GUIDANCE DOCUMENT

Use of GC/MS Analysis to Distinguish Between Vapor Intrusion and Indoor Sources of VOCs – Standardized Protocol for On-Site Evaluation of Vapor Intrusion

ESTCP Project ER-201119

July 2014

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 07-2014	**2. REPORT TYPE** User's Guide	**3. DATES COVERED** *(From - To)* 03-2011-07-2014

4. TITLE AND SUBTITLE
Use of Compound-Specific Stable Isotope Analysis to Distinguish Between Vapor Intrusion and Indoor Sources of VOCs - Standardized Protocol for On-Site Evaluation of Vapor Intrusion

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER
ER-201119

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER
ER-201119

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
SERDP/ESTCP
4800 Mark Center Drive, Suite 17D08
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)
SERDP/ESTCP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This guide provides a standardized protocol for the use of on-site gas chromatography/mass spectrometry (GC/MS) analysis to evaluate the potential for vapor intrusion in a building, including the ability to distinguish between vapor intrusion and indoor or other sources of volatile organic chemicals (VOCs). This vapor intrusion investigation approach provides an alternative to the conventional investigation method of indoor air and sub-slab testing using Summa canisters and off-site laboratory analysis. The protocol was developed and validated as part of Environmental Security Technology Certification Program (ESTCP) Project No. ER-201119 (GSI, 2013).

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**		43	Carmen Lebron
					19b. TELEPHONE NUMBER *(Include area code)* 713-522-8010

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Table of Contents

TABLES

FIGURES

1.0 INTRODUCTION

This guide provides a standardized protocol for the use of on-site gas chromatography/mass spectrometry (GC/MS) analysis to evaluate the potential for vapor intrusion in a building, including the ability to distinguish between vapor intrusion and indoor or other sources of volatile organic chemicals (VOCs). This vapor intrusion investigation approach provides an alternative to the conventional investigation method of indoor air and sub-slab testing using Summa canisters and off-site laboratory analysis. The protocol was developed and validated as part of Environmental Security Technology Certification Program (ESTCP) Project No. ER-201119 (GSI, 2013).

This investigation protocol relies on use of a commercially-available off the shelf (COTS) field-portable GC/MS instrument and real-time decision making. The use of on-site analysis significantly improves an investigator's ability to distinguish between vapor intrusion and other sources of VOCs detected in indoor air.

This standardized investigation protocol includes:

- Building operating procedures to minimize air mixing prior to sample collection;
- Systematic sample collection and analysis to determine the distribution of VOCs within the building and to identify likely indoor sources of VOCs and/or vapor entry points;
- Procedures to test specific sources and entry points;
- Confirmation sampling following source isolation and/or removal; and
- Optional procedures for additional testing under controlled building pressure conditions to further evaluate VOC sources as well as potential temporal variability in vapor intrusion.

2.0 APPLICABILITY

Building-specific investigations of vapor intrusion are typically required when VOCs have been detected above applicable screening concentrations within 30 to 100 feet (ft) of the buildings and the results of subsurface testing (i.e., groundwater and/or soil gas) indicate a potential vapor intrusion concern (USEPA, 2002; ITRC, 2007).

When a building-specific investigation is required, the on-site GC/MS investigation procedure is broadly applicable to a wide variety of building types and constituents of concern (COCs). The investigation procedure can be applied either i) as an **initial investigation tool** at buildings without prior vapor intrusion testing or ii) at buildings where preliminary testing of indoor air has identified VOC concentrations above regulatory screening values and there is some **uncertainty concerning the source of the VOCs**. Specific considerations for the selection of this investigation procedure are discussed in Section 2.1-2.4 below.

2.1 Building-Specific Considerations

The use of on-site analysis relies on the difference in COC concentrations within a building in order to identify sources (e.g., vapor entry points or specific products and/or materials within the building). As a result, the method is most effective in buildings comprised of discrete spaces (i.e., rooms). However, even in buildings that consist of large, open spaces (e.g., warehouses), the concentration gradients observed within the building are commonly large enough so that the source can be identified. The effectiveness of the method is improved when mixing of air within the building can be minimized (i.e., doors closed and heating, ventilation and air conditioning (HVAC) system turned off).

2.2 Vapor Intrusion COCs

On-site GC/MS analysis is most effective for the identification of sources of chlorinated VOCs (cVOCs). Indoor sources of cVOCs typically contain high concentrations of one or two individual chlorinated compounds (i.e., strong sources). Additionally, an individual building typically contains only a small number of sources. These sources (e.g., tube of glue) cannot often be identified by standard methods (e.g., visual inspection), but can usually be identified based on the observed distribution of cVOCs within the building.

In contrast to cVOCs, petroleum VOCs typically occur in complex mixtures where the risk drivers (e.g., benzene and ethylbenzene) are present only in low concentrations (i.e., weak sources). Buildings may contain a large number of these indoor sources of petroleum VOCs resulting in a distribution within the building that makes it difficult to identify all of the individual sources. On-site analysis can be used to identify strong indoor sources of petroleum VOCs or significant vapor entry points. However, for petroleum VOCs, the method has a greater potential to yield equivocal results. Because petroleum VOCs are found in a wide range of consumer products, the background level is also likely to be higher, making it more difficult to isolate weak or moderate sources.

