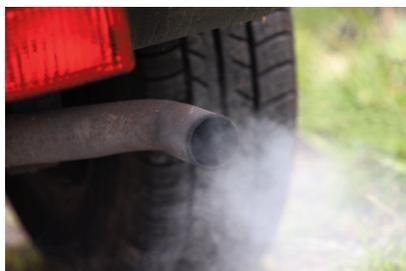


## Application Note 514<sup>†</sup>

# Analysis of polycyclic aromatic hydrocarbons from vehicle exhaust using TD-GC-TOF MS and TargetView software

### Summary

This Application Note describes how BenchTOF time-of-flight mass spectrometers and TargetView compound identification software can be used to accurately identify trace-level polycyclic aromatic hydrocarbons (PAHs) in a complex vehicle exhaust particulate sample.



### Introduction

Polycyclic aromatic hydrocarbons (PAHs) are potentially carcinogenic species present in the environment. In ambient air, the most toxic PAHs tend to be bound to airborne particulate matter, such as that generated from combustion processes. One major source of such particulates is the exhaust emissions of vehicle engines (particularly older diesel engines). In view of the continued need to reduce vehicle emissions and the toxicity of PAHs in the environment, it is important to be able to monitor the PAHs present in particulate matter from diesel exhaust.

In this Application Note, we build upon previous work<sup>1</sup> to demonstrate how established methods for the sampling and pre-concentration of PAHs using thermal desorption (TD)<sup>2</sup> can be enhanced by using BenchTOF time-of-flight mass spectrometers in conjunction with the innovative TargetView compound identification software package.

### Background to BenchTOF instruments

PAHs are often present at trace levels, and accurate identification and measurement in complex samples such as diesel particulate matter can prove challenging. However, Markes' BenchTOF™ time-of-flight mass spectrometers are ideally suited for the analysis of such samples, the following three features being of particular importance:

- **Sensitivity:** Sensitivity: Highly efficient direct-extraction technology allows BenchTOF instruments to acquire full-range spectra with SIM-like sensitivity, allowing them to reliably detect trace-level analytes in a single run, which would be difficult or impossible on a quadrupole system.
- **Spectral quality:** Spectral quality: The 'reference-quality' spectra produced by BenchTOF are a close match for those in commercial libraries such as NIST or Wiley. This enables quick and confident matching of both targets and unknowns.
- **Speed:** The ability to record full-range mass spectral information to extremely high densities (10,000 transient spectral accumulations per second) enables advanced spectral deconvolution and 'data-mining' algorithms to extract maximum information from weak, matrix-masked signals.

### Background to TargetView

The advantages of BenchTOF are enhanced by TargetView, a sophisticated post-run data processing package that allows accurate and automated identification of trace compounds in complex GC-MS profiles.

TargetView uses sophisticated algorithms to eliminate background interference and deconvolve co-eluting components into individual analyte peaks. The mass spectra produced for each deconvolved component can then be rapidly matched against library spectra using advanced chemometric techniques, which allow both target and 'unknown' compounds to be identified confidently, even at trace levels. Total ion chromatogram (TIC) profiles can either be searched against a target library (a 'target search'), or screened against the full NIST library (an 'all-component search').

TargetView is easy to learn, simple to operate, and compatible with common GC-MS file types from major vendors.

### Experimental

Following ignition of the diesel engine, a stream of exhaust gas was sampled for one minute onto a quartz filter. A portion of this quartz filter (4 cm long × 4 mm wide) was placed in an empty glass TD tube and analysed using the following conditions:

<b>TD:</b>	
Instrument:	UNITY™ (Markes International)
Focusing trap:	High-boilers trap
Pre-purge time:	1.0 min
Desorption:	300 °C, 15.0 min (20 mL/min to trap, 40 mL/min to split)

<sup>†</sup> Formerly ALMSCO Application Note 014.



