The use of thermal desorption with optimized sampling tubes for quantifying polycyclic aromatic hydrocarbons (PAHs) in air

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Summary

This poster describes the use of thermal desorption (TD) with gas chromatography (GC) for the quantitation of polycyclic aromatic hydrocarbons (PAHs), as an alternative to solvent-based sampling techniques. We show how a range of PAHs from naphthalene to benzo[ghi]perylene can be readily captured on to specially-optimized sorbent tubes, and released from them quantitatively. Using this technique, low detection limits are obtained for airborne PAHs with minimal breakthrough and excellent linearity, even when the total sampling volume exceeds 400 L.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely recognized as a particularly harmful group of organic compounds. Resulting from the incomplete combustion of coal, gasoline and other organic materials, they are particularly prevalent in urban and industrial environments, which combined with their toxicity, has resulted in very low limit levels for urban and workplace air.

Although PAHs can be analyzed by GC–MS, they cover a relatively wide volatility range, from naphthalene (b.p. 218°C) to benzo[ghi]perylene (b.p. 500°C). This means that the lower-volatility PAHs tend to occur bound to particulate matter, as well as being present in the air. This is reflected in global standardized methods for the analysis of PAHs (including US EPA Method TO-13A, ISO 16000-13, ISO 16362, ISO 12884 and Chinese EPA Method HJ 584), some of which require the use of a quartz filter to trap the particulates, backed-up with a sorbent cartridge to collect the vapour-phase fraction. However, analysis of these cartridges is labour-intensive, making it difficult to automate, and prone to errors in sample handling and data logging. In addition, the use of solvent risks the more volatile analytes being lost during the evaporation stage, raises the possibility of cross-contamination between samples, and means that the protocol is not environmentally responsible.

Consequently there is demand for more efficient techniques for the sampling of PAHs and their introduction to the GC system. Thermal desorption offers a number of well-known advantages over solvent extraction methods for a wide range of VOCs and SVOCs, the major one being the greatly improved sensitivity due to the avoidance of dilution, the high extraction efficiency, and efficient transfer/injection into the GC. This sensitivity advantage means that the 1000+ litre volumes (and very large sampling flows) required for traditional methods can be substantially reduced, simplifying the sampling process.

In this poster, we describe the outstanding performance offered by a new sorbent tube developed by Markes International that is dedicated to the analysis of PAHs, employed in conjunction with an optimized TD–GC–MS method.

Experimental

Sample: A standard solution of PAHs (1 µL, 10 ng per compound) was spiked into a 'PAH' TD tube (Markes International) using a Calibration Solution Loading Rig™. Following injection, the tube was flushed with either 40, 119, 158, 455 or 475 L of real air at 330 mL/min using an ACTI-VOC™ pump (Markes International) to simulate the high-volume sampling needed to achieve the necessary detection limits. The real air samples were collected in Shanghai, P.R. China, using pumped sampling onto a 'PAH' TD tube at 250 mL/min for 12 h, giving a total volume of 180 L.

TD: Instrument: TD100-xr™ (Markes International). Sorbent tube: PAH (Markes International part no. C2-AAXX-5138). Desorption: 12 min at 320°C at 50 mL/min. Trap: PAH trap (Markes International part no. U-T19PAH-2S). Trap temp.: Low 25°C; high 380°C. Trap heating rate: Max. Trap hold: 8 min. Outlet split flow: 10 mL/min. GC: Column: DB-5MS™, 30 m × 0.25 mm × 0.25 µm. Carrier gas: Helium, 3.0 mL/min constant flow. Oven: 50°C (1 min), 15°C/min to 100°C, then 20°C/min to 240°C, then 10°C/min to 260°C (6 min), then 50°C/min to 310°C (5 min).

Quadrupole MS: Source: 250°C. Transfer line: 320°C.

Results and discussion

Carryover and reproducibility

The chromatogram of a standard PAH mix is shown in Figure 1, with the sharp peaks indicating the efficiency of trap desorption – and hence optimum sensitivity.

