Thermal Desorption Technical Support

Note 97: Analysis of polycyclic aromatic hydrocarbons from vehicle exhaust using TD–GC/MS

Keywords:

PAHs, fuel, exhaust, diesel, particulates

Summary

This Application Note describes how Markes International's UNITY 2™ thermal desorber, in conjunction with GC/MS, can be used to detect polycyclic aromatic hydrocarbons in vehicle exhaust in a real-world situation.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are potentially carcinogenic species present in the environment. In ambient air, the most toxic PAHs tend to occur 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.

PAHs can be difficult to analyse by TD–GC/MS. These semi-volatile species require high linear velocities in the flow path and the absence of cold spots for efficient transfer through the analytical system. Furthermore, the lack of distinctive fragmentation patterns means they can be difficult to distinguish from one another based on their mass spectra alone. Therefore, well-resolved chromatography is essential for identification, and by using Markes' thermal desorption technology it is possible to obtain excellent results, as previously demonstrated for PAHs and other high-boiling compounds[1].

Here we build upon previous work[2] to demonstrate how Markes' UNITY 2 thermal desorber can be used for the direct analysis of PAHs in a particulate sample collected from the exhaust of a diesel engine. A key benefit of using direct thermal desorption is that it is much quicker and easier than traditional solvent extraction protocols. Furthermore, in this case, the UNITY 2 was coupled to GC/TOF MS and used in conjunction with TargetView™ data-mining software, providing further analytical power to deal with this challenging sample.

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 a clean glass TD tube and analysed using the following conditions:

TD:

Instrument:	UNITY 2 (Markes International)
Cold trap:	U-T1HBL-2S (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)
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-dx (ALMSCO International)
Transfer line:	300 °C
Ion source:	300 °C
Mass range:	40–400 amu
Data rate:	2 Hz with 5000 spectra per data-point

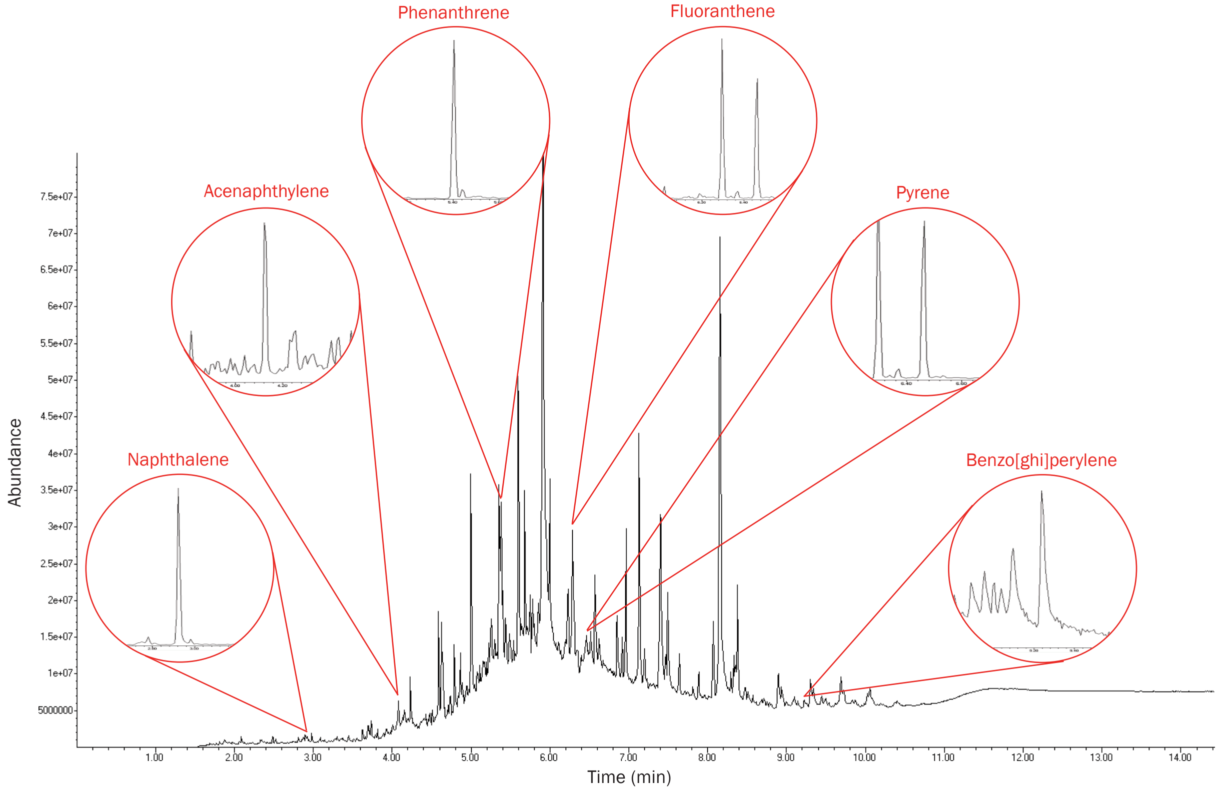


Figure 1. Chromatogram of the diesel exhaust sample collected on a quartz filter and analysed by (direct desorption) TD–GC/MS. Extracted-ion chromatograms of the six identified PAHs are provided in the insets (in each case, the peak in the centre of the inset is the labelled compound)

