A mean concentration for each compound was calculated and the standard deviation ( $\sigma_{n-1}$ ) of this mean was then determined. The LOD was then calculated by multiplying the standard deviation with the value (3.14) for the Students t-test at 99 % confidence level. The repeatability of the six replicates of 0.3 µg/ml (0.3 ng on-column) was calculated as the % relative standard deviation against the mean concentration. **Table 2** reports the retention times, LODs and repeatability for the analysis with both hydrogen and air detector gases obtained from hydrogen cylinder/ air compressor and those generated by Parker domnick hunter products.

Detector gases generated by Parker domnick hunter products benefited from a lower baseline compared to the cylinder/compressor gases, as can be seen in **Figure 4**.



**Figure 4:** Non offset chromatograms of the standard mix analysed with a GC-FID at a concentration of 0.05 µg/ml analysed with a GC-FID using FID hydrogen and air detector gases obtained from cylinder/compressor compared with those produced from Parker domnick hunter generators.

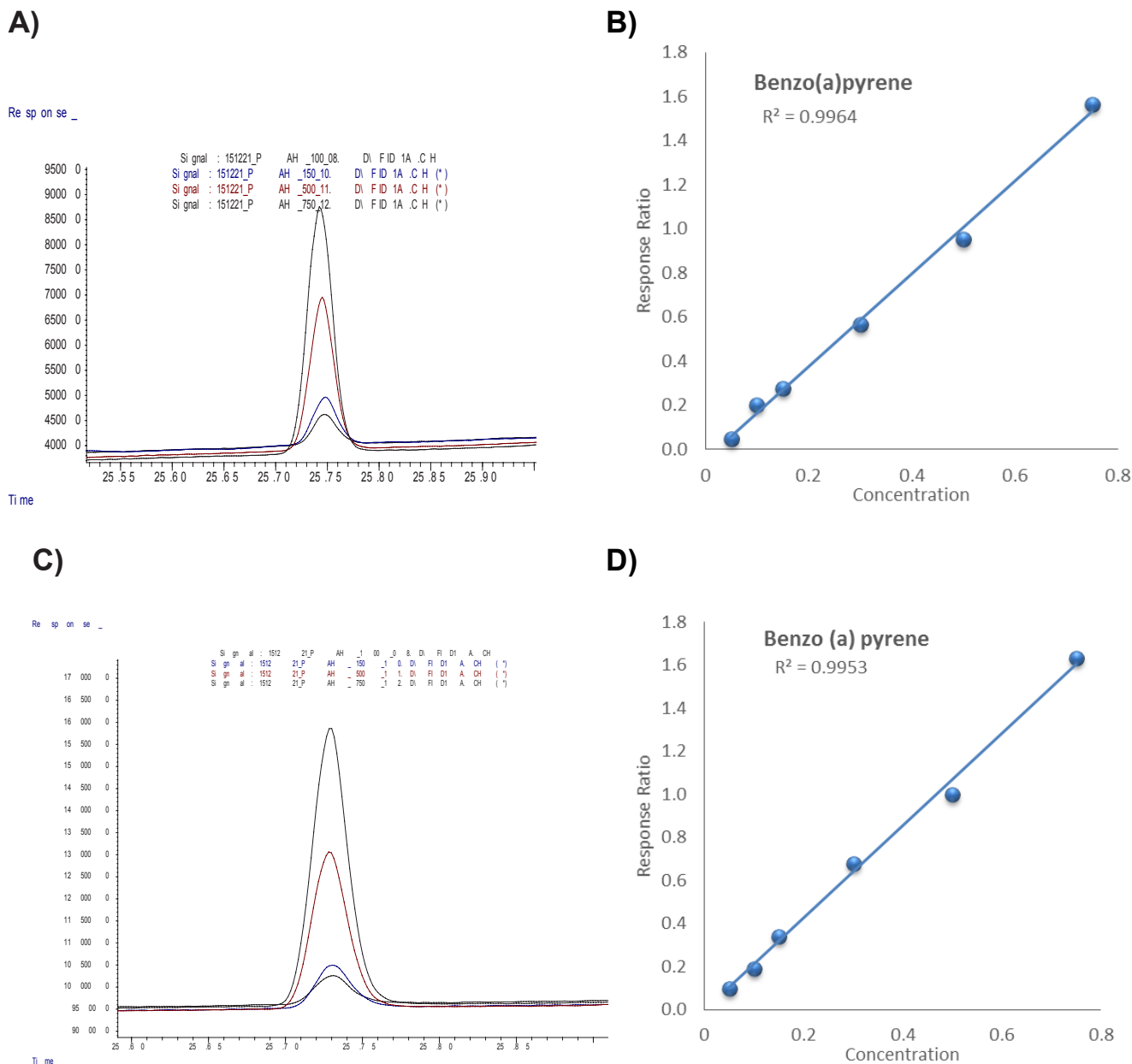
LODs with generated detector gases were between 2.4 – 9.7 pg (0.024 – 0.097 µg/ml) with similar results for the detector gases from the cylinder/compressor with LODs between 1.8 – 8.0 pg (0.018 – 0.080 µg/ml). LODs could further be improved by employing large volume injection (LVI) if required.

