Thermal Desorption Technical Support

Note 80: Evaluation of a 'Soil Gas' sorbent tube for improving the measurement of volatile and semi-volatile fuel vapors in soil contaminated land

Keywords:

Environmental, Petroleum, Contaminated land, Soil gas, Vapor intrusion

Acknowledgement

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Introduction

When investigating fuel-contaminated sites, soil gas measurements are used to assess the potential risk to human health from vapor intrusion into nearby buildings and to identify fuel sources for mitigation and liability management. Measurement of the most toxic individual petroleum-related compounds, such as benzene and naphthalene, and characterization of the total petroleum hydrocarbon (TPH) profile are both usually required as part of the risk assessment. In addition, a comprehensive list of hydrocarbons and an evaluation of the TPH profile are important to identify the source of the contamination.

TPH and related compounds are normally determined by collecting samples of the soil gas from suspect sites and carrying out an off-line laboratory analysis. Canisters or tubes have been used to sample soil gas with subsequent analysis by thermal desorption (TD)-GC/MS along the lines of US EPA Compendium Methods TO-15 or TO-17 respectively[1-3]. However, some of the heavier fuel types classified as middle distillates – diesel, jet fuels and kerosene, for example – 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' – that is 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 ~n-C_{14} and diesel up to ~n-C_{18}.

Comparison of soil gas sampling options

Heavier organic species (compounds less volatile than n-C_{10}) are routinely monitored using TD-compatible sorbent tubes. Many tube-based monitoring methods include both volatiles and semi-volatiles and quantitative recovery is reported for compounds to n-C_{32} and above[4-6].

In contrast to this, canisters are prone to incomplete recovery of compounds less volatile than n-C_8[7, 8] or n-C_{10}[3] (depending on storage conditions). If canisters are used to collect fuel-contaminated soil gas, selective loss of lower volatility compounds will compromise quantification and identification of the middle distillate fuels. This can adversely affect the health risk assessment and make it difficult to get the canister clean again.

The high concentration of fuel vapours on some heavily contaminated site can aggravate canister cleaning issues. Once used for high concentration samples, canisters can be very expensive and time consuming to clean again[8, 9], especially if contaminants are high boiling. In comparison, multi-sorbent tubes and traps are available offering quantitative recovery and release of petroleum fuel components from gasoline to heavy diesel (n-C_3 to n-C_{20}). They are also cleaned thoroughly and automatically, during the thermal desorption analytical process (no additional conditioning steps are required) and are compatible with trace and high concentration vapours[10, 11]. (For other differences between tubes and canisters see Markes TDTS Note 79[10].)

Study objectives

Hayes *et al.* (2007)[3] demonstrated that sorbent tubes can be successfully applied to soil gas measurements and that, if sites were contaminated with middle distillate fuels (*e.g.* No.2 diesel), more accurate/representative fuel fingerprints were obtained using sorbent tubes compared to Method TO-15 canisters (Figures 1 and 2). The main aim of the study reported in this application note was to build on this work by designing a specific sorbent tube for fuel vapors in soil gas and evaluating the performance of this 'soil gas' tube (trapping efficiency and recovery) under both dry and humid conditions.

A secondary objective was to test whether the sampled 'soil gas' tubes could be quantitatively 'analysed' using a Markes analytical thermal desorber configured for air toxics work (TO-17 and TO-15) and connected to GC/MS (Figure 3). If this proved possible, it would mean that a laboratory equipped for TO-17 air toxics analysis could also offer a soil gas monitoring service without additional capital investment.

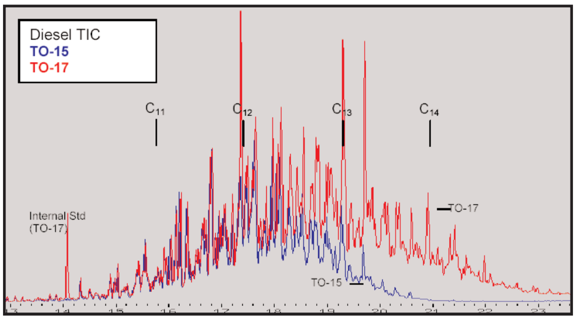

Figure 1: Profiles of soil gas contaminated with diesel obtained using:

a) canister sampling and TO-15 analysis (blue)

b) sorbent tube sampling with TO-17 analysis (red)

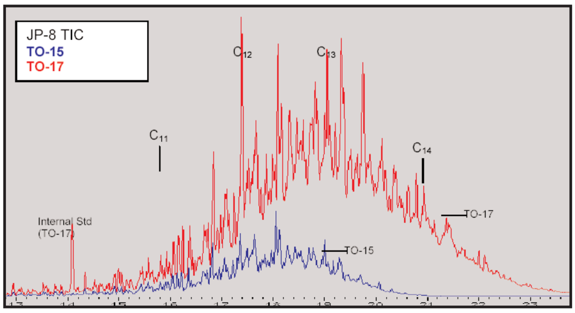

Figure 2: Profiles of soil gas contaminated with kerosene obtained using:

a) canister sampling and TO-15 analysis (blue)

b) sorbent tube sampling with TO-17 analysis (red)

