

Evaluation of Sorbent Methodology for Petroleum-Impacted Site Investigations

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ABSTRACT

Soil gas measurements are often used for risk assessment in vapor intrusion investigations. In the case of petroleum-contaminated sites, total petroleum hydrocarbon (TPH) characterization may be required to effectively measure the associated risk. One of the common strategies employed to characterize TPH for risk assessment includes the quantitation of indicator compounds of significant toxicological effects as well as the quantitation of hydrocarbon fractions of similar toxicity and mobility characteristics. While EPA Compendium Method TO-15¹ is commonly used to assess gasoline-impacted sites, heavier fuel types may not be effectively characterized using whole air collection methods. The low vapor pressures associated with fuels such as diesel and other middle distillates may result in poor recovery and precision using Method TO-15 canister methodology due to condensation effects in the canister.

An alternative sorbent-based method based on EPA Compendium Method TO-17² is evaluated for TPH soil gas measurements, specifically at sites contaminated with middle distillate fuels. A sorbent-based approach offers the inherent advantage of trapping the compounds before condensation occurs. Various adsorbent materials are evaluated for retention of fuel-related target compounds. Results between soil gas measurements from co-located TO-15 canisters and TO-17 sorbent tubes are compared for several fuel types.

INTRODUCTION

Sites requiring an evaluation of the vapor intrusion pathway may be contaminated with petroleum fuels heavier than the typical gasoline range of C₆ to C₁₀. The predominant carbon ranges for middle distillate fuels can span the C₉ to C₂₀ range and include kerosene, jet fuels, diesel fuels, and light fuel oils. Several regulatory agencies have established soil gas screening levels for middle distillate TPH as well as compounds with low volatility such as naphthalene and other light polyaromatic hydrocarbons. In addition to the measurement of TPH and select indicator compounds, some investigators are also interested in quantifying aromatic and aliphatic carbon ranges up to C₁₆ in the soil vapor to assess fate and transport as well as toxicological impacts of TPH.

To date, little attention has been given to the collection and analysis of middle distillate TPH and its associated compounds. For many active soil gas investigations EPA Method TO-15 is the standard analytical method for TPH measurements in soil gas. While Method TO-15 is generally limited to volatile compounds with vapor pressures greater than 0.1 Torr, carbon ranges for middle distillates can exhibit vapor pressures below Method TO-15 specifications. Heavier compounds and carbon ranges can exhibit poor or

erratic recovery during vapor collection, sample storage, and analysis. Preparation of accurate vapor-phase calibration standards is also difficult and stability can be a significant concern.

Sorbent-based methods offer an advantage to whole air methods in collecting and storing compounds with low vapor pressures since compounds are stabilized by adsorption onto the sorbent tube. Various sorbent methods using pumps for sample collection have been published in the EPA Compendium Methods for Ambient Air and in the NIOSH Manual of Analytical Methods³. EPA Compendium Method TO-17 describes sample analysis using thermal desorption (TD) GC/MS while NIOSH methods apply solvent extraction of the sorbent tube and analysis by GC/FID. Both methods have been applied to compounds in the middle distillate range in ambient air. Due to the sensitivity advantage of thermal desorption over chemical extraction, the definitive nature of mass spectrometry detection, and the wide range of TD adsorbent materials available, Method TO-17 is a more suitable option than NIOSH methods for soil gas measurements. While Method TO-17 has been applied to soil gas investigations, the focus has been on volatile petroleum hydrocarbons up to the C₁₀ fractions⁴. Little published data is available on naphthalene and middle distillate TPH measurements in soil gas using Method TO-17.

Since the publication of Method TO-17 in 1999, the newest commercially available TD instruments have overcome some of the drawbacks traditionally associated with TD methods. One of the major limitations has been the "one-shot" nature of thermal desorption. During desorption, sample compounds were released from the sorbent tube onto the re-focusing trap and GC/MS, eliminating the option for sample dilution or re-analysis. The newest TD units have a re-collection feature by which a portion of the desorbed sample is re-collected on a clean sorbent tube, allowing for sample re-analysis or archival. The advances in TD instrumentation and the applicability of TD methods to a wide volatility range (C₃ to C₂₀) make Method TO-17 an appropriate solution for TPH-related soil gas measurements.