2.3 Use of On-Site GC/MS Analysis for Initial Building Investigations

As indicated above, on-site GC/MS analysis may be used i) for **initial building investigations** or ii) at buildings where preliminary testing of indoor air has identified VOC concentrations above regulatory screening values, and there is some **uncertainty concerning the source of the VOCs**. The presence of the three site conditions discussed below would favor the use of this method as an initial investigation tool. However, other factors are also likely to be important at some sites. The decision of whether to use on-site analysis for initial investigation or follow-up will inevitably involve professional judgment.

- <u>Likely Indoor Source of Target VOCs</u>: The prevalence of indoor sources varies significantly for different chlorinated VOCs. For example, tetrachloroethylene (PCE) is used in a wide variety of consumer products including hobby craft glues, oven cleaner, silver polish, water-proofing spray, lubricant spray, and other products. 1,2-dichloroethane (1,2-DCA) is commonly emitted from plastic decorations present in most houses (Doucette et al., 2010). Trichloroethylene (TCE) is less common but is found in gun cleaner, "industrial strength" cleaner, self-defense "pepper" spray, and other products. In contrast, cis-1,2-dichloroethene (cis-1,2-DCE), 1,1-dichloroethene (1,1-DCE), and vinyl chloride (VC) are rarely present in consumer products, although low concentrations of some of these VOCs can be generated by the reaction of bleach with other organic materials in bleach cleaners (Odabasi, 2008). The relative potential for indoor sources of various VOCs to result in exceedances of indoor air screening concentrations is illustrated in Table 1.

Table 1: Likelihood of VOC to be a Problematic Indoor Source

Higher	Benzene, 1,2-DCA (EDC), Naphthalene
	Ethylbenzene, Carbon Tetrachloride, Chloroform
↕	PCE
	TCE, trans-1,2-DCE
	Toluene, Xylenes, 1,1,1-TCA
Lower	1,1-DCE, cis-1,2-DCE, Vinyl Chloride, methyl tertiary butyl ether (MTBE)

Note: “Problematic” source based on potential for indoor source to result in an exceedance of the indoor air screening value. Although toluene and xylene are commonly detected in indoor air, the concentrations are typically well below the indoor air screening value. The analysis is qualitative and is based on field experience and comparison of typical background range from literature (e.g., Dawson and McAlary, 2009) to indoor air screening values (USEPA, 2013). See Gorder and Dettenmaier, 2011, for information on indoor sources of trans-1,2-DCE. Although benzene, ethylbenzene, and naphthalene commonly have problematic indoor sources, the on-site analysis method may be less effective for these constituents (see Section 2.2). Carbon tetrachloride can be an ingredient in adhesives. However, carbon tetrachloride and chloroform are also associated with household cleaning products containing chlorine bleach (Odabasi, 2008).

If the VOCs for the vapor intrusion investigation include one or more VOCs where indoor sources are likely to result in exceedances of the applicable indoor screening concentrations, then on-site analysis is favored due to its ability to identify indoor sources which can then be removed prior to collection of indoor air samples for vapor intrusion decision-making.

- <u>High Stakeholder Concern</u>: At sites with high stakeholder concern regarding vapor intrusion, the investigation results are usually interpreted with a higher level of conservatism. For example, at sites with high concern, a foundation attenuation factor of 0.1 to 1 may be used for evaluation of sub-slab samples rather than the more common range of 0.01 to 0.1. Alternatively, multiple rounds of conventional testing may be required to evaluate potential temporal variability in vapor intrusion. High stakeholder concern favors the use of the on-site analysis method because a highly conservative evaluation of the results from conventional testing is more likely to yield inconclusive results.

- <u>Need for Rapid Source Identification and Mitigation</u>: For some buildings (e.g., schools), the identification of VOCs in indoor air at concentrations above screening levels could cause an immediate concern. The on-site analysis method allows the identification and removal of indoor sources during the initial testing. In cases of vapor intrusion, the

> method allows the identification of specific vapor entry points or areas which may allow immediate measures to reduce vapor intrusion. The need for rapid mitigation of indoor air exceedances favors the use of the on-site analysis method. In the event that immediate measures must be taken, the on-site analysis method also allows the user to quickly evaluate whether these measures are improving indoor air quality.

If conventional testing is used for the initial building-specific vapor intrusion investigation, then the on-site analysis method may be used for follow-up testing at buildings where the conventional program did not yield definitive results.