Figure 3: Series 2 ULTRA-UNITY-CIA 8 system offering cryogen-free, method compliant air toxics analysis via TO-15 (canisters) or TO-17 (tubes)

Sorbent tube selection for fuel-contaminated soil gas

Some sorbent tubes (*e.g.* incorporating 3 or 4 sorbents) offer compatibility with an almost universal analyte volatility range ($C_{2/3}$ to n-C_{30}). However, real world soil gas samples don't contain the lightest (gas-phase) fuel components (*e.g.* propane and butane from gasoline) as these quickly disappear from a fuel leak or spill under normal ambient conditions. This means that a simpler combination of sorbents can be used for soil gas monitoring.

Theoretically, a stainless steel tube packed with Tenax TA™ (sampling end) and Carbotrap X™ or Carbograph 5TD™ at the rear would provide an ideal soil gas sampler. It would provide the following key features:

- Quantitative retention and recovery of compounds over a wider volatility range than that found in fuel-contaminated soil gas *i.e.* from one of the most volatile and toxic C_4 hydrocarbons (1,3-butadiene) to n-C_{26}
- Hydrophobic (*i.e.* allows water vapor to break through during sampling)
- Low inherent artifacts (*i.e.* suitable for trace as well as higher levels)
- Robust – allowing cost-effective repeat use (>100 monitoring cycles)

Note also that this combination of sorbents is relatively inert and could be provided in a Silcosteel™ tube if reactive components were of interest in the soil gas.

Experimental

In order to evaluate the performance of the 'soil gas' samplers described above, a batch of freshly packed tubes was prepared and used to sample vapors purged from sand spiked with a range of fuels. Markes' novel Micro-Chamber/ Thermal Extractor (μ-CTE) device was used as a simple means of exposing the soil gas tubes to the contaminated soil under controlled conditions of temperature, humidity and air flow. The μ-CTE offers 6 separate, ~45 ml sample chambers which can operate simultaneously for optimum throughput (figure 4).

Sample preparation: Approximately 15 g replicate samples of sand were weighed into 20 ml headspace vials and 1 μL of fuel (gasoline, kerosene or diesel) was injected onto the top of each sand sample. Wet samples were prepared by adding 1 ml of HPLC grade water to the sand. The headspace vials were subsequently sealed and the vapors allowed to permeate through the wet or dry sand for approximately 48 h. The prepared sand samples were then placed into individual micro-chambers and incubated at either 30°C or 50°C to simulate a range of worst case conditions. Each micro-chamber was purged with a flow of 50 ml/min pure air for 5 minutes. Vapors exhausting from each micro-chamber (250 ml total) were collected on the attached soil gas sorbent tubes.

Figure 4: Markes Micro-Chamber/Thermal Extractor (μ-CTE) for simultaneous sampling/purging of 6 material samples - in this case, sand

The tubes were subsequently analysed using a Markes 100-tube capacity series 2 ULTRA-UNITY thermal desorption system configured with an electrically-cooled 'Air Toxics'/'Soil Gas' trap and GC/MS.

Analytical conditions were as follows:

μ-CTE parameters

Air flow:	50 ml/min
Sample time:	5 min
Temperature:	30 or 50°C

TD parameters

Soil gas tubes:	Tenax TA/Carbopack X
Prepurge time:	3 min (trap in line)
Tube desorb time:	5 min
Tube desorb temp:	300°C
Desorb flow:	40 ml/min
Cold trap:	Air Toxics trap
(designed for TO-15/17 analysis – see TDTS Note 81)	
Cold trap low temp:	25°C
Cold trap high temp:	310°C (3 min)
Split flow:	50 ml/min during trap desorption only
TD flow path temp:	200°C

GC parameters

Carrier gas:	He
Column:	VF-5ms 30 m x 0.25 mm x 0.25 µm
Constant pressure:	13 psi
Temp program:	50°C (1 min), 5°C/min to 140°C, 15°C/min to 300°C (1 min)
Column flow:	1.5 ml/min @ 50°C

MS conditions

MS Source temp:	230°C
MS Quadrupole temp:	150°C
MSD transfer line temp:	280°C
Mass Scan Range:	35 to 600 amu

Results and discussion

Each of the three fuels were tested on multiple sand samples under both wet and dry conditions and with the microchambers held at 30 and 50ºC. A subsequent repeat desorption of one of each of the fuel samples is also shown to demonstrate recovery during the thermal desorption process.

