Abstract

Thermal desorption is the technique used to measure atmospheric concentrations of volatile organic compounds (VOCs) in many industrial and urban environments as a measure of air quality. VOCs monitored can range in volatility from acetylene to hexachlorobutadiene & trichlorobenzenes and include some polar as well as apolar compounds. Several national and international standard methods have been developed for air toxics and related applications including US EPA method TO-15 (canister sampling) and TO-17 (sorbent tube sampling). Thermal desorption can be used, in addition to these approaches, for continuous on-line measurements such as those carried out as part of the Photochemical Assessment Monitoring Stations (PAMS) program for ozone precursor analysis.

This poster will report on the use of a new generation of automated thermal desorption instrumentation providing improved performance in a diverse range of air monitoring applications including TO-15, TO-17, ozone precursor monitoring and TPH analysis.

Markes series 2 UNITY[™] with automated air sampling

The series 2 Air Server[™] and 8-channel Canister Interface Accessory[™] (CIA 8[™]), shown below, add to any series 2 (ULTRA-) UNITY[™] system to allow a controlled flow of whole-air or gas to be introduced directly into the electrically-cooled focusing trap of the desorber. The combined systems operate cryogen-free (to minimise running costs/maintenance) and offer optimum analytical performance/sensitivity.



UNITY/Air Server (far right) UNITY/CIA 8 (right)



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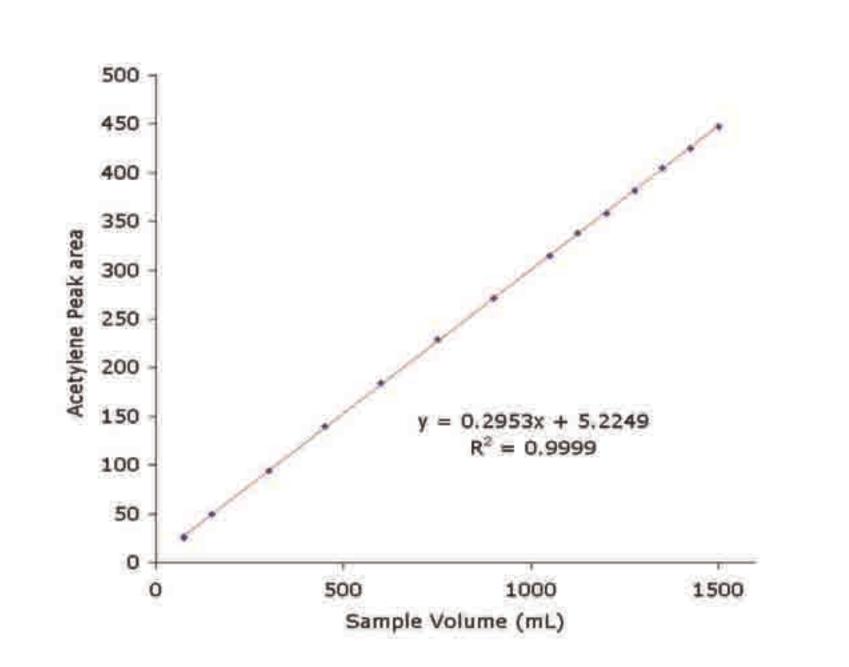
Recent advances in monitoring volatiles in air by thermal desorption