2.4 Tools for On-site GC/MS Analysis

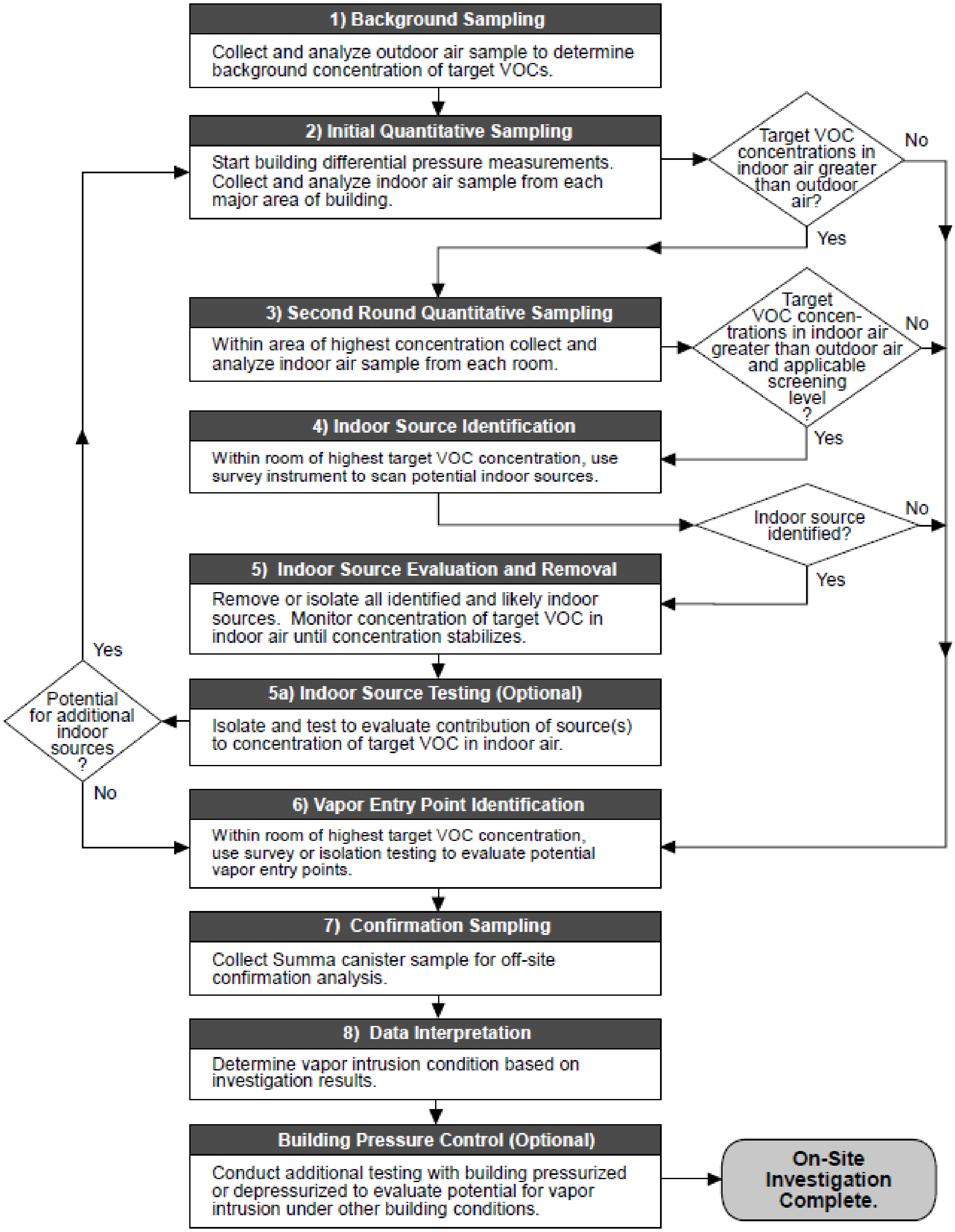
This investigation protocol requires a field-portable instrument that provides i) sufficient compound specificity and sensitivity to measure VOCs in indoor air at levels of regulatory concern (i.e., <1 ug/m^3 for cVOCs, and <5 ug/m^3 for petroleum VOCs), with ii) sufficient precision to measure concentration gradients within a building. The general investigation procedures (Section 3.0) can be implemented using any field-portable instrument meeting these requirements.

This investigation protocol was developed using the Smart Plus model of the HAPSITE GC/MS as the on-site analysis tool. Additional information specific to the HAPSITE is provided in Section 5.0. This information includes analytical method specifications, calibration procedures, and costs.

3.0 GENERAL INVESTIGATION PROTOCOL

The investigation protocol for use of on-site GC/MS analysis for the evaluation of vapor intrusion is illustrated in Figure 1.

Figure 1: On-Site GC/MS Analysis Building Investigation Process



Notes: 1) QA steps are not shown in the flowchart. 2) The last step of the process (on-site investigation complete) refers to the field investigation program. Preliminary interpretations regarding vapor intrusion can be made based on on-site results. Additional investigation of the building may or may not be required, depending on final evaluation of the results including results from confirmation samples (collected in Step 7) analyzed by an off-site laboratory. 3) The flow chart illustrates the recommended investigation process. Deviations from the process may be warranted based on site-specific factors.

3.1 Pre-Sampling Activities

The technical team should determine the activities to be completed prior to mobilization. These pre-sampling activities include:

1) **Identify specific structures for sampling**: Select specific structures based on factors such as the distance from and nature of the potential subsurface source.