Note that the repeat analysis of each desorbed soil gas sample tube demonstrated negligible carryover in every case (<0.1%). This was true under all conditions (humidity, temperature) and for all fuel types. This indicates that the analytical system and the method parameters selected offered quantitative and complete recovery of all compounds of interest in one run and that the soil gas tubes would be ready for immediate reuse *i.e.* without additional conditioning.

Note also that, as expected, increasing the temperature and humidity of the spiked sand sample, increased the relative proportion of higher boiling fuel components present in the soil gas which would exacerbate recovery concerns if canisters were used for soil gas monitoring under these extreme conditions.

Conclusions

Soil gas tubes, as described, have been shown to provide suitable samplers for soil gas samples contaminated with a range of petroleum fuels under worst case real-world conditions of humidity and surface temperature. Both lighter hydrocarbons and polyaromatic/longer chain hydrocarbons were detected, confirming the results shown by Hayes *et al*. (2007) that sorbent tubes provide a representative TPH profile of light and middle distillate fuels in soil gas.

The soil gas tubes have also been shown to be compatible with complete quantitative recovery of even the heaviest fuel components, allowing for cost-effective immediate repeat use without additional conditioning.

Furthermore, the Markes TD system configured for air toxics analysis has also been shown to be compatible with soil gas contaminated with middle distillate fuels, offering complete recovery in one analysis.

Trademarks

Tenax TA® is a registered trademark of Buchem B.V., The Netherlands.

Carbograph 5TD™ is a trademark of LARA s.r.l., Italy.

Carbotrap X™ is a trademark of Sigma-Aldrich, Inc., USA.

SUMMA® is a registered trademark of Molectrics, USA.

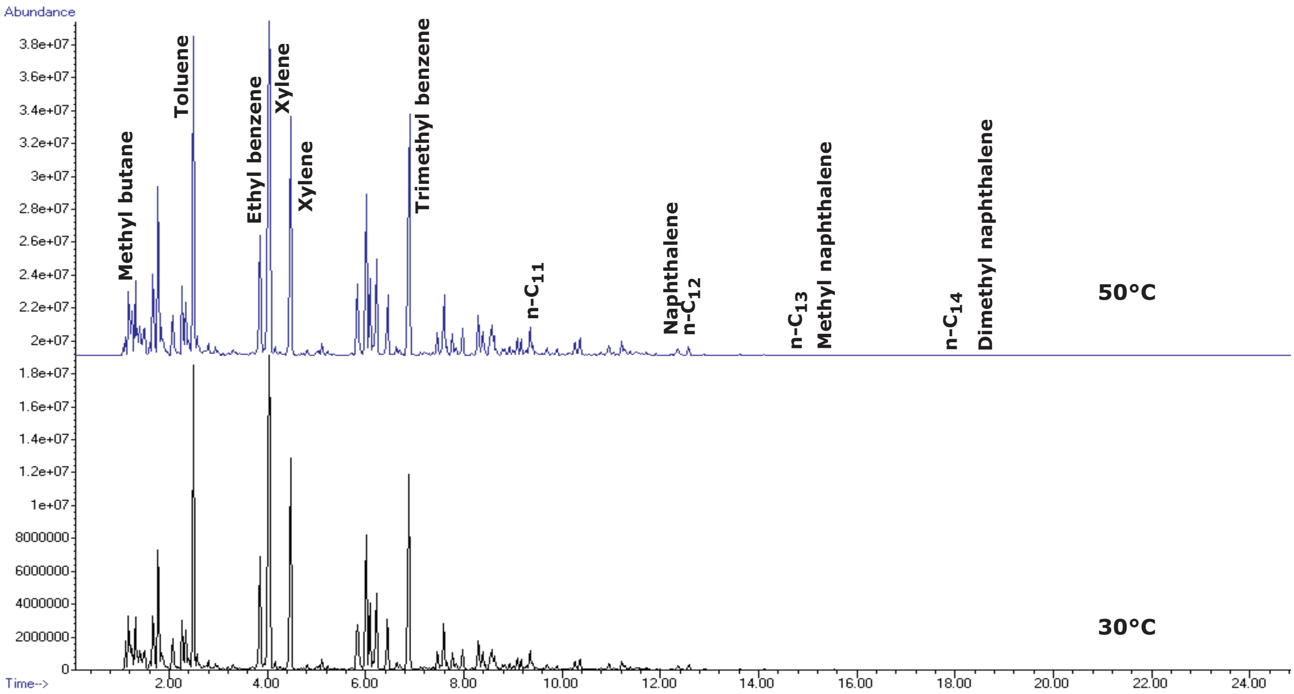

Figure 5: Gasoline vapor collected from dry sand samples at 30°C and 50°C using soil gas tubes

