



## 7.8 SOIL VAPOR OR INDOOR AIR SAMPLE ANALYSIS

The analytical methods selected for analyzing soil vapor or indoor air samples depends on the conceptual migration model, intended use of the data (i.e., characterization versus exposure pathway assessment), and site-specific field conditions. In Hawai'i, soil vapor or indoor air samples are typically forwarded to a fixed analytical laboratory. Different levels or required precision often dictate whether on-site analysis is feasible, as on-site methods are generally less precise and contaminants cannot be quantified at extremely low levels. Analytical methods should be consistent within each sampling event as well as for different sampling events to assist in the interpretation of the analytical data.

The physical state of specific chemicals (i.e., whether a chemical is considered "volatile" or "non-volatile" by the Hawai'i Department of Health (HDOH) Hazard Evaluation and Emergency Response Office [HEER Office]) is presented in the document Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater (HDOH, 2008). The Physical State column presented in Table H in Appendix 1 (HDOH, 2008) lists "V" for volatile chemicals (based on the Henry's Law Constant and molecular weight) or "NV" for non-volatile chemicals.

### 7.8.1 Analytical Method Selection

Soil vapor or indoor air samples collected to assess petroleum contamination must always be analyzed for Total Petroleum Hydrocarbons (TPH) in addition to targeted, individual chemicals (HDOH, 2008). TPH is the volatile component of petroleum contamination, specifically six to twelve carbon chains in length, which overlaps between methods for gasoline and diesel.

As indicated in Section 9, several volatile components of petroleum are identified as target indicator compounds, which should be included when conducting soil vapor or indoor air investigations. The target indicator compounds recommended for analysis at petroleum contaminated sites are listed in Table 9-5.

The USEPA's air toxic program (USEPA, 1999b), solid waste program (USEPA, 1998b), and other promulgated methods (USEPA, 1996c; USEPA, 2002c) also provide recommendations for analytical methods.



The American Petroleum Institute publication titled *Collecting and Interpreting Soil Gas Samples from the Vadose Zone* (API, 2005) recommends that prior to the selection of analytical methods, the following questions should be answered:

- What are the specific chemicals of concern or other analytes (e.g., natural attenuation parameters) that need to be identified by the analysis? The specific analytes (e.g., benzene, naphthalene) for the subsurface-vapor-to-indoor-air exposure pathway should be identified. Generally, these will be the volatile and semi-volatile chemicals of concern identified during the overall site investigation. Many regulatory agencies have identified specific chemicals of concern that should be included in the analyte list. However, if specific chemicals of concern are not identified, an analytical method should be selected based on its ability to detect the range of analytes (e.g., VOC, SVOCs) that may be present at a site.

Even though risk-based pathway assessment is based on concentrations of chemicals of concern, it is important to also measure the total petroleum hydrocarbon concentration in soil vapor at petroleum hydrocarbon impacted sites. This is necessary to understand adequately the subsurface processes, especially as they relate to biodegradation. For example, the attenuation by biodegradation of any single chemical is influenced by the presence of all hydrocarbons in the soil vapor, as they determine the total oxygen demand and oxygen-penetration depth. The total petroleum hydrocarbon measurement should be the full range of detectable hydrocarbons, not of a specific product range of carbon numbers (e.g., as in a soil or water analysis that quantifies “gasoline range organics”).

- What analytical method reporting limits are required to adequately assess the potential exposures? It is important to determine the smallest concentrations of chemicals of concern in soil vapor or other analytes that are expected to be required for purposes of evaluating the subsurface-vapor-to-indoor-air exposure pathway. To evaluate this exposure pathway, indoor air target levels for chemicals of concern or other analytes should be identified. These indoor air target levels can be used to identify the necessary detection limits for the soil vapor analyses. Generally, the detection limits



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for concentrations of chemicals of concern in soil vapor should be no more than 100 times the target indoor air concentration so that non-detect concentrations can be conclusively evaluated.

- Do soil or groundwater analytical results, or other field data, indicate that concentrations of chemicals of concern in soil vapor will be high? If concentrations of chemicals of concern or other analytes in soil vapor are anticipated to be high, then the analytical method selected should address high concentrations. In cases where high concentrations are anticipated, solid waste program methods (USEPA, 1998b) may be appropriate. There is some concern that the solid waste program methods may be biased low for some chemicals of concern. Hartman (2004a) indicates that for BTEX, and chlorinated hydrocarbons the solid waste program methods and air toxics methods produce similar results.
- How are the samples to be collected? The analytical method selected, in many cases, will define the collection method (e.g., Summa canister) that should be used and typically the sample preparation that is required to analyze a sample.
- Do the regulatory agencies require certification of the laboratory or that specific analytical methods be used? Some state or federal regulatory agencies require that samples be analyzed by specific methods. They may also require the laboratory that is conducting the analysis to be certified under a state or national program. In some cases, this may limit the use of field analytical methods. HDOH does not currently require analysis labs in Hawai'i to be certified for soil vapor analyses; however, the HEER Office recommends that lab certifications and/or other lab quality control measures be carefully considered when selecting an analysis lab.
- Are there short turnaround times required for analytical results? Turnaround times will be influenced by shipping requirements, holding times, laboratory backlog, and analytical methods. Depending on the priorities of the subsurface-vapor-to-indoor-air exposure pathway evaluation, field analysis may be preferable to shipment to a laboratory. Field analysis can provide nearly real time results.