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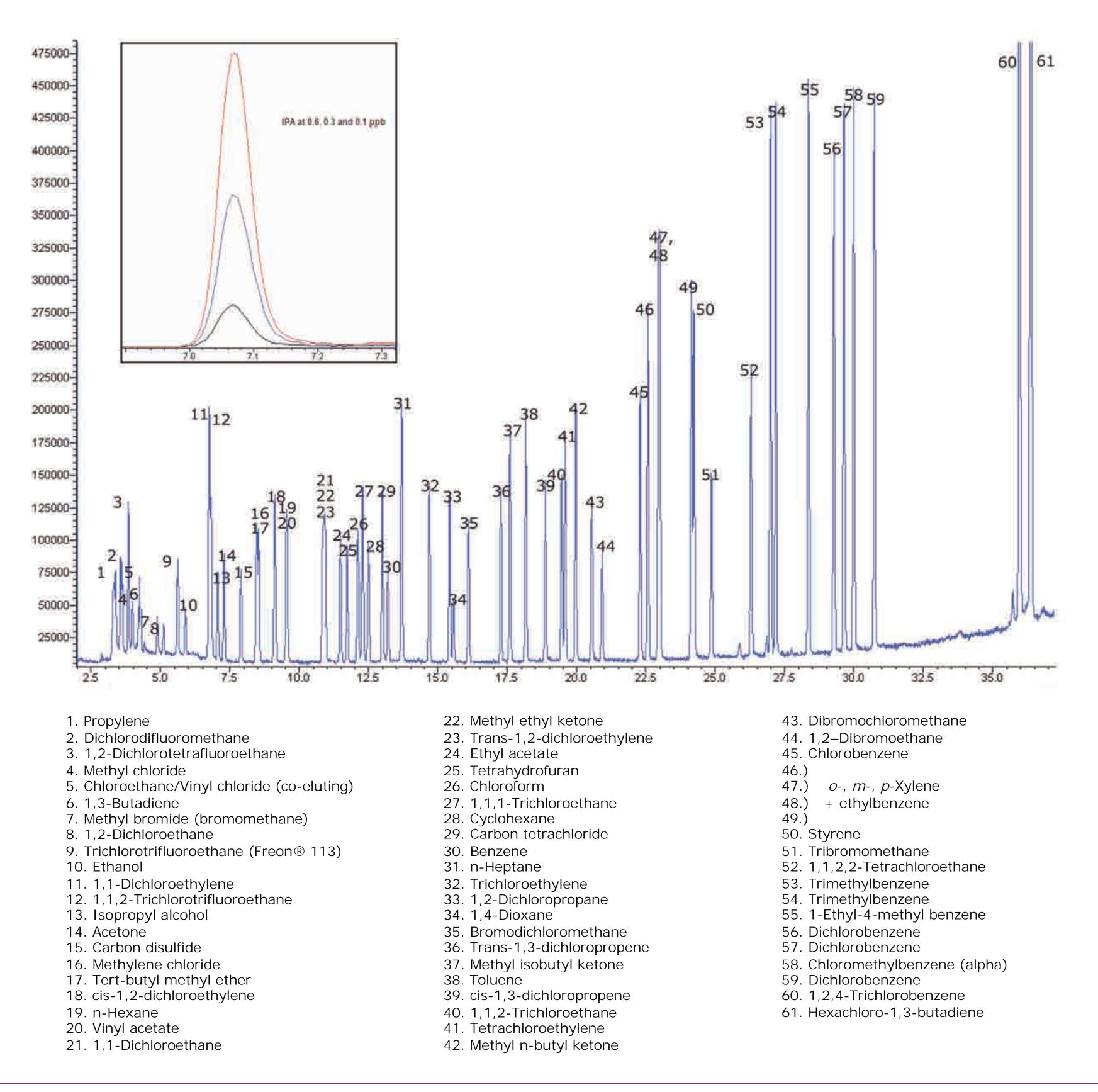
Ozone precursor analysis

The graph below shows peak area versus sampled volume of calibration gas for acetylene. The data shows that there is good reproducibility and negligible breakthrough for acetylene even up to 1500 ml of sampled gas.



EPA method TO-15: Canister analysis

Splitless analysis of 500 ml of a 10 ppb TO-15 standard using a 60 m x $0.32 \text{ mm} \times 1.80 \text{ }\mu\text{m}$ column for purgeable volatiles and scan mode. The Markes "air toxic analyser" trap was used in combination with a 25°C cold trap temperature.