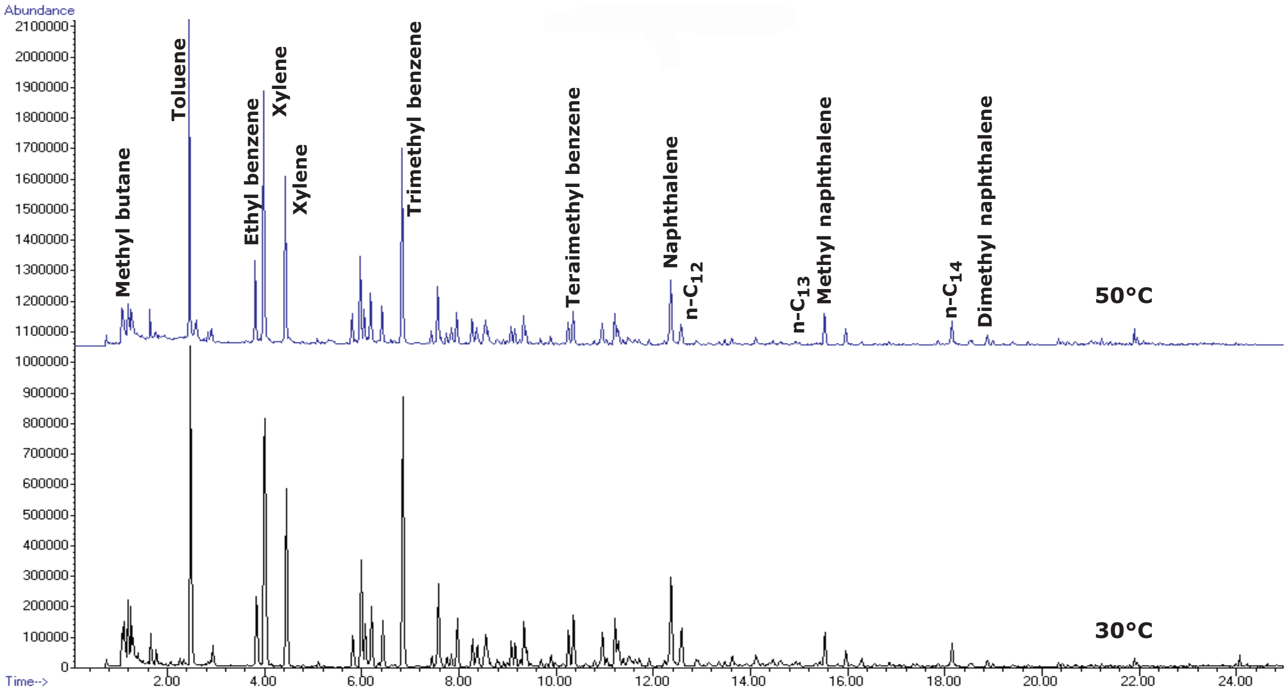

Figure 6: Gasoline vapor collected from wet sand samples at 30°C and 50°C using soil gas tubes