SORBENT TUBE EVALUATION

Selecting the appropriate adsorbent material for sample collection is one of the key requirements for Method TO-17. The material must retain the compounds of interest yet efficiently release the compounds during the thermal desorption step. A wide range of adsorbents is commercially available, and typically classified as "weak", "medium", or "strong". As a rule, the stronger adsorbent materials have a larger surface area and are generally used to retain the most volatile compounds such as C₂ to C₅ carbon ranges. Weak adsorbents are used for heavier carbon ranges, generally C₆ to C₃₀. Tubes can be packed with single adsorbents to target a specific carbon range or with multiple adsorbents of increasing strength to target a wider volatility range, depending on the anticipated complexity of the mixture of compounds in the gas of interest.

The retention of a compound onto an adsorbent material is often measured in terms of breakthrough volume. Breakthrough volume is the volume of sample pumped through the sorbent tube such that the compound is no longer retained by the adsorbent. As a rule

of thumb, for a given material, the lower the boiling point, the lower the breakthrough volume. Safe sampling volumes are typically defined as two-thirds of the breakthrough volume and are used to determine the maximum sample volume that can be collected to ensure breakthrough does not occur. While breakthrough volumes and safe sampling volumes for various adsorbents and compounds are available in the literature as a guideline for adsorbent selection, the breakthrough volume also depends on the concentrations, which are generally not well-known in advance. Therefore, Method TO-17 recommends the assessment of breakthrough using typical field conditions and sample matrix.^{2,5}

Adsorbents can also be characterized by their affinity to water. The uptake of water by adsorbent materials can be significant, specifically for some of the strong carbon molecular sieve sorbents.^{6,7} Retention of water on the sample sorbent tube can present a challenge during sample analysis and can compromise the analytical results. Because of the high relative humidity of soil gas vapor, the performance of the sorbent under similar conditions must also be evaluated as part of the breakthrough study.

Testing Protocol

A wide variety of sorbents were evaluated for breakthrough and performance under high humidity conditions. Table 1 summarizes the adsorbent materials and their properties. A total of five single and multi-bed sorbent tubes of varying adsorptive strength and affinity to water were tested. The two single-bed sorbents were Tenax TA and Tenax GR. Carbograph 1TD was combined with Tenax TA to create a two-bed sorbent tube (T1). Additionally, two three-bed sorbents were tested. The first was a custom tube comprised of Tenax TA, Carbograph 1TD, and Carbograph 5TD (T15). A commercially available three-bed tube, Carbotrap 300 from Supelco, was also tested. The Carbotrap 300 contained Carbotrap C, Carbotrap B, and Carbosieve SIII.

Table 1. Sorbent Properties

Sorbent	Material	Classification ⁸	Volatility range ⁸	Affinity to water ^{7,8}
Tenax GR	Porous Polymer with Graphitized Carbon	Weak	~C _{6/7} to C ₃₀	Low
Tenax TA	Porous Polymer	Weak	~C _{6/7} to C ₃₀	Low
Carbograph 1TD Carbotrap B	Graphitized Carbon	Medium/Weak	~C _{5/6} to C ₁₄	Low
Carbograph 5TD	Graphitized Carbon	Medium/Strong	~C _{3/4} to C ₈	Low
Carbotrap C	Graphitized Carbon	Very weak	~C ₈ to C ₂₀	Low
Carbosieve SIII	Carbon Molecular Sieve	Very Strong	Ethane to C ₅	High

Performance was tested by connecting two sorbent tubes of the same materials in series. The front tube was spiked with a multi-component volatile mix. Each compound was spiked at a concentration of 1.0 µg for a total mass loading on the tube of 50 µg. The

front tube inlet was connected to a humidified air source, and the outlet end of the back tube was connected to an SKC Air Check Pump calibrated to pull a flow of approximately 100 mL/min through the tube pair. Humidified air was generated by pulling ambient air through a midjet impinger filled with de-ionized water. The relative humidity (RH) of the air stream sampled by the tube pair measured approximately 72 to 75% RH using a hygrometer (ROTRONIC HygroPalm). For each sorbent type, three tube pairs were prepared. Sample volumes of 1 L, 2 L and 4.5 L were pumped through each pair. After sample collection, the front and back tubes were analyzed separately by Method TO-17.