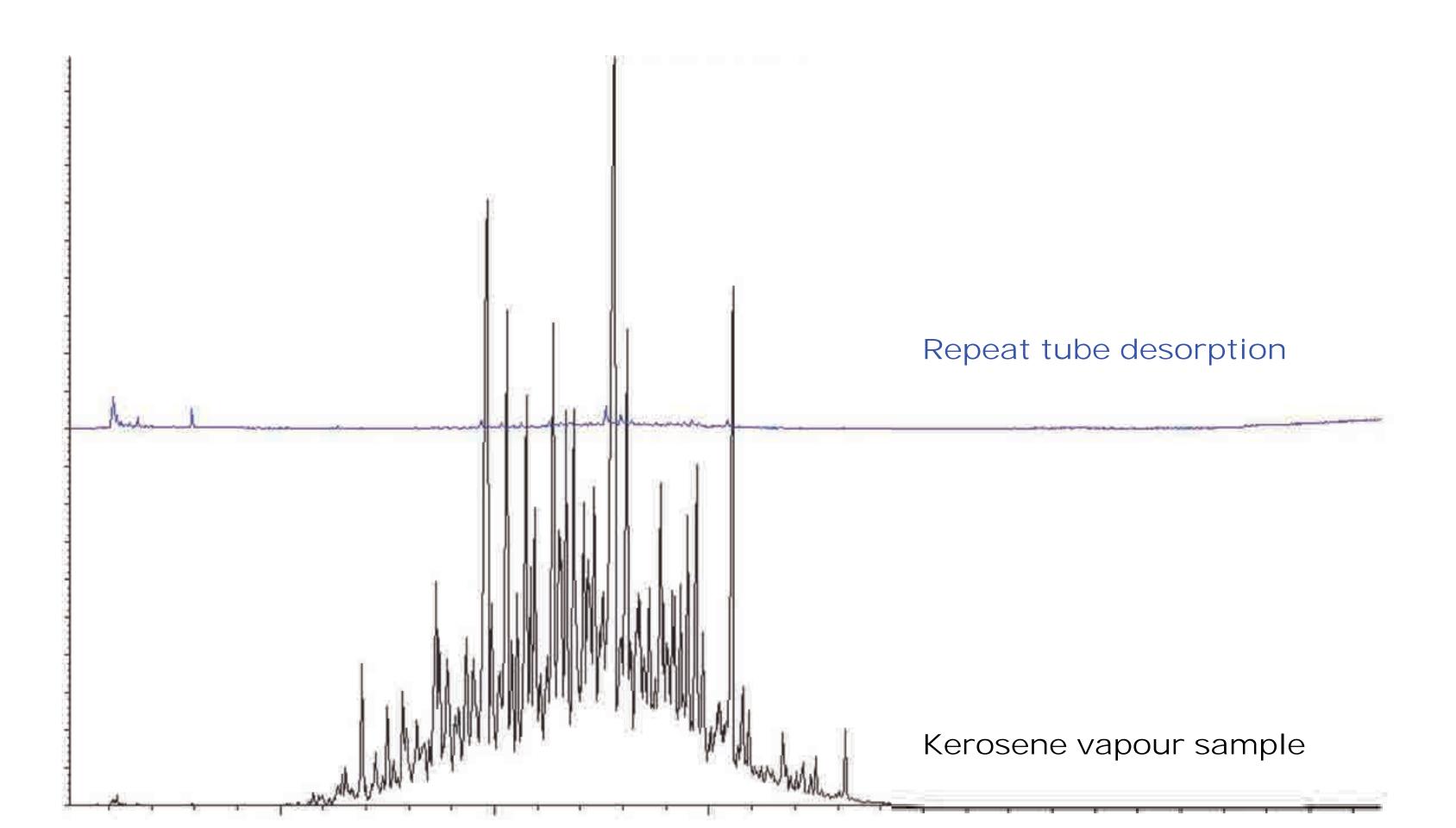


The TO-15 method has also been applied to total petroleum hydrocarbon (TPH) analysis, which is often required to effectively determine the associated human health risk from petroleum contaminated sites, and is achieved by collection and analysis of the soil gas from the contaminated site. However, some of the heavier fuel types classified as middle distillates (*e.g.* diesel, jet fuels and kerosene) contain a significant fraction of components that fall outside the applicability of Method TO-15 and the scope of TO-17. Both of these EPA methods are targeted at ambient air levels of 'air toxics' (*i.e.* organic chemicals ranging in volatility from methyl chloride to hexachlorobutadiene/n- C_{10}), whereas fuels such as kerosene and jet fuel range in volatility up to $\sim n-C_{14}$ and diesel up to $\sim n-C_{18}$.

An alternative sorbent tube based method may be employed to provide more accurate fuel fingerprints at sites contaminated with middle distillate fuels (e.g. No.2 Diesel) compared to Method TO-15.

The figure below shows a kerosene vapour analysis run using a VF-5ms 30 m x 0.25 mm x 0.25 µm column with repeat desorption of the tube showing negligible carryover.