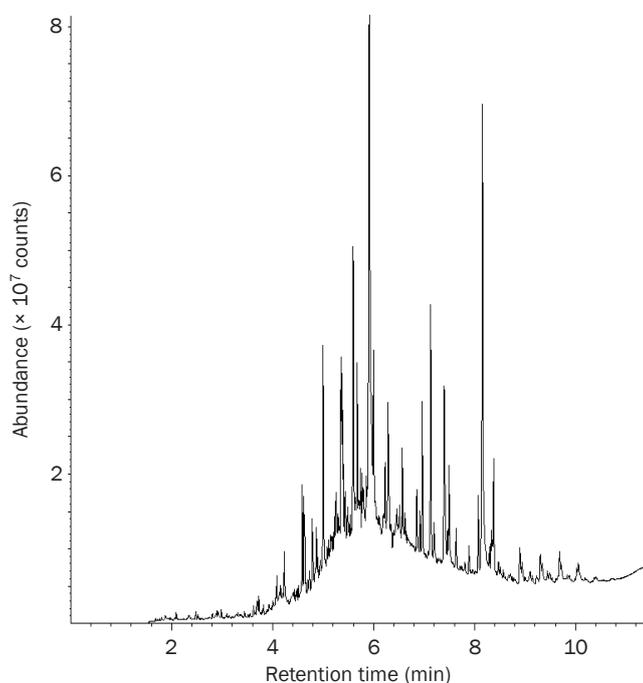
Pre-trap fire purge: 1.0 min  
 Trap low temp.: 30 °C  
 Heating rate: Maximum (~100 °C/s)  
 Trap high temp.: 320 °C  
 Trap high time: 5.0 min  
 Secondary split flow: 200 mL/min  
 Flow path temp.: 210 °C

**GC:**

Column: BTX-5: 15 m × 0.25 mm × 0.1 µm  
 Carrier gas: He, constant flow 1.5 mL/min  
 Oven: 50 °C (0.5 min), 30 °C/min to 370 °C (5.0 min)

**MS:**

Instrument: BenchTOF (Markes International)  
 Transfer line: 300 °C  
 Ion source: 300 °C  
 Mass range: m/z 40–400  
 Data rate: 2 Hz (5000 spectral accumulations per data point)



**Figure 1:** Total ion chromatogram of the diesel exhaust sample collected on a quartz filter and analysed by (direct desorption) TD–GC–MS.

Target compound	Retention time (min)	Expected retention time (min)	Match coeff.	Peak sum
Naphthalene	2.923	2.92	0.811	578 967
Acenaphthylene	4.125	4.14	0.745	263 566
Phenanthrene	5.404	5.45	0.880	12 883 091
Fluoranthene	6.297	6.32	0.954	4 973 663
Pyrene	6.461	6.48	0.937	4 523 126
Benzo[ghi]perylene	9.240	9.24	0.841	13 015

**Table 1:** Report identifying six PAHs in the diesel exhaust.

## Results and discussion

Figure 1 shows the total ion chromatogram (TIC) obtained for the diesel particulate sample. An overall split ratio of approximately 400:1 was used to prevent potential contamination of the analytical systems with high-abundance components. The drawback of using a high split is that the already low levels of PAHs present in the sample are reduced even further. However, the inherent sensitivity of BenchTOF combined with the post-run processing power of TargetView still allowed confident identification of multiple target PAHs in the sample.

### Matching against a PAH target library

PAHs are often structural isomers, and therefore have very similar ion patterns in their mass spectra. To obtain accurate matches for PAHs, it is therefore often necessary to know their elution order (retention index) or their specific retention times, which in this case were obtained by analysing a standard PAH solution (spiked onto a sorbent tube and analysed under the same TD & GC conditions). TargetView contains a function that allows matches to be penalised if they fall outside a pre-set ‘window’ of expected retention times. In this way, accurate matches of compounds with similar spectra but differing chromatographic retentivity can be obtained.

Initially, the chromatogram was searched against a library of the 16 PAHs in the US EPA 610 list<sup>3</sup>. A spectral match factor limit of 0.70 was imposed on the search, and expected retention times for each compound were added to the library with an accompanying narrow retention time window. Following interrogation of the spectra obtained, six PAHs were confidently identified (Table 1).