Results and Discussion

Breakthrough for each compound was calculated as the percentage of the back tube concentration compared to the total concentration measured on the front and back tube combined. The breakthrough results for several representative fuel-related compounds were evaluated including methyl tert-butyl ether (MTBE), benzene, toluene, ethyl benzene, xylenes, trimethylbenzenes, and naphthalene. (Although MTBE and benzene may be present at negligible concentrations in most middle distillate fuels, they are often included on the target list at fuel-impacted sites.) Of the compounds evaluated, breakthrough was tabulated for only MTBE and benzene because there was essentially no breakthrough for the other fuel-related compounds by any sorbent tested for all collection volumes. The results are summarized in Table 2.

Table 2. Breakthrough (BT) Results

Sorbent	Volume (Liters)	%BT MTBE	%BT Benzene
Tenax GR - 200 mg	1	4.0	<0.5
	2	4.0	<0.5
	4.5	13	15
Tenax TA - 200 mg	1	2.5	1.0
	2	3.2	0.9
	4.5	5.3	13
Tenax TA/Carbograph 1TD (T1) – 350 mg total	1	1.0	<0.5
	2	3.2	<0.5
	4.5	12	<0.5
Tenax TA/Carbograph 1TD/Carbograph 5TD (T15) – 430 mg total	1	<1	<0.5
	2	<1	<0.5
	4.5	<1	<0.5
Carbotrap 300 – Supelco 3.5” tube	1	<1	0.62
	2	N/A	N/A
	4.5	N/A	N/A

The TO-17 sorbent sample collection is considered valid if breakthrough of the target compounds is less than 5%. All sorbents tested met this breakthrough criterion for sample volumes of 1 L and 2 L. The weak sorbents, Tenax TA and GR, exceeded 5%

breakthrough for MTBE and benzene at a volume of 4.5 L. The two-bed sorbent comprised of Tenax TA coupled with the medium-strength Carbograph 1TD retained benzene even at the higher volume of 4.5 L, but did not show a significant improvement for the retention of MTBE over Tenax GR or TA alone. The three-bed sorbent containing Tenax TA, Carbograph 1TD and Carbograph 5TD demonstrated no measurable breakthrough even when collecting a 4.5 L sample.

The breakthrough data for the Carbotrap 300 adsorbent could not be calculated for the 2 L and 4.5 L sample because internal standard and target compound area recoveries from the front tube were low and accurate concentrations could not be reported. To determine the source of the low recoveries, the test was repeated along with a control group for which the sampled source was not humidified. The relative humidity of the air pumped through the control group tubes was approximately 50% RH. The internal standard and target compound areas were within method limits for each of the Carbotrap 300 tubes in the control group including the tube sampled with 4.5 L of air. In contrast, the results from the Carbotrap 300 tubes sampled with humidified air demonstrated low internal standard area recoveries for the 2 L and 4.5 L consistent with the original test. The second 4.5 L test also demonstrated a severe loss of sensitivity for the early eluting compounds. Several investigators have reported analytical interferences due to excessive water uptake of Carbosieve SIII, one of the adsorbents comprising the Carbotrap 300 tube.⁷

While the breakthrough data indicated that Carbotrap 300 tubes should be used with caution even when sampling soil gas volumes less than 2 L, the volume limitation of Tenax TA and GR for the lighter compounds does not eliminate their application to most middle distillate petroleum-impacted soil gas investigations. Most often, with TD-GC/MS analytical reporting limits of 0.005 to 0.010 μg for individual target compounds and 0.50 to 1.0 μg for fuels, screening levels for petroleum-related VOCs and middle distillate fuels can be met with soil gas volumes of less than 0.2 L. Volumes of 1 to 2 L may be needed when screening levels are less than 10 $\mu\text{g}/\text{m}^3$. It is important to note that although breakthrough was not significant at volumes less than 2 L in our study, soil gas containing TPH concentrations on the order of several hundred mg/m^3 can significantly reduce safe sampling volumes. To mitigate breakthrough, soil gas samples can be collected using two tubes in series. If breakthrough is suspected due to high concentrations measured on the front tube, then the back tube can be analyzed.