2) **Determine target VOCs for on-site analysis and screening concentrations for field decision-making**: Identify the VOCs to be included in the on-site investigation program. The target VOCs should be the one or two vapor intrusion COCs of greatest concern based on consideration of subsurface concentrations and indoor air screening concentrations. Additionally, consider the sensitivity of the on-site analysis tool relative to the desired screening concentrations (e.g., concentrations less than or equal to regulatory screening levels).

   As shown on Figure 1 and discussed further below, concentrations of target VOCs are compared to screening concentrations or levels at different points in the investigation process. This is done to interpret whether vapor intrusion is occurring or not. For the purposes of this protocol, "vapor intrusion" is defined as VOCs migrating from a subsurface source into a building at levels above the screening concentrations.

   Note that buildings may contain a large number of the indoor sources of petroleum VOCs resulting in a distribution of petroleum VOCs within the building that makes it difficult to identify all of the individual sources. On-site analysis can be used to identify strong indoor sources of petroleum VOCs or significant vapor entry points. However, for petroleum VOCs, the method has a greater potential to yield equivocal results.

3) **Obtain necessary equipment**: Equipment typically required to implement the on-site analysis procedure is listed in Table 2 below. The list should be modified to reflect site-specific requirements. At a minimum, the procedure requires a HAPSITE or other instrument for quantitative on-site analysis and chemical-specific qualitative analysis. The user should confirm that analytical methods are available and appropriate for the target VOCs identified in Item 2 above.

   Additional equipment is required for other procedures such as product/vapor entry point isolation testing and building depressurization.

4) **Building access**: Request permission to access the building, determine an acceptable schedule, describe the procedure to building owner/operator, and inform the owner/occupant how and when they may be able to obtain the results. The building owner/operator may also be able to provide information on the building history, use, and chemical storage for general context prior to the investigation. Occupants should be asked to avoid use of materials containing target VOCs prior to testing.

Table 2: Typical Equipment Requirements for On-Site Analysis Procedure

Program	Equipment/Supplies
On-site GC/MS Analysis	Quantitative Analysis: Inficon HAPSITE portable GC/MS or equivalent quantitative instrument, and related supplies Survey Mode: Inficon HAPSITE MS survey mode or equivalent continuous-read instrument, and related supplies
Confirmation Sampling	Certified clean, evacuated Summa canisters for indoor confirmation sampling, and related supplies
Product/Vapor Entry Point Isolation Testing (Optional)	Container for testing potential indoor VOC sources (see Section 5.3.1). Container or plastic sheeting for testing potential vapor entry points (see Section 5.3.2). Related supplies (e.g., 3-way valves, tubing, tape [e.g., painters tape])
Building Depressurization (Optional)	Box or floor fan(s), depending on building size
	Related supplies (e.g., plastic sheeting, tape)
	Pressure transducer, and related supplies

3.2 Analytical Methods

Analytical methods for the on-site analysis should be prepared and tested prior to mobilization. HAPSITE method descriptions are provided in Section 5.1, for reference.

Quantitative Analytical Methods: The on-site instrument should use a quantitative analytical method that detects and quantifies the target VOCs. If possible, the analytical method should have a sensitivity below the applicable indoor air screening concentration for the target VOCs. However, because the VOC concentrations are higher in close proximity to the source (either an indoor source or a vapor entry point), a sensitivity that is 2-3 times above the screening level should be sufficient for the identification of sources causing an exceedance of the screening level within the bulk indoor air.

Qualitative Analytical Methods: The instrument used for continuous-reading qualitative analysis should use a method or methods that provide a compound-specific response for the target VOCs.

3.3 Instrument Calibration and QC

This protocol uses the on-site results primarily for source identification (i.e., vapor intrusion vs. indoor source) and uses the confirmation results from the off-site lab as the primary data for comparison of VOC concentrations in indoor air to regulatory screening values. As a result, there are fewer QA requirements than would be needed if the on-site results were being used for definitive decision-making. Note that, although the on-site instrument's analytical methods may include several VOCs, the QA requirements apply to the 1-2 target VOCs identified for the site (see Section 3.1).

Prior to on-site use, startup protocols recommended by the GC/MS instrument manufacturer should be followed. These include automated self-checks and instrument tuning. In addition, continuing calibration verification (CCV) analyses are recommended each day prior to on-site use. If the results of the CCV analyses demonstrate an error greater than the acceptable limit previously established by the operator, the instrument should be recalibrated. Calibration curves should be developed using a standard gas mixture containing known concentrations of the target VOCs. The standard gas is diluted with nitrogen gas or blank air to create a series of samples with known concentrations that span the range of typical indoor air VOC concentrations (e.g., 0 to 10 ppbV). The calibration curve is fit to the results from these samples, and the fit is checked to determine whether the calibration is acceptable.