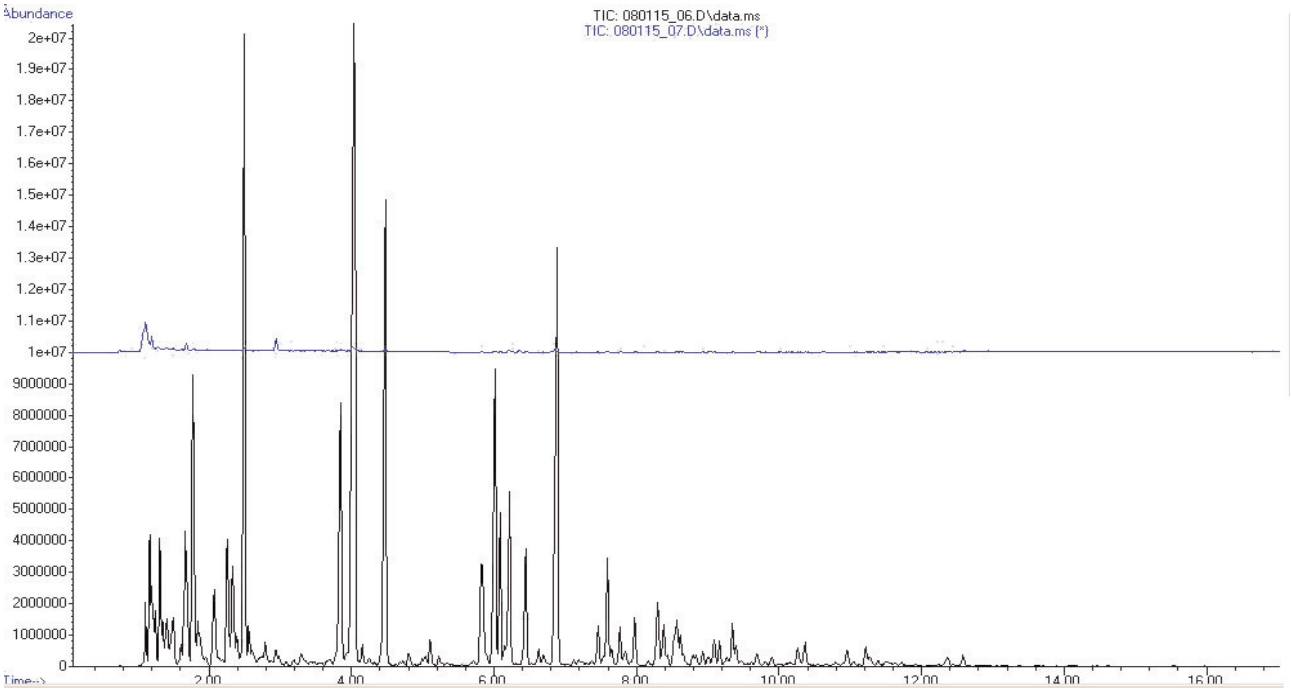

Figure 7: Gasoline vapor analysis with repeat desorption of tube showing negligible carryover

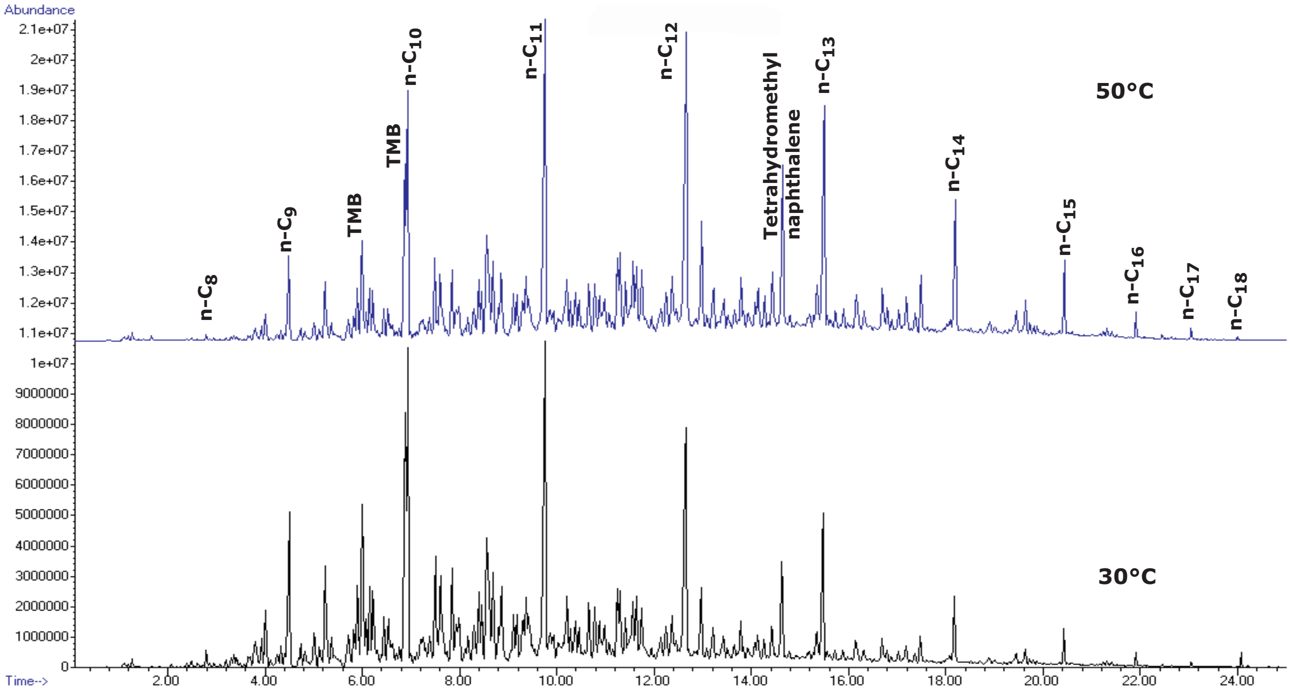

Figure 8: Diesel vapor collected from dry sand samples at 30°C and 50°C using soil gas tubes