METHOD COMPARISON

Testing Protocol

To compare the performance of Method TO-17 to Method TO-15 for the measurement of middle distillate fuels in soil gas, a "bench-top" TPH soil gas standard was prepared. A mixture of 0.2 L of de-ionized water and 0.1 mL of middle distillate fuel was added to a 4 L container filled with silica sand. The container was sealed for approximately 24 hours to allow the vapors from the water/fuel mixture to permeate through the sand. A 1/4" rod was inserted in the center of the container, and a 1/4" Teflon tube probe was inserted in its place and capped. The top of the soil gas container was loosely covered, and the soil

mixture was allowed to age for approximately 2 weeks. During the aging process, the soil mixtures were exposed to heat by placing them in the direct sunlight for 2 to 3 hours.

The goal of the "bench-top" soil gas was to simulate the partitioning of the fuel components between the soil, water, and vapor phases. The measured composition of a vapor phase fuel calibration standard can differ significantly from the composition of the same fuel in a soil environment. To best compare the performance between Method TO-17 and Method TO-15 for middle distillate-impacted soil gas, the "real-world" TPH pattern is more relevant than comparing calibration standards.

To sample the soil gas, a Swagelok "T" fitting was attached to the soil gas probe. Equal lengths of Teflon tubing were attached to each end of the "T". One end of tubing was attached to a 3.5" Tenax TA sorbent tube packed with 200 mg of adsorbent. The other end was attached to a critical orifice 50 mL/min flow controller connected to a 1 L SUMMA canister. An SKC Air Check pump calibrated to a flow of approximately 50 mL/min was used to sample the tube. To commence sampling, the pump was started at the same time as the canister valve was opened. The sampling duration was 5 minutes, collecting 0.25 L on the tube and approximately 0.25 L in the canister. The canister was pressurized with UHP nitrogen to 15 psig and analyzed by Method TO-15. The Tenax tube sample was analyzed by Method TO-17.

To provide a direct comparison of the TPH patterns, the GC column and parameters were matched such that compound retention times between the two methods were within about 0.1 minutes. Additionally, sample loading volume on the TO-15 unit was fine-tuned such that similar area counts were achieved for most of the target compounds through naphthalene.

Three different types of fuels were used to prepare the "bench-top" soil gas samples. To verify that the soil gas sampling procedures and analytical parameters yielded comparable results for TO-15 and TO-17 samples, gasoline was used to generate one of the soil gas samples. Also, two middle distillate fuels, No. 2 Diesel Fuel and Jet Fuel 8 (JP-8), were spiked. The predominant carbon range is C₁₀ to C₂₀ for No. 2 Diesel and C₉ to C₁₆ for JP-8. JP-8 is a kerosene-based fuel similar to JP-5. Although the middle distillate fuels were aged prior to sampling, the gasoline-spiked soil gas was sampled and analyzed approximately 24 hours after preparation. Samples for each fuel were collected in duplicate.