The quality of each calibration curve is assessed by examining the relative standard deviation (RSD), which is a measure of the linearity of calibration curve, and the Response Factor, which is a measure of the relative response (ion count) of a compound compared to that of an internal standard. For use in the protocol, the curve is acceptable if the RSD is less than 20% and the RSD of the Response Factor is less than 30%. An R^2 criteria (≥ 0.98) can also be used to evaluate the quality of the calibration curve (see Section 5.2).

After recalibration, a standard sample (i.e., CCV sample) should be analyzed to further confirm the instrument response. Other quality control samples include method blanks (i.e., samples consisting of nitrogen or blank air).

During the course of the field investigation, field duplicates can be collected to confirm that the on-site GC/MS instrument is operating correctly. This can be done on a prescribed basis (i.e., 1 duplicate for every 20 samples). However, note that an optional part of the protocol involves sampling during a period when the building pressure is intentionally manipulated. Because VOC concentrations can change quickly during pressure manipulation, it is not recommended that duplicates be analyzed while this part of the test is being conducted.

After completion of the day's work, additional CCV and blank samples should be run to confirm the results and determine the degree to which the instrument maintained calibration during the course of the day.

3.4 Building Operating Conditions

The on-site investigation procedure relies on differences in VOC concentrations within the building to locate sources (either indoor sources or vapor entry points). As a result, the building operating conditions should minimize the mixing of indoor air prior to and during the investigation program. This serves to maximize the differences in VOC concentrations within the buildings with the highest concentrations occurring in the areas of indoor sources or vapor entry points. The desired operating procedures include:

- Doors and Windows: Interior and exterior doors and windows should be kept closed to the extent possible. Both interior and exterior doors may be opened during the investigation to allow ingress and egress of investigators and other building occupants. However, the doors should be closed when not in use.

- HVAC System: The HVAC system (including the circulating fan) may need to be turned off. Air circulation within the building should be minimized, but the baseline building pressure should be considered before making the decision to turn off the HVAC system.

- Other Fans: Any other fans that circulate air through the building or within individual rooms should be turned off.

The pressure difference between indoors and outdoors should be measured at the beginning of the investigation. If the building is depressurized under normal operating conditions, consider not changing these conditions right away (i.e., by manipulating the HVAC system), and proceeding with the baseline sampling. Note that depressurized building conditions are conducive to vapor intrusion. Artifically pressurizing a building during the baseline sampling may result in reduced VOC concentrations, and may make subsequent sample results more difficult to interpret.

Procedures used during the investigation should be implemented to the extent practicable without compromising safe building conditions. Building occupants may remain in the building during the investigation and normal building activates can continue.

3.5 Sampling Program

The sampling program involves an iterative procedure to find and evaluate VOC sources. This program includes: i) initial quantitative sampling, ii) second round quantitative sampling, iii) qualitative screening for source identification, and iv) source evaluation. If one or more sources are identified and removed or isolated, then the process may need to be repeated (see Figure 1).

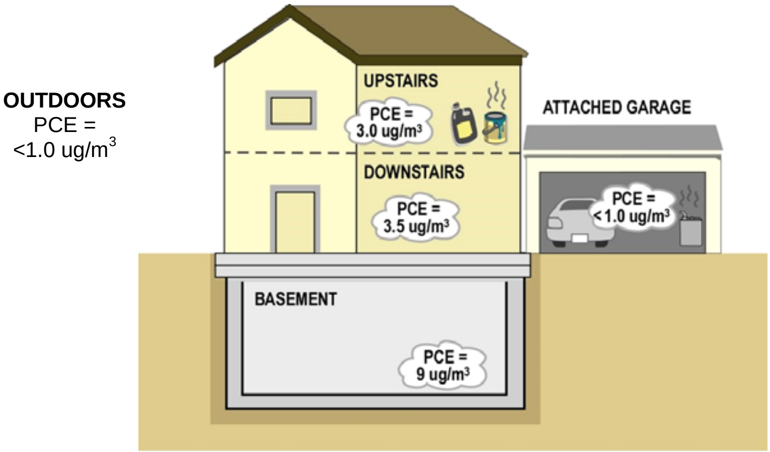
1) Background (Outdoor Air) Sampling: In order to define the ambient (outdoor) concentration of the target VOCs, collect and analyze an outdoor air sample upwind of the building.

   Consider collecting additional outdoor air samples at different locations (e.g., ground level near upgradient outdoor VOC source, near HVAC intake, etc.), depending on site conditions. Also consider collecting additional samples during the course of the building investigation (e.g., between Steps 2 and 3) to account for potential temporal variability in outdoor air VOC concentrations.

2) Initial Quantitative Sampling: The initial sampling and analysis program is conducted using the on-site GC/MS instrument. A sample for quantitative analysis should be collected from each major space within the building, for example, from the basement, main floor, and second floor of a residence (see Figure 2). Additional samples may be collected from likely source areas such as an attached garage.

If the concentration of target VOCs in all areas is less than or equal to the outdoor air concentration, then this portion of the investigation is complete; there is no evidence of current vapor intrusion. If desired, the potential for vapor intrusion under other building conditions can be evaluated by i) screening potential vapor entry points (see Step 6, below) and/or ii) using building depressurization to create conditions favorable for vapor intrusion (See Section 3.6). If the concentration of target VOCs in one or more areas is greater than the outdoor air concentration, then proceed to Step 3.