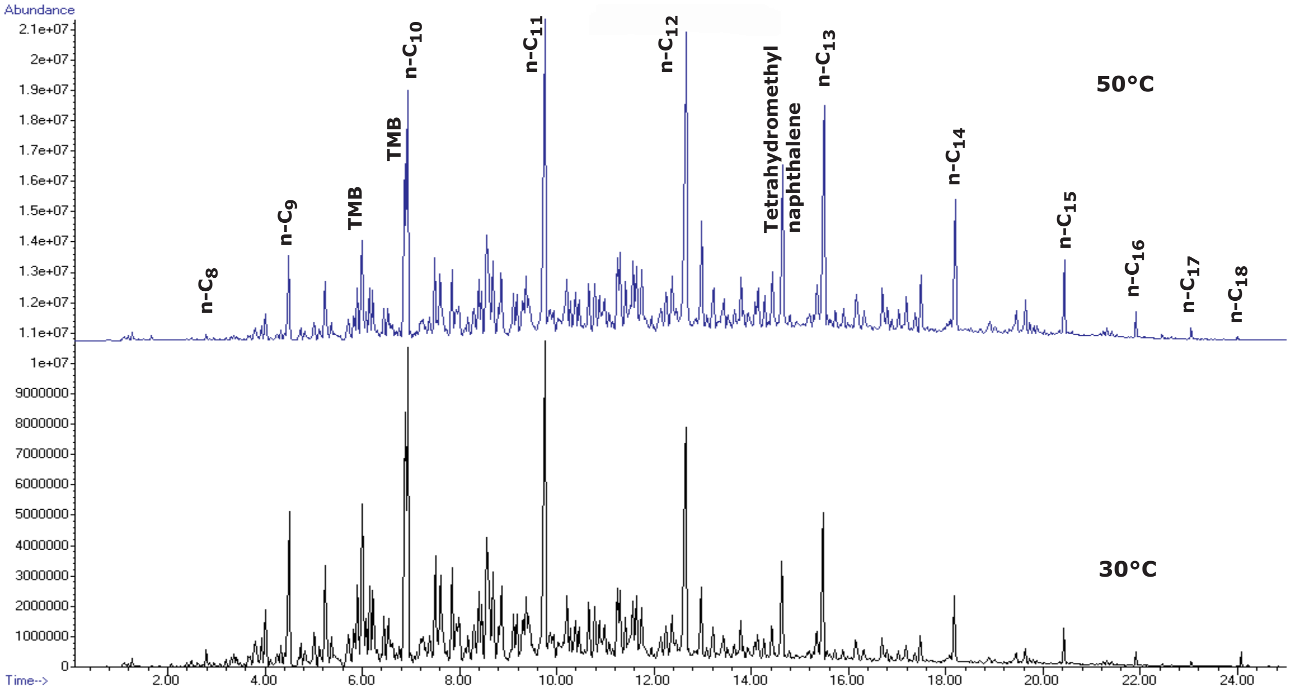

Figure 9: Diesel vapor collected from wet sand samples at 30°C and 50°C using soil gas tubes

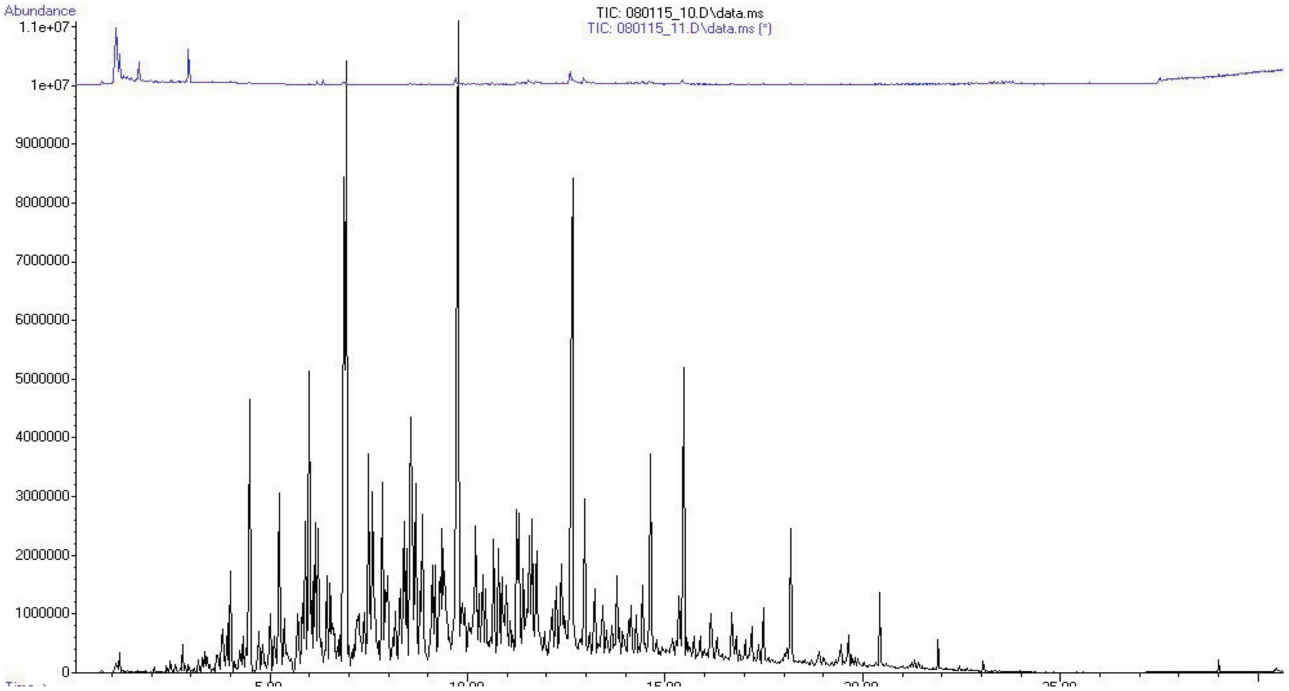

Figure 10: Diesel vapor analysis with repeat desorption of tube showing negligible carryover