- Are the analytical methods appropriate for the soil vapor samples? The analytical methods often are updated with newer techniques. It is suggested that the user consult with the regulatory agency and a qualified analytical laboratory to identify analytical methods appropriate for the specific site.

### **7.8.2 Field Analytical Methods**

Field analytical methods range from qualitative (e.g., using a PID) to quantitative (e.g., using a portable gas chromatograph [GC] or mass spectrometer [MS]). As indicated above, the specific sampling objectives should define the required data precision, which may influence the selection of field versus laboratory analytical methods. Different levels of required precision often dictate whether on site analysis is feasible as on site methods are generally less precise and cannot be quantified at extremely low levels. Mobile laboratories in the field should follow the same analytical and quality control procedures as used in fixed laboratories.

### **7.8.3 Laboratory Analytical Methods**

Laboratory analytical methods are quantitative and can generally achieve low detection limits. Laboratory quantitation limits are critical for risk-based decision-making in indoor air analysis. Therefore project planners should work closely with both the analytical laboratory and toxicologists to ensure that the analytical data meet the project requirements. For indoor air samples, method TO-15 in selected ion mode may be the required analysis to achieve the required quantitation limits that are below the risk-based action levels. For soil vapor samples, the contaminant concentrations are expected to be higher than the indoor air, so less-stringent quantitation limits are required and method TO-14 may be sufficient to meet the project requirements.

The following laboratory analytical methods are recommended for contaminants commonly detected during site investigations in Hawai'i:



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**Table 7-1 Recommended Laboratory Analytical Methods for Soil Vapor or Indoor Air Contaminants**

Analyte	Analytical Method	Reference
TPH	TO3, 8015B	USEPA, 1998b
BTEX, MTBE	TO15, 8260B	USEPA, 1998b
VOCs	TO14, TO15, TO1, TO2, TO17	USEPA, 1998b
SVOCs	8270C	USEPA, 1998b
Oxygen, CO <sub>2</sub> , Nitrogen, Methane	3C, ASTM D-1946	USEPA, 2002c
Polynuclear aromatic hydrocarbons (PAHs)	TO13A	USEPA, 1999b

Other analytical methods not listed above may be utilized on a site-specific basis. A description of the alternate analytical method, rationale for its selection, and analytical results should be fully documented in the final soil vapor or indoor air investigation report.

**7.8.4 Quality Control Samples**

**7.8.4.1 Field Quality Control**

Field duplicate samples should be collected at a minimum of 10% of the soil vapor or indoor air samples collected per sampling day per laboratory (if more than one laboratory is used). If less than ten samples are collected during each day or sampling event, a minimum of one duplicate sample is recommended per sampling day or event.

In general, a field duplicate is a second sample collected in the field simultaneously with the primary sample at one single location. The duplicate sample is collected in a separate sample container from the same location and depth as the primary sample. Collection of a duplicate simultaneously with the primary sample utilizing a “T” sample inlet is recommended. However, specific configurations of sample collection inlets may be discussed with the analytical laboratory and be fully documented in the soil vapor or indoor air sampling report. The results of the duplicate field sample can be used to calculate a relative percent difference to provide information on consistency and reproducibility of field sampling procedures. Figure 7-9 shows two types of laboratory-supplied



apparatus used to collect duplicate samples in the field, a tubing “Y” for sorbent tube media, and a stainless steel “T” manifold for summa canisters.

For soil vapor or indoor air samples shipped to a fixed laboratory, a trip blank should be included for VOC samples at a minimum of one trip blank per sampling day or shipment cooler. The trip blanks should consist of laboratory grade ultra pure air. The results of the trip blank sample can be used to evaluate if the shipping and handling procedures are introducing contaminants into the samples, and if cross contamination in the form of VOC migration has occurred between the collected VOC samples. The trip blank containers and media should be identical as the normal samples. Trip blanks are not required for the use of Summa canisters as they do not provide meaningful data.

#### ***7.8.4.2 Laboratory Quality Control***

The accuracy of an analytical method depends on sample handling and preparation and maintenance of the analytical equipment (API, 2005). Most analytical methods recommended by the USEPA include minimum quality control measures designed to assess the performance of the analytical procedures. Minimum quality control measures should include the calibration of instruments and an assessment of the analytical accuracy and precision (USEPA, 2000d). Analytical accuracy and precision is typically assessed through the use of method blanks, laboratory control samples, and matrix spike samples (see Section 10). Additional details on quality control measures for analytical methods are included in the method’s documentation (USEPA, 1998b; USEPA, 1999b; USEPA, 2002c) or as stipulated in SW-846 (USEPA, 1986).