Figure 2: Example Initial Sampling Program Results



<u>3) Second Round Quantitative Sampling</u>: Additional quantitative samples are collected from within the area[1] found to contain the highest concentrations of the target VOCs. A sample should be collected from the room or other discrete space within the area with highest target VOC concentration identified from the first round (see Figure 3). For example, if the VOC concentrations from the first round were highest in the basement, each room in the basement would be sampled in the second round. In order to minimize air exchange within the building and to decrease the invasiveness of the investigation program, samples can be collected from individual rooms by inserting a sample collection tube under the closed door of the room.

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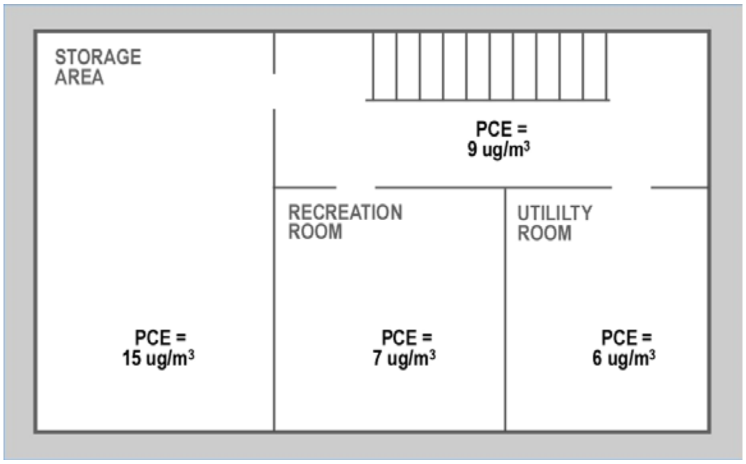
[1] The protocol is designed to prioritize and focus sampling on the area with the highest target VOC concentrations. More than one area may need to be sampled if multiple VOC sources are found, as discussed further below.

Figure 3: Example Second Round Sampling Results



If, based on this additional testing, the concentration of target VOCs in all areas are consistent with or greater than the outdoor air concentration but are less than indoor screening concentrations[2], then there is no evidence of vapor intrusion under current building conditions. If desired, the potential for vapor intrusion under other building conditions (i.e., temporal variability) can be evaluated by i) screening potential vapor entry points (see Step 6) and/or ii) using building depressurization to create conditions favorable for vapor intrusion (See Section 3.5).

If the concentration of target VOCs in one or more locations is greater than the outdoor air concentration and applicable indoor air screening concentrations, then proceed to Step 4.

<u>4) Indoor Source Identification</u>: Consumer products and household items are commonly found to be significant sources of VOCs in indoor air (See Table 3). Some products contain significant amounts of VOCs not identified on the ingredient label.

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[2] Note that if indoor air concentrations are marginally less than indoor air screening concentrations, additional sampling should be considered to address sampling or temporal variability.

Table 3: Example Indoor Sources of VOCs

Chemical [1]	General Categories	Examples of Brand Name Products containing Chemical [2]
Benzene	Motor vehicle exhaust, tobacco smoke	ExxonMobil Unleaded Automotive Gasoline, Classic Aerosol Wax
1,2-DCA	Molded plastic products, air freshener	Bravo Platinum Series Metered Air Freshener, Time Mist Fragrance of the Islands
Naphthalene	Insect repellant, diaper pail and toilet deodorizer	STP Auto Products, Enoz Moth Balls and Flakes
Ethylbenzene	Some paints	Many Sherwin Williams and Krylon Paint products
Carbon Tetrachloride	Aerosol cans, refrigerants, dry cleaned clothes, varnish	Radio Shack Plastic Bonder, Radio Shack Anti Static Foaming Cleaner
Chloroform	Dry cleaned clothes, fire extinguishers, adhesive remover, chlorinated drinking water	Time Mist Air Freshener, Evercare Glass Wipes
PCE	Dry cleaned clothes, automotive brake cleaners, metal degreasers, hobby craft glue	Plumbers Goop Adhesive and Sealant, Lectra Motive Auto Care, Sprayway Cleaners and Fabric Protector
TCE	Self-defense pepper spray, degreaser, rug-cleaners	Sprayway Cleaners and Degreasers, Lectra Clean, Trouble Free Rust Buster
Trans-1,2-DCE	Taxidermy foam, refrigerants, cleaning solutions	3M Novec 71DE Engineered Fluid
Toluene	Some paints and adhesives	SprayPAK Enamel, Minwax Wood Finish
Xylenes	Adhesives, paints, gasoline	Bonide Tree Sprays and Insecticides
1,1,1-TCA	Cleaners, adhesive, aerosol cans	Evercare Glass Wipes

Notes: 1) Data sources: U.S. Department of Health and Human Services. Household Products Database. 2012. Available at http://hpd.nlm.nih.gov/index.htm. Accessed 1/23/2012; Gorder and Dettenmaier, 2011. 2) Partial list; many other products may contain VOCs.