Generated gases demonstrated improved repeatability (<3.3 %) over gases obtained from the cylinder/compressor (<5.9 %) at the 0.3 µg/ml (0.3 ng) level.

			Detector gases from generator (Hydrogen & Air)		Detector gases from cylinder/ compressor (Hydrogen & Air)	
No.	Compound name	RT (min)	LOD (pg)	Repeatability (% RSD @ 0.3 ng)	LOD (pg)	Repeatability (% RSD @ 0.3 ng)
	Tetradecane (Internal Standard)	15.91	-	-	-	-
1	1,2,3-Trimethylbenzene	6.71	2.9	0.6	3.8	0.8
2	Naphthalene	9.23	2.8	0.5	3.5	0.6
3	2-Methylnaphthalene	10.79	2.0	0.2	7.5	0.8
4	Acenaphthylene	12.83	3.0	0.6	4.7	0.5
5	Acenaphthene	13.27	4.6	0.6	6.7	0.6
6	Fluorene	14.44	4.6	0.9	2.5	0.7
7	Phenanthrene	16.63	4.9	0.7	7.7	1.1
8	Anthracene	16.73	5.7	0.9	2.8	1.3
9	Fluoranthene	19.41	7.9	1.7	1.8	2.1
10	Pyrene	19.91	6.9	2.7	5.6	2.0
11	Benz(a)anthracene	22.74	9.3	2.7	6.9	4.0
12	Chrysene	22.83	9.3	2.6	8.0	3.6
13	Benzo(b)fluoranthene	25.11	9.5	3.3	5.5	3.7
14	Benzo(k)fluoranthene	25.16	6.5	3.3	4.0	3.2
15	Benzo(a)pyrene	25.75	9.7	2.9	5.9	4.4
16	Indeno(1,2,3-cd)pyrene	27.82	8.9	2.4	4.8	4.6
17	Dibenz(a,h)anthracene	27.87	3.1	2.2	3.8	5.9
18	Benzo(ghi)perylene	28.23	4.5	2.0	3.5	5.7

**Table 2:** Compounds analysed, retention times, LODs and repeatability values.

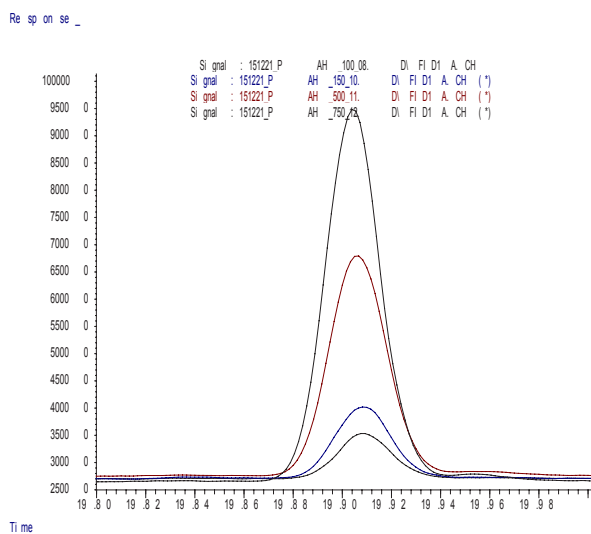
The chromatograms for benzo(a)pyrene for the Parker domnick hunter generated and cylinder/compressor detector gases are shown in **Figure 5** along with their respective correlation coefficients. Similarly **Figure 6** illustrates the plots for pyrene. For both compounds, the calibration curve correlation coefficient was good for both sources of detector gases.



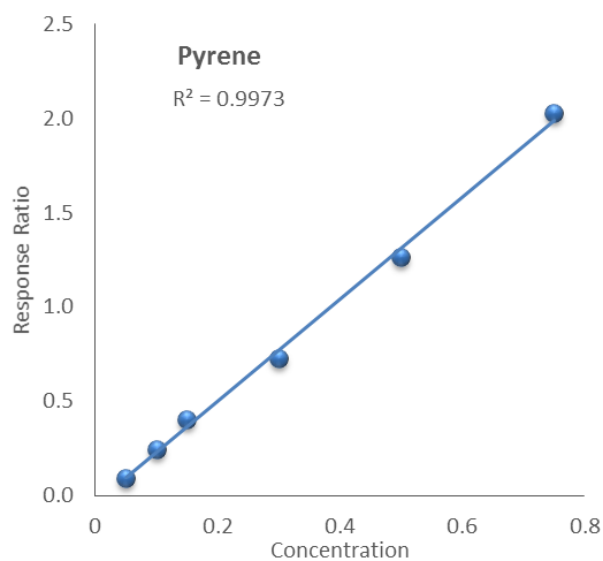
**Figure 5:**

- A) Chromatograms of benzo(a)pyrene analysed with a GC-FID using generated detector gases at concentrations of 0.1, 0.15, 0.5 and 0.75 µg/ml (Retention time 25.75 min).
- B) A linear calibration curve of the compound with a correlation coefficient of 0.9933.
- C) Chromatograms of benzo(a)pyrene analysed with a GC-FID using cylinder/compressor detector gases at concentrations of 0.1, 0.15, 0.5 and 0.75 µg/ml (Retention time 25.75 min).
- D) A linear calibration curve of the compound with a correlation coefficient of 0.9953.