### Accurate identification of PAHs with near-identical spectra

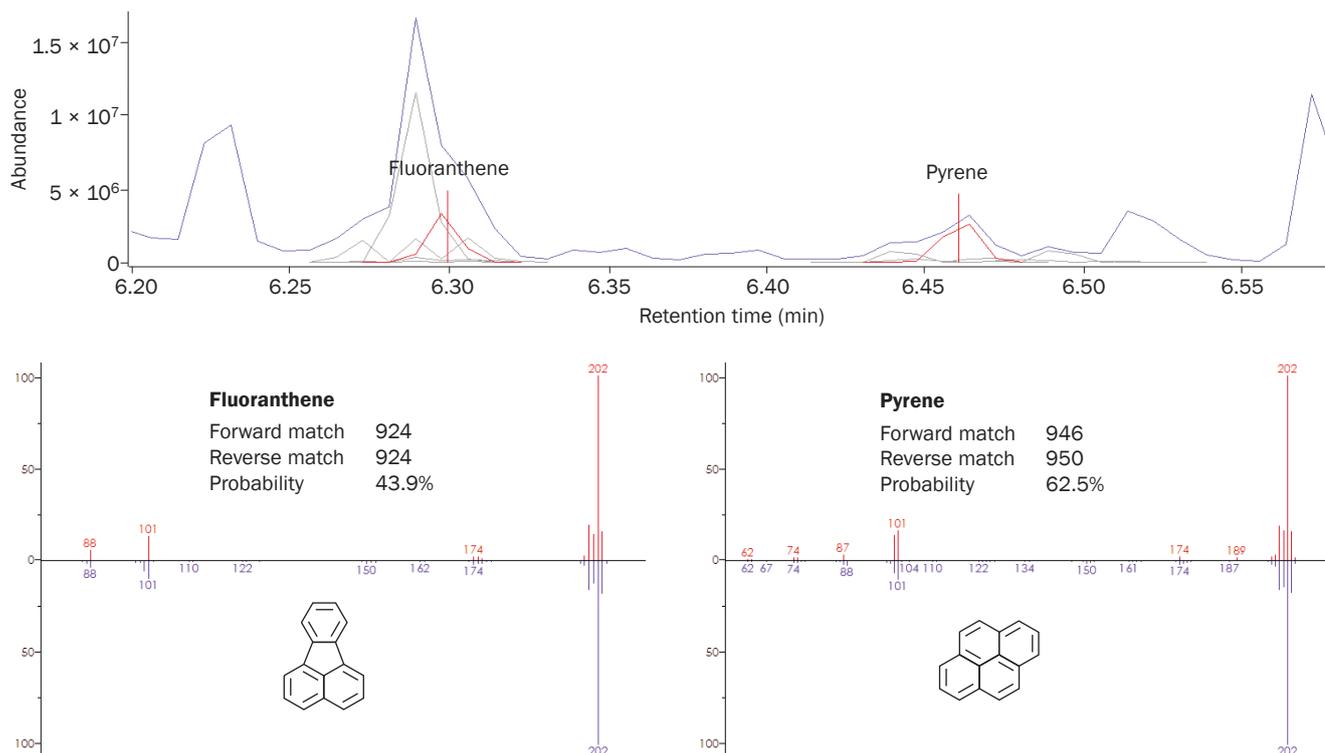
A good example of how TargetView can be used to accurately identify compounds with almost identical spectra is the determination of fluoranthene and pyrene. The deconvolved peaks for each compound (shown in red within the TIC) are displayed in Figure 2 alongside the respective spectra from the NIST library. Match factors of 924 and 946 for fluoranthene and pyrene respectively demonstrate both the inherent quality of the spectra produced by BenchTOF instruments and the excellent performance of the TargetView deconvolution algorithm. Knowledge of their retention times (6.32 min for fluoranthene and 6.48 min for pyrene) provides additional confirmation of identification.