The indoor source identification procedure involves using a combination of i) continuous-read qualitative analysis with the on-site instrument, ii) visual inspection, and iii) isolation and further testing of potential sources (see Section 5.3).

When using the HAPSITE, source identification includes real-time screening of potential sources using a continuous reading mode. The HAPSITE provides a real-time chemical-specific semi-quantitative response. In continuous-reading mode, the instrument intake port is used to scan potential sources for the specific target analyte. When using a mobile laboratory for GC/MS analyses, this step involves a real-time screening using an alternate instrument such as a PID with ppb-level sensitivity. When conducting real-time screening with a PID or other instrument that does not provide a chemical-specific response, additional investigation will be required to confirm that responses are associated with the target VOC rather than a non-target VOC. This confirmation may include identification of the target VOC on the product label and/or flux or emission testing (Step 5; see also Section 5.3). An alternative to this testing is to remove the potential VOC source and re-sample the indoor air to see if the concentrations change.

Using the real-time screening instrument, scan storage units (e.g., cabinets, closets, storage containers, etc.) and product containers found in the room(s) with the highest concentration of the target VOCs. If an instrument response is observed for a storage unit, screen individual items and containers within the unit. Also examine the product labels to see if the target VOC is identified on the label.

If one or more items are identified as potential indoor sources, then proceed to Step 5. Otherwise, proceed to Step 6.

5) Indoor Source Evaluation and Removal: All potential indoor sources should be removed from the building, if possible. If removal is not possible, then the sources should be isolated to the extent possible by placement in a tight container or covering with plastic. Many plastics are permeable to VOCs, so isolation may only serve to temporarily reduce the release from the source. Following source removal, indoor air concentrations should be measured to observe any changes in target VOC concentrations (e.g., every 10 to 15 minutes at the beginning, then less often thereafter [every 15 to 30 minutes until concentrations stabilize]. Three building air exchanges are typically needed for the VOC concentration in indoor air to attain a new steady-state concentration following source removal. This would require three hours or less for a building with 24 or more air exchanges per day (common for commercial/industrial buildings), but could require 12 hours for a building with 6 air exchanges per day (low end for an energy efficient residential building). Also, note that VOCs from indoor sources may still be detectable in indoor air after concentrations stabilize. The steady state concentration could reflect off-gassing of VOCs from sink materials (e.g., rugs or building materials which may sorb and desorb VOCs), or could reflect off-gassing from unidentified, low-grade sources distributed in the building (e.g., individual sources that off-gas at levels below instrument sensitivity, but collectively emit measureable quantities of target VOCs).

Optionally, the target VOC emission rate from the indoor source(s) can be measured in order to determine if the identified source(s) are likely the primary source(s) of target VOCs in indoor air. The testing procedure is provided in Section 5.3.

Following the removal of identified indoor sources, if the concentrations of target VOCs in all areas are consistent with the outdoor air concentration or are below indoor screening concentrations, then this portion of the investigation is complete[3]; there is no evidence of current vapor intrusion. If desired, the potential for vapor intrusion under other building conditions can be evaluated by i) screening potential vapor entry points (see Step 6, below) and/or ii) using building depressurization to create conditions favorable for vapor intrusion (See Section 3.6). If the concentration of target VOCs in one or more locations is greater than the outdoor air concentration, then either i) repeat Steps 2 to 5 if additional indoor sources are suspected or ii) proceed to Step 6 if vapor intrusion is suspected.

6) Vapor Entry Point Identification: Using the continuous-read survey instrument, scan potential vapor entry points such as floor drains, expansion joints, plumbing penetrations, or cracks.

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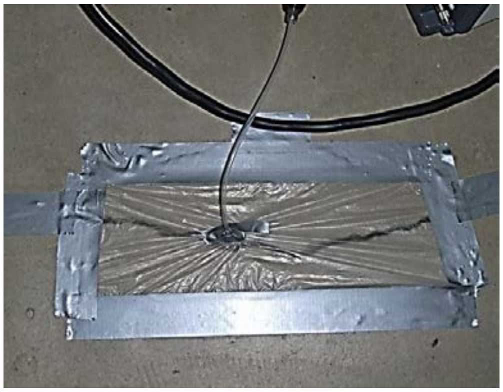
[3] Note that if indoor air concentrations are marginally less than indoor air screening concentrations, additional sampling should be considered to address sampling or temporal variability.

Potential entry points can also be covered with plastic (Figure 4; see also Section 5.3) or with a metal isolation device and the air in the space can be sampled quantitatively. Use of plastic to isolate the crack is acceptable, but a metal device is more reliable because VOCs can diffuse through plastic. Electrical outlets or wall cracks can be screened to check for elevated concentrations of target VOCs in the wall space.