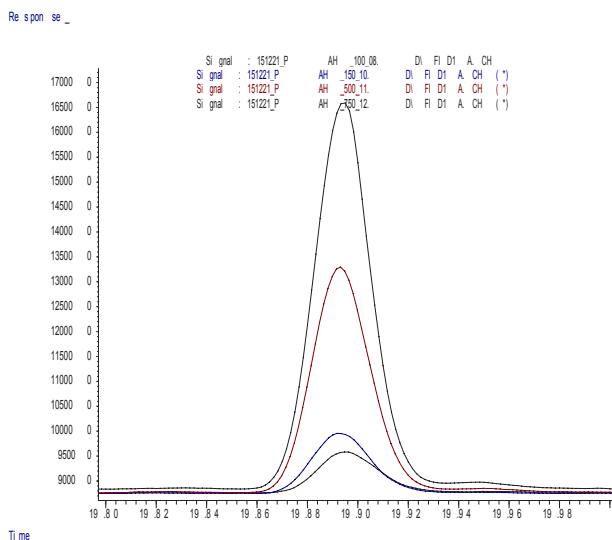
A)



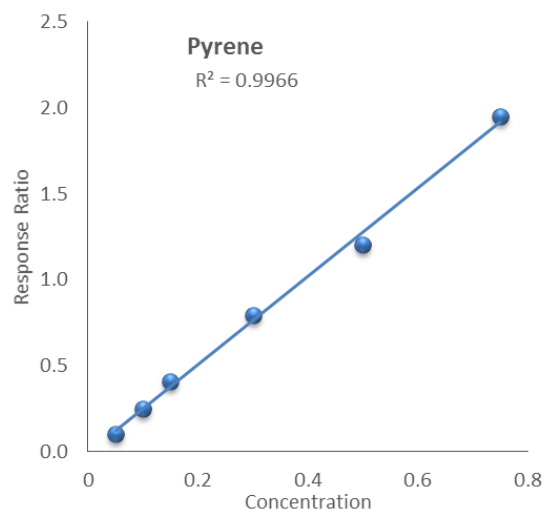
B)



C)



D)



**Figure 6:**

- A) Chromatograms of pyrene analysed with a GC-FID using generated detector gases at concentrations 0.1, 0.15, 0.5 and 0.75 µg/ml (Retention time 19.91 min).
- B) A linear calibration curve of the compound with a correlation coefficient of 0.9973.
- C) Chromatograms of pyrene analysed with a GC-FID using cylinder/compressor detector gases at concentrations 0.1, 0.15, 0.5 and 0.75 µg/ml (Retention time 19.91 min).
- D) A linear calibration curve of the compound with a correlation coefficient of 0.9966.



## Conclusion

The detection of USEPA Method 610 PAHs by GC-FID with PTV injection with generated detector gases shows similar method performance to those obtained with cylinder/compressor gases, in terms of detection limits, repeatability and calibration curve correlation coefficients. Further method optimisation could improve the performance further. The analysis with generated gases benefited from a significantly lower baseline. A higher baseline for the compressor/cylinder gases could indicate that these gases were not as clean as the generated gases, which could have a long-term impact on the instrument, such as a requirement for more frequent detector maintenance.

Ultra-pure hydrogen (>99.99995 %) was supplied from a Parker domnick hunter 110H-MD hydrogen generator and Parker UHP-75 ZA-S zero air generator for the fuel. The ultra-high purity hydrogen gas employed in this application note was generated on-site from deionised water, using proton exchange membrane technology.

Parker domnick hunter gas generation systems, such as the hydrogen and zero air generators outlined, are designed to eliminate the high cost, inconvenience and safety concerns associated with high pressure gas and liquid cylinder storage and handling. A gas generator will also eliminate equipment downtime due to gas interruption (cylinder change out), inconsistent gas purity and dependence upon delivery from outside vendors. Parker domnick hunter hydrogen generators only require the supply of electricity and deionised water to produce consistent, high purity, gas.

In addition to use of hydrogen as a fuel gas for Flame Ionisation detectors, there exists the potential for hydrogen to be used as a carrier gas. For many GC applications, hydrogen carrier gas permits higher resolving power than helium over a larger velocity range and volumetric carrier gas flows, thus improving the quality and speed of chromatographic separation. With helium becoming prohibitively expensive for routine analysis and the clear advantages offered by hydrogen, many chromatographers are transitioning to hydrogen carrier gas. Parker domnick hunter analytical gas generators are also used in LCMS, FTIR, NMR and TOC applications.

## References

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