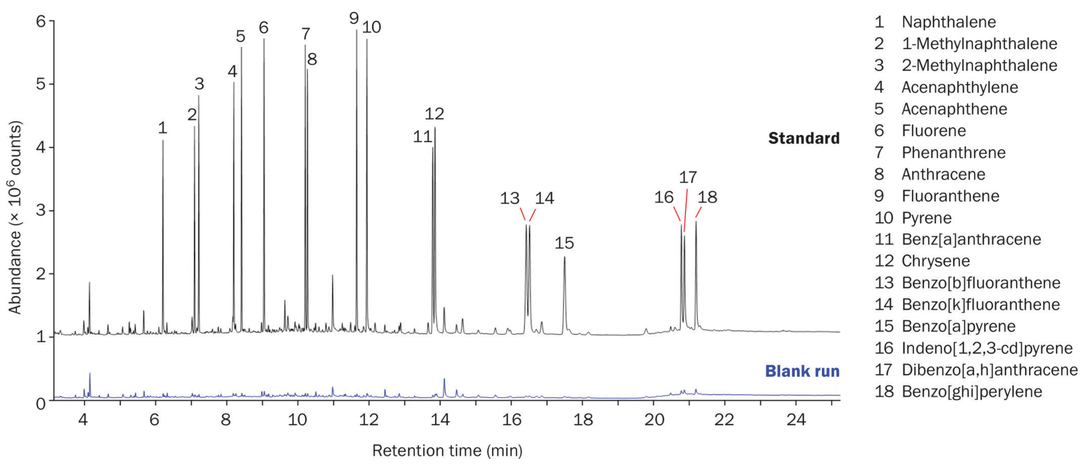


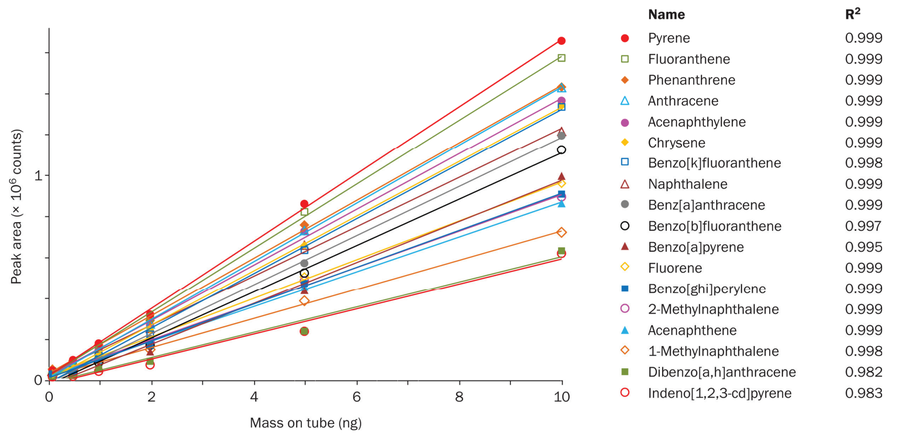
Figure 1: Top: Analysis of a PAH standard (10 ng on-tube per compound), following flushing with 40 L of nitrogen to simulate a high-volume sample. Bottom: Analysis of a subsequent blank tube, showing negligible carryover.

The efficient transfer of all the PAHs through the TD system is shown by the negligible response from a subsequent run of a blank tube – average values of 2–3% were obtained for the majority of the PAHs for a set of five identical tubes. The reproducibilities for the same five tubes were also excellent, with response RSDs varying from 1–4%.

Linearity

Linearities were calculated using five tubes loaded with 0.1–10 ng of a PAH standard and flushed with 455 L of nitrogen to simulate a high-volume sample (Figure 2). The linearities were excellent – all R^2 values were found to be above 0.98.

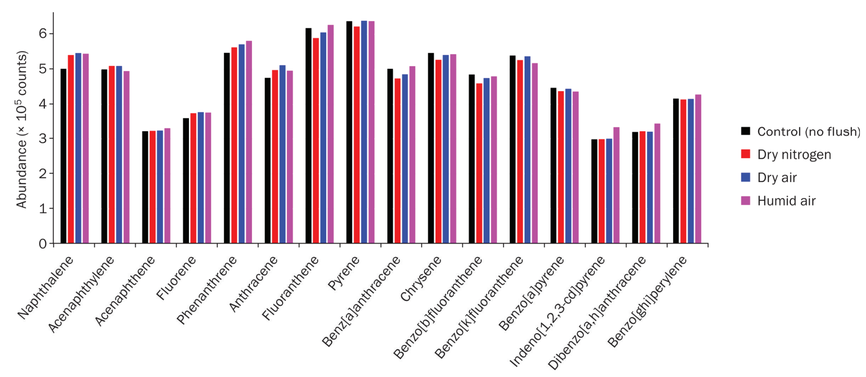
Figure 2: Linearities for each component of a PAH standard, following flushing of the sorbent tube with 455 L of nitrogen to simulate a high-volume sample.



Breakthrough

To check for breakthrough of the analytes during sampling under different conditions, four tubes were spiked with the same quantity of a PAH standard (10 ng per component), with a blank tube placed in series in each case. Three of these tube setups were flushed with gas, and very similar responses were obtained from all four tubes under conditions of different flush gases (Figure 3). Excellent results were also obtained with a real-air flush volume of 475 L (Figure 4).

Figure 3: Assessment of breakthrough for each member of a PAH standard, by flushing a set of four sorbent tubes with 40 L of nitrogen or air (dry or humid) to simulate high-volume samples under different conditions.