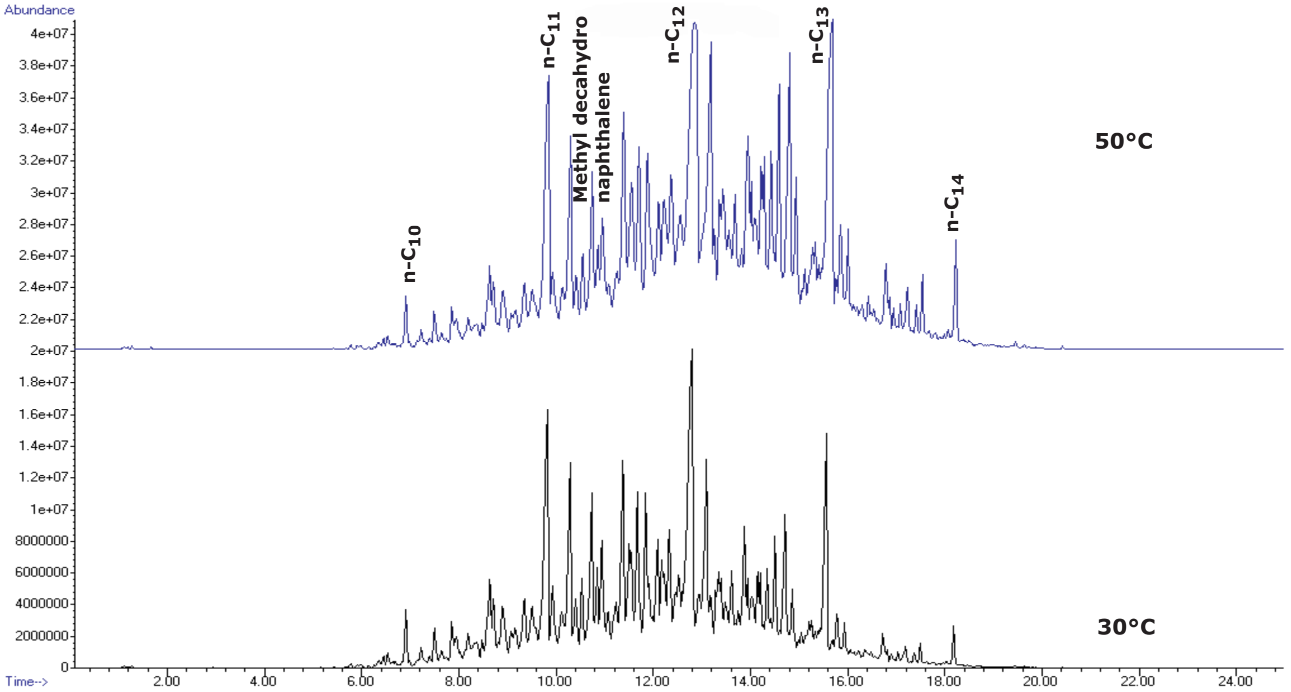

Figure 11: Kerosene vapor collected from dry sand samples at 30°C and 50°C using soil gas tubes