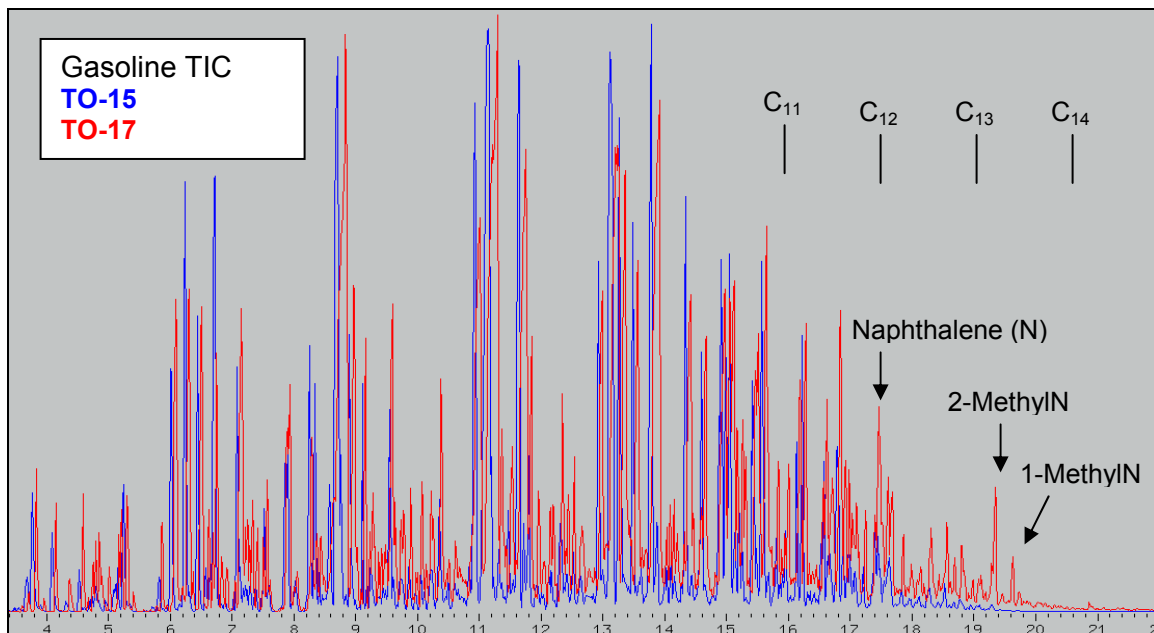
Results and Discussion

The data generated from the "bench-top" soil gas samples was intended to provide both a qualitative and quantitative comparison between Method TO-15 and Method TO-17 performance. The quantitative comparison was focused primarily on BTEX (minor components of middle distillates), naphthalene, and 2-methylnaphthalene. Naphthalene was of particular interest since it is an emerging compound of concern for many fuel-impacted sites. In California, naphthalene has been re-classified as a carcinogen, and the California Human Health Screening Level (CHHSL) for shallow soil gas at residential sites is now 32 µg/m³.⁹ Similarly, the 2002 EPA OSWER draft guidance lists a generic

screening level for naphthalene of $30 \mu\text{g}/\text{m}^3$ at the 10^{-6} risk level.¹⁰ Unfortunately, neither the diesel nor the JP-8 samples contained concentrations of BTEX and naphthalene high enough to provide a statistical comparison. The replicate gasoline samples did contain measurable target concentrations; however, definitive conclusions could not be made due to the small data set. Additional work is on-going to generate soil gas data to quantitatively compare TO-15 performance to TO-17, specifically for naphthalene.

The soil gas data collected did allow for qualitative comparisons between the methods. Figure 1 shows an overlay of the total ion chromatograms for the TO-15 and TO-17 gasoline soil gas samples. Approximate carbon ranges based on the elution of the corresponding n-alkanes are indicated on the chromatograms. As expected, the two methods generated a similar TPH pattern for gasoline-range TPH in the C_6 to C_{10} range. However, the peaks in the region of the chromatogram after C_{11} showed a reduced response for the TO-15 run compared to the TO-17 run, including the 2- and 1-methylnaphthalene peaks.

Figure 1. TO-15 and TO-17 Total Ion Chromatogram overlay: gasoline-spiked soil gas



The total ion chromatograms for diesel and JP-8 are shown in Figures 2 and 3. In the case of diesel, the TO-15 chromatogram matched the TO-17 trace very closely for the earliest eluting compounds with the chromatograms diverging near the C₁₂ range. Compared to diesel, the JP-8 chromatograms showed less comparability between TO-15 and TO-17 in the region prior to C₁₂ and greater overall divergence between the two chromatograms. The TO-17 TPH pattern for both diesel and JP-8 included a significant area in chromatographic region after C₁₃ elution as compared to the TO-15 pattern.