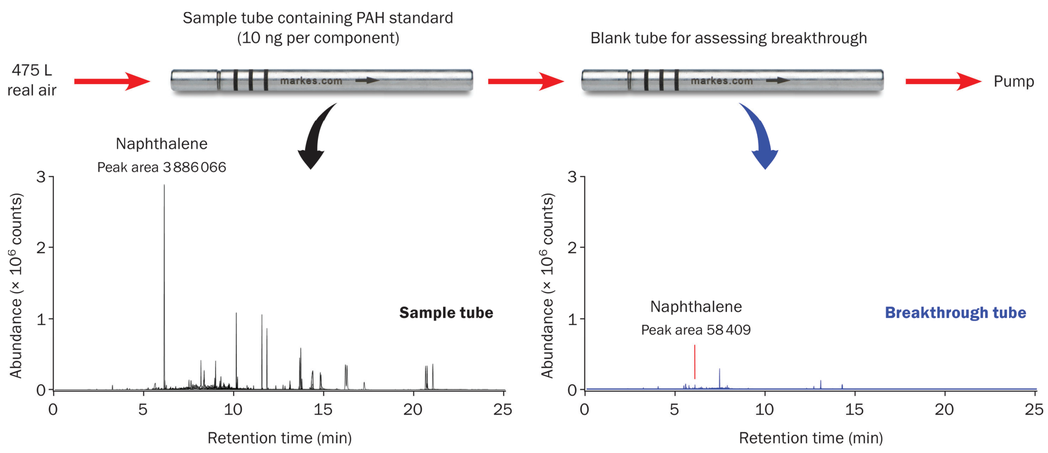


Figure 4: Assessment of breakthrough for a PAH standard, by flushing a sorbent tube with 475 L of real air, configured with a blank tube in series. Even the most abundant PAH in the breakthrough tube, naphthalene, has a response that is just 1.5% of that in the sample tube.

Limits of quantitation and detection

Limits of quantitation and detection were determined based on the analysis of tubes spiked with the PAH standard (0.5 ng per component) by calculating the signal-to-noise ratio at this level and extrapolating the calibration curve to the concentration at which the signal-to-noise ratio was equal to 10 (LOQ) and 3 (LOD). Values obtained were below 20 pg in all instances, extending down to just 3 pg for chrysene.

Real air sample

To assess the performance of the analytical setup, 180 L of urban air was pumped onto a conditioned 'PAH' tube (with a clean tube placed in series), and analyzed as described previously. The results (Figure 5) show that despite the complexity of the air sample, very low levels of PAHs were measured.

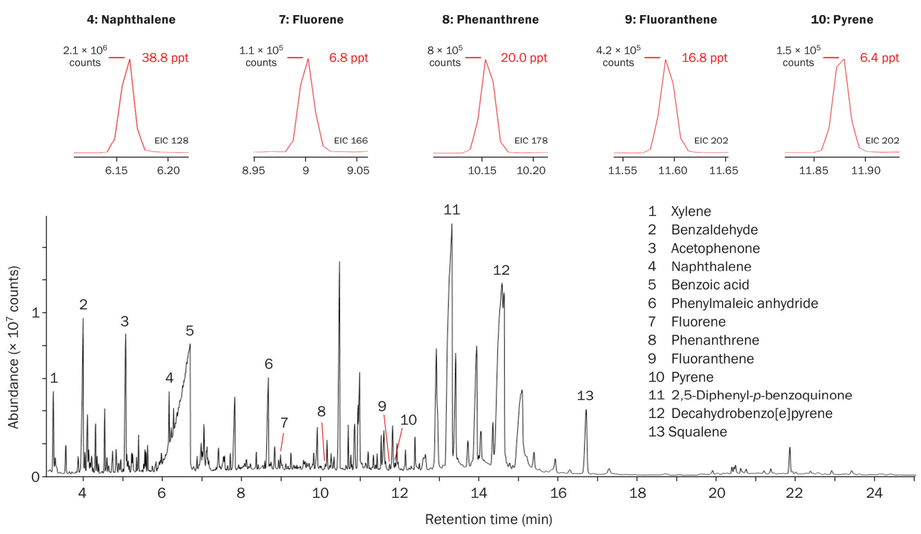


Figure 5: Analysis of 180 L of urban air, with insets showing EICs for the five most abundant PAHs detected.

Conclusions

This poster demonstrates that sampling using sorbent tubes, with analysis by TD–GC–MS, offers a reliable, less labour-intensive alternative to existing methods for the analysis of PAHs in air.

Particular strengths of this approach are (a) the high volumes of air that can be collected on these tubes with minimal carryover for the target SVOC analytes; (b) the low-picogram limits of detection; (c) the excellent reproducibility and linearity for all the target PAHs, ranging from naphthalene to benzo[ghi]perylene.

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