Results and discussion

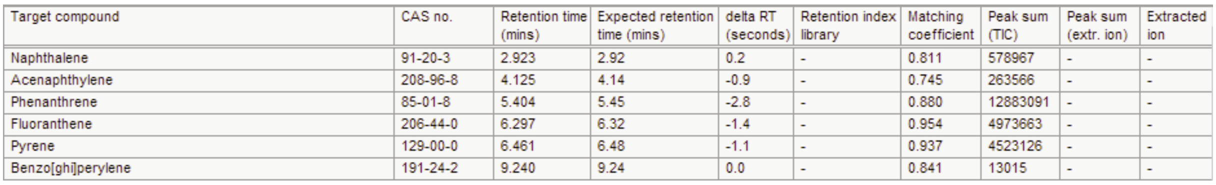
Figure 1 shows the chromatogram of the diesel particulate sample, which is extremely complex. Despite this, it is possible to obtain good peak shapes from the extracted-ion chromatograms for the six components identified, as shown in the insets.

An overall split ratio of approximately 400:1 was used so that potential contamination of the GC would be avoided. Although this presents a challenge to the analytical system because it makes the already low levels of PAHs even lower, this is not a problem if post-run processing software such as TargetView™ (from ALMSCO International) is used to eliminate matrix interferences and identify target analytes.

With this processing complete, details of retention times of the target analytes were obtained from a standard PAH solution (for an example of this, see Markes' TDTS 53[1]). Ordinarily, it would not be necessary to know retention times in order to identify the analytes by GC/MS, but in this case, because the analytes are structurally very similar, there is in some cases very little difference between the pattern of fragment ions in their mass spectra. Knowledge of the retention times therefore provides additional confirmation of the assignment.

A good example in this case is fluoranthene and pyrene, which have almost identical spectra. However, their different retention times (6.32 min and 6.48 min, respectively) allow an extra degree of confidence in the assignment from the mass spectral matching. Note also that the target compounds detected cover the full volatility range of compounds of interest in this case.

Finally, the identification of benzo[ghi]perylene in the diesel exhaust sample is a good example of the power of TD–GC/MS to analyse trace high-boiling components. Not only do the peak sums provided in the TargetView report (Figure 2) indicate that it is present at levels 1000 times lower than the most abundant target component (phenanthrene), but it has a strong match coefficient, and the retention time exactly matches that in the library.



Target compound	CAS no.	Retention time (mins)	Expected retention time (mins)	delta RT (seconds)	Retention index library	Matching coefficient	Peak sum (TIC)	Peak sum (extr. ion)	Extracted ion
Naphthalene	91-20-3	2.923	2.92	0.2	-	0.811	578967	-	-
Acenaphthylene	208-96-8	4.125	4.14	-0.9	-	0.745	263566	-	-
Phenanthrene	85-01-8	5.404	5.45	-2.8	-	0.880	12883091	-	-
Fluoranthene	206-44-0	6.297	6.32	-1.4	-	0.954	4973663	-	-
Pyrene	129-00-0	6.461	6.48	-1.1	-	0.937	4523126	-	-
Benzo[ghi]perylene	191-24-2	9.240	9.24	0.0	-	0.841	13015	-	-

Figure 2. TargetView report identifying six PAHs in the diesel exhaust

Conclusions

The UNITY 2 thermal desorber provides an excellent means of analysing PAHs in vehicle exhaust. The fast trap heating, patented valving and optimised flow path design provide high performance for these high-boiling analytes, with the excellent peak shape greatly aiding successful analysis. These benefits are used to the full by employing the UNITY 2 in conjunction with the BenchTOF-dx mass spectrometer and TargetView data-mining software. This combination offers unbeatable sensitivity and analytical performance for the analysis of semi-volatile PAHs in diesel exhaust.

References

1 TDTS 53: Quantitative recovery of high boiling point (>450 °C) semi-volatiles (SVOCs) using thermal desorption–GC/MS, Markes International, http://www.markes.com/Downloads/Application-notes.aspx. This Application Note describes the use of Markes' UNITY 2 thermal desorber as well as the TD-100™, which allows automated sampling and (optional) re-collection of up to 100 samples.

2 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.

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