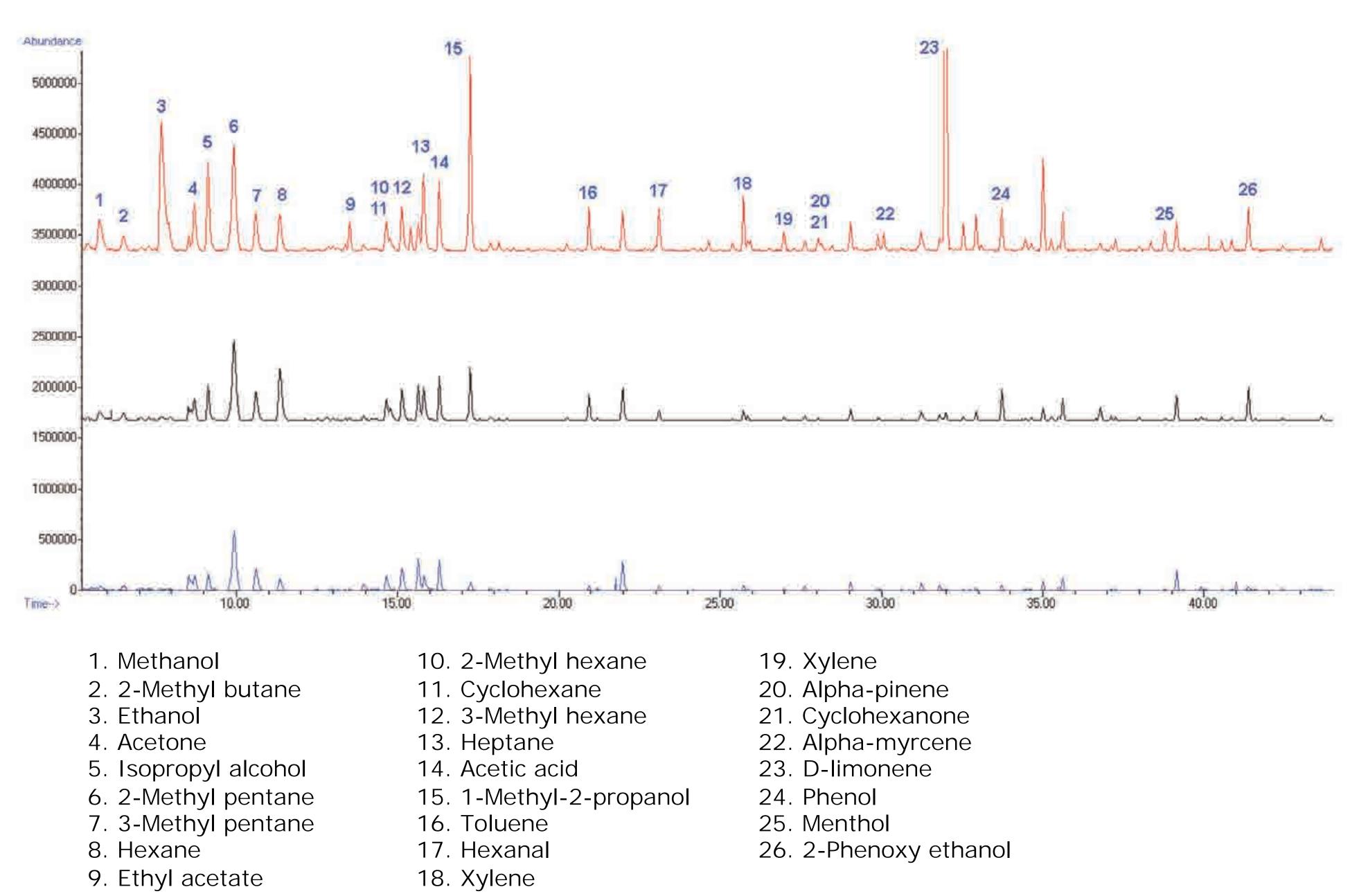
Soil gas analysis





EPA method TO-17: Tube analysis

The chromatograms below show three 1 L real air samples collected using Markes 'universal' sorbent tubes and desorbed splitless using a 60 m x 0.32 mm x 1.80 µm column for 'purgeable volatiles'.



These results illustrate the excellent chromatographic performance of the Markes series 2 UNITY system for TO-15, TO-17, soil gas and PAMS, operating cryogen-free. Quantitative detection of air toxics ranging from methyl chloride to hexachloro-1,3-butadiene has been demonstrated at levels down to 0.1 ppb in canisters and sorbent tubes.

Soil gas analysis with tubes has been shown to provide suitable samplers for soil gas samples contaminated with a range of petroleum fuels. Both lighter hydrocarbons and polyaromatic/longer chain hydrocarbons were detected confirming the results shown by Hayes et al. (2007)¹ that sorbent tubes provide a representative TPH profile of light and middle distillate fuels in soil

Conclusions

Evaluation of sorbent methodology for petroleum impacted site investigations: Hayes HC et al., Proceedings of the Air and Waste Management Association conference on vapor intrusion, Sept