### Detection of trace-level high-boiling PAHs

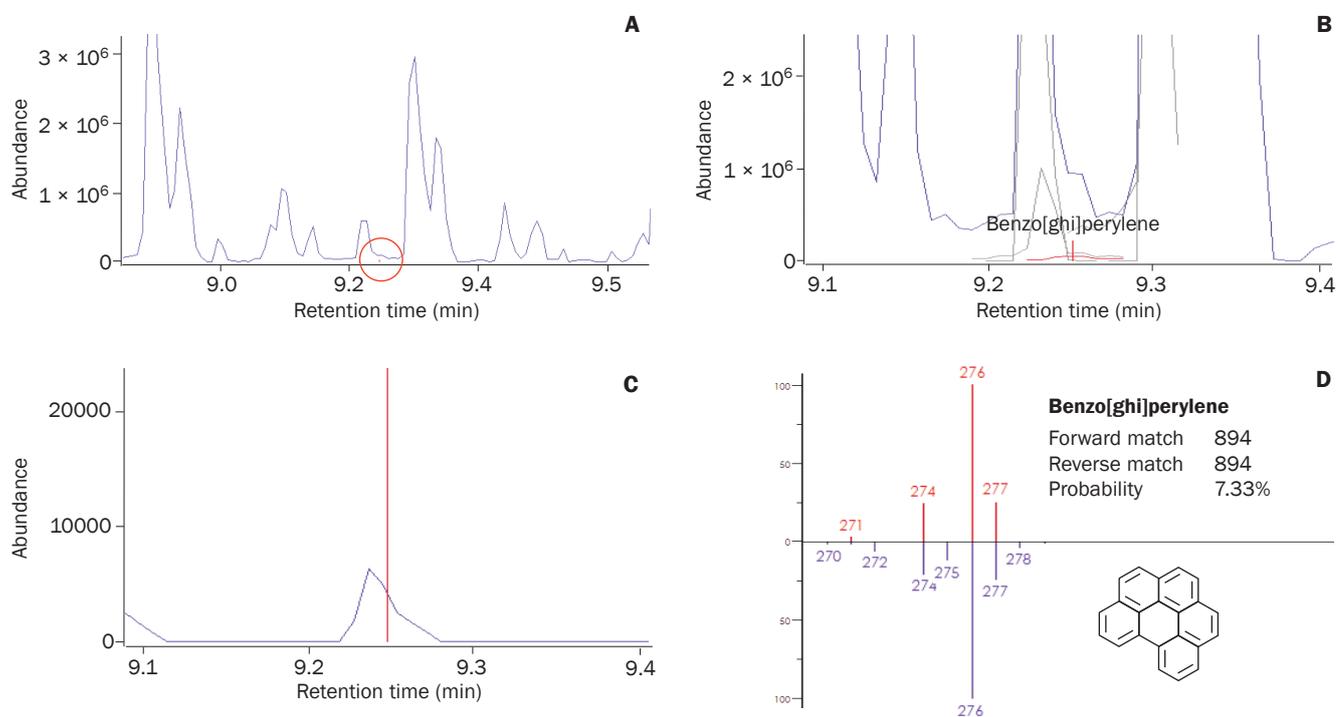
The identification of benzo[ghi]perylene in the diesel exhaust is a good example of the power of TD–GC–TOF MS to analyse trace-level high-boiling components (Figure 3). The peak sums provided in the TargetView report (Table 1) indicate that it is present at levels 1000 times lower than the most abundant target component (phenanthrene) – but it nevertheless has a high match coefficient of 0.841.

As before, the use of expected retention times in the TargetView library allows this isomer to be assigned with confidence.

The traditional approach to detection of trace target analytes in complex chromatographic profiles involves the use of selected ion monitoring (SIM), but this precludes the analysis of unknowns.



**Figure 2: Top:** Detection of the deconvolved peaks for fluoranthene and pyrene (red traces) amongst closely-eluting compounds (grey traces). Bottom: The corresponding mass spectra (top, red) compared to those in the NIST library (bottom, blue).



**Figure 3: (A)** Detection of benzo[ghi]perylene in the TIC (circled). **(B)** Deconvolved elution profile of benzo[ghi]perylene in the TIC (red trace). **(C)** Elution profile of benzo[ghi]perylene in the EIC for m/z 276. **(D)** The corresponding mass spectrum (top, red) compared to that in the NIST library (bottom, blue).

## Conclusions

This quick study illustrates how the sensitivity, spectral quality and speed of BenchTOF instruments work together with TargetView's sophisticated algorithms to enhance the detection of trace-level compounds in highly complex samples.

When this approach is used in conjunction with the inherently sensitive technique of thermal desorption-GC, excellent analytical performance can be obtained even in the most challenging of scenarios, as demonstrated here for the detection of semi-volatile PAHs at trace levels in a complex diesel exhaust matrix.

## References

1. See, for example: (a) E. Wauters, P. Van Caeter, G. Desmet, F. David, C. Devos and P. Sandra, Improved accuracy in the determination of polycyclic aromatic hydrocarbons in air using 24 h sampling on a mixed bed followed by thermal desorption capillary gas chromatography-mass spectrometry, *Journal of Chromatography A*, 2008, 1190: 286-293; (b) M. Bates, P. Bruno, M. Caputi, M. Caselli, G. de Gennaro and M. Tutino, Analysis of polycyclic aromatic hydrocarbons (PAHs) in airborne particles by direct sample introduction thermal desorption GC-MS, *Atmospheric Environment*, 2008, 42: 6144-6151.
2. See, for example, Application Note 053.
3. Appendix A to Part 136 (Methods for organic chemical analysis of municipal and industrial wastewater), *Method 610 - Polynuclear aromatic hydrocarbons*, US EPA, December 1996.

## Trademarks

BenchTOF™, TargetView™, TD-100™ and UNITY™ are trademarks of Markes International.

*Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.*