Figure 2. TO-15 and TO-17 Total Ion Chromatogram overlay: diesel-spiked soil gas

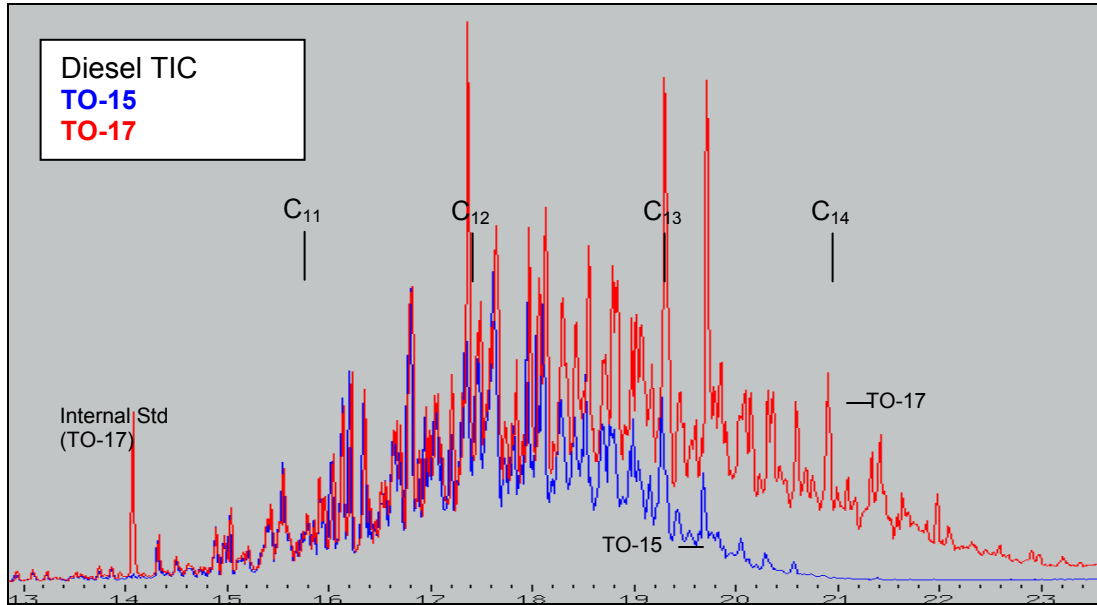
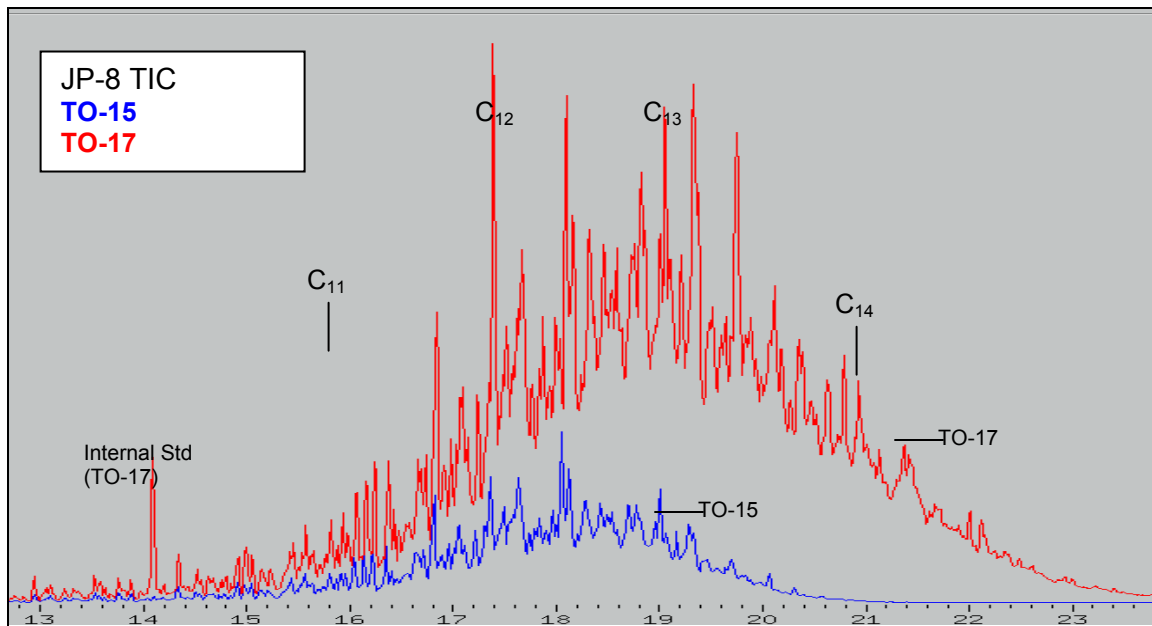
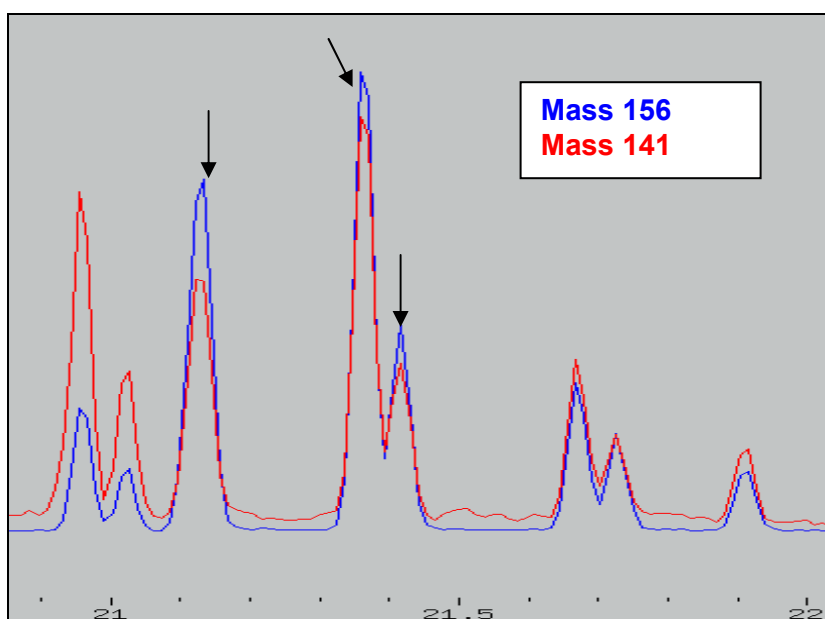