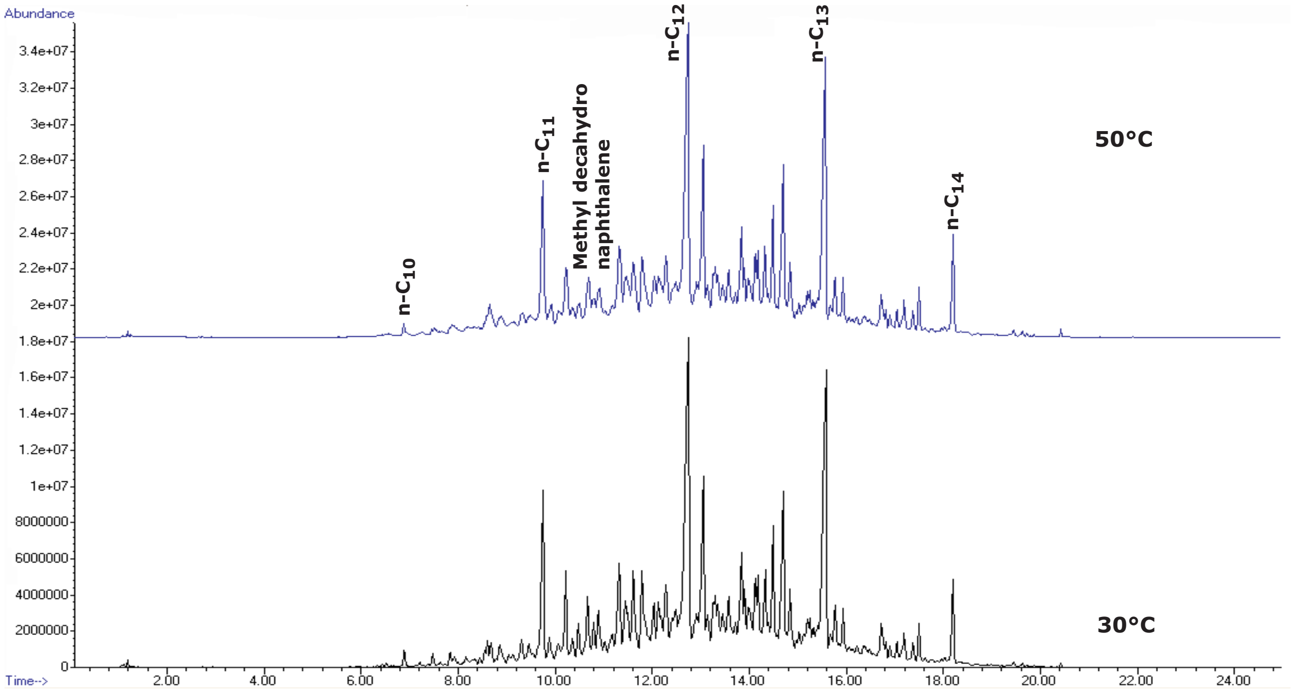

Figure 12: Kerosene vapor collected from wet sand samples at 30°C and 50°C using soil gas tubes

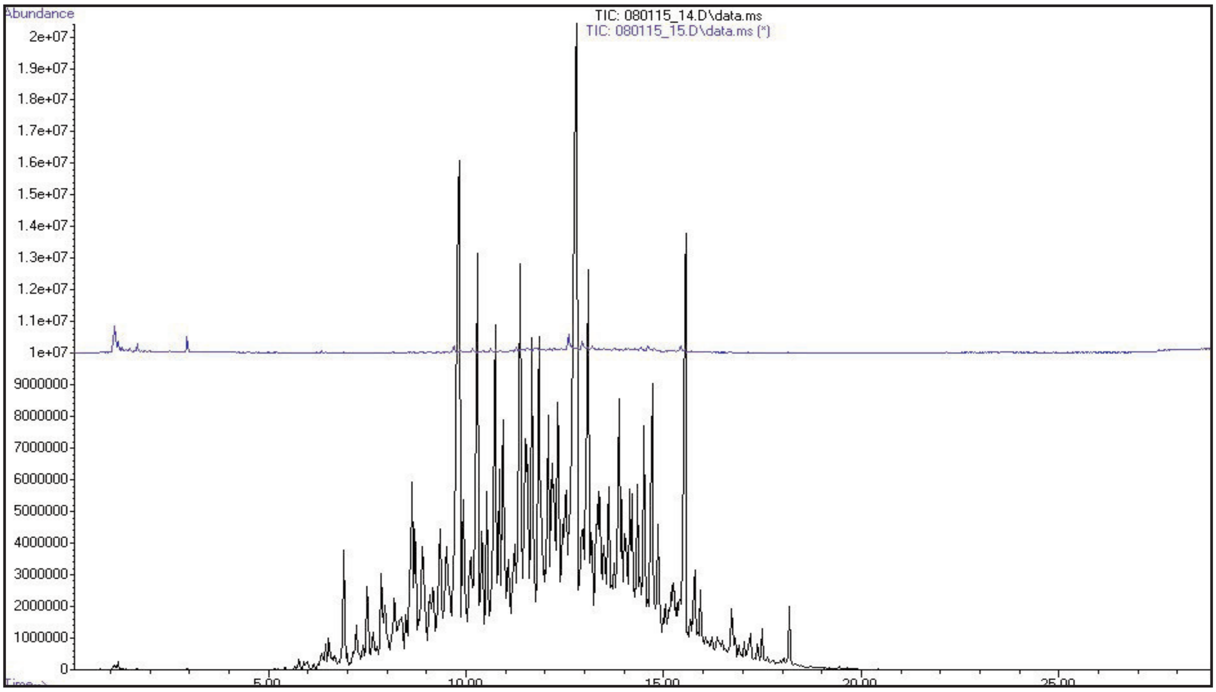

Figure 13: Kerosene vapor analysis with repeat desorption of tube showing negligible carryover

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