Figure 3. TO-15 and TO-17 Total Ion Chromatogram overlay: JP8-spiked soil gas



Despite the low vapor pressure of hydrocarbons in the C₁₃ to C₁₆ volatility range, the TO-17 data demonstrated that these hydrocarbons can constitute a significant fraction of the TPH in soil vapor, which would not be evident with the TO-15 analyses. Evaluation of the mass spectral information of peaks in this chromatographic region indicates the presence of alkyl naphthalenes, branched and straight chain alkanes, and other hydrocarbons. As an example, several dimethylnaphthalene isomers and other C₁₂ aromatics were identified in both the diesel and JP-8 samples. The characteristic mass ions of 156 and 141 for the dimethylnaphthalene isomers were extracted from the total ion chromatogram, and estimated concentration for each isomer in the soil vapor phase ranged from 75 to 200 µg/m³. The extracted ion profile for JP-8 is shown in Figure 4. The data was also evaluated to determine the presence of the light polyaromatic hydrocarbons such as acenaphthene, acenaphthylene, and fluorene. None were detected in either sample.

Figure 4. JP-8 Extracted ion profile – Dimethylnaphthalene isomers



CONCLUSION

With the proper selection of sorbent tube and sampling parameters, Method TO-17 can be successfully applied to soil gas measurements. Due to the sensitivity of thermal desorption technique, relatively small volumes of soil gas are needed to meet most screening levels. Additionally, Method TO-17 provides more accurate fuel fingerprints heavier than gasoline at sites contaminated with middle distillate fuels. Naphthalene and other light polyaromatic hydrocarbons, as well as hydrocarbons through the C₁₆ range, can be reliably and accurately measured using Method TO-17. Studies to provide a quantitative comparison between Method TO-15 and Method TO-17 for fuel-related compounds of concern are on-going.

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