Figure 4: Testing a Sealed Crack in a Concrete Floor



Advection is the most common vapor entry mechanism. Less commonly, diffusion through the concrete floor can occur. Diffusion through a concrete (or dirt) floor can be tested by sealing a section of floor under plastic sheeting or a metal device and sampling the trapped air (see Section 5.3.2).

<u>7) Confirmation Sampling</u>: At the end of the baseline on-site investigation program (i.e., before manipulating building pressure conditions), a confirmation sample should be collected to verify the accuracy of the on-site analysis. If one or more indoor sources were removed during the investigation, the confirmation sample should be collected after the concentration of the target VOC has decreased and stabilized following source removal. One confirmation Summa sample should be collected from the room with the highest concentration of target VOC at that time. The confirmation sample may be a grab sample, an 8-hr sample, or a 24-hr sample, depending on regulatory requirements and other project considerations.

<u>8) Data Interpretation</u>: Data interpretation answers two primary questions: i) what is the source of the target VOC (i.e., vapor intrusion vs. indoor or ambient source), and ii) are VOC concentrations above applicable indoor air screening values.

<u>Source Identification</u>: At the end of the baseline characterization (and after concentrations have stabilized after indoor source removal), the investigators make a preliminary interpretation of the source of VOCs using the following guidelines:

1. <u>Comparison of target VOC concentrations in indoor air to ambient (outdoor) air</u>: Do indoor concentrations of the key VOC exceed outdoor concentrations? A “Yes” response is evidence of vapor intrusion and/or an indoor source of the target VOC.
2. <u>Baseline building pressure</u>: Is baseline building pressure negative (i.e., less than ambient [outdoor] pressure)? A “No” provides evidence of an indoor source because a positive building pressure does not support the flow of soil gas into the building. A “Yes”

response is potentially consistent with vapor intrusion. However, this line of evidence is not definitive with respect to vapor intrusion because negative building pressure does not eliminate the possibility of an indoor source.

3. Remaining indoor sources: Were any known or discovered indoor sources of target VOCs removed prior to the end of the baseline period such that no (known) indoor sources remain in the building? If no known indoor sources remain in the building then target VOC concentrations above ambient concentrations is consistent with vapor intrusion. If known indoor sources remain, and these indoor sources may be the primary source(s) of VOCs in indoor air. This question does not apply if the on-site results for the target VOC are below detection limits or equal to ambient concentrations.
4. Vapor entry point: Were vapor entry points found? If "Yes", then vapor intrusion could contribute to target VOCs in indoor air. However, if VOC concentrations at the identified entry points are only modestly above indoor air concentrations, then it is possible that indoor sources are also contributing.

These lines of evidence and any other relevant information are considered together to determine the source of the target VOC and the level of confidence in the source determination.

Exposure Concentration: Within the context of a regulatory response action, the determination of whether or not target VOC concentrations exceed an applicable screening level typically requires the use of concentration data that meet defined data quality standards. Therefore, the confirmation results from an analytical laboratory should be used for comparison with regulatory criteria. Many regulatory guidance documents recommend the use of 8 hr or 24 hr samples for the evaluation of exposure concentrations; however, the grab confirmation samples should be suitable for making a preliminary estimate of the exposure concentration. Due to concerns regarding temporal variability in vapor intrusion, some regulators require more than one indoor air sampling event regardless of whether the sample duration is grab, 8 hr, or 24 hr. Additional measures to address temporal variability are discussed in Section 3.6 below.

Although the QA documentation for the on-site results may not support their use for definitive decision-making, the result will provide supporting evidence regarding the exposure concentration by serving to document the spatial and short-term temporal variability within the building.

Note that, while sufficient QA/QC steps *can* be taken to support on-site analysis for definitive decision-making, it may not be practical to do in the field. Additionally, the power of the on-site analysis protocol is rooted in high precision of the instrument which allows the user measure relative concentration differences in a building. These differences are used locate sources of VOCs during building characterization. As the protocol is designed, instrument accuracy and developing "definitive" data using the on-site instrument (e.g., HAPSITE) are less important.

3.6 Building Pressure Control (Optional)

Basis for Pressure Control Lines of Evidence

Changes in building pressure relative to the subsurface can cause temporal variations in vapor intrusion. As a result, a one-day investigation program with uncontrolled building conditions may not identify vapor intrusion that could occur under other building pressure conditions.

Building pressure control can be used as a tool to control the advective flow of soil gas into the building. If advection (rather than diffusion) is the primary mode of vapor intrusion for a building, then building pressure control can be used to provide an improved understanding of the potential for vapor intrusion under other building operating conditions (McHugh et al., 2012, USEPA, 2011). If VOC concentrations in indoor air are below screening levels under both baseline (uncontrolled) conditions and depressurized conditions, then this provides strong evidence that vapor intrusion is not a concern. If VOC concentrations in indoor air are below screening levels under baseline (uncontrolled) conditions but above screening levels under depressurized conditions, then additional evaluation may be required to determine if temporally-variable unacceptable vapor intrusion may occur under realistic building operating conditions.

Lines of evidence for the optional pressure control evaluation focus on change in target VOC concentrations relative to baseline, and relative to the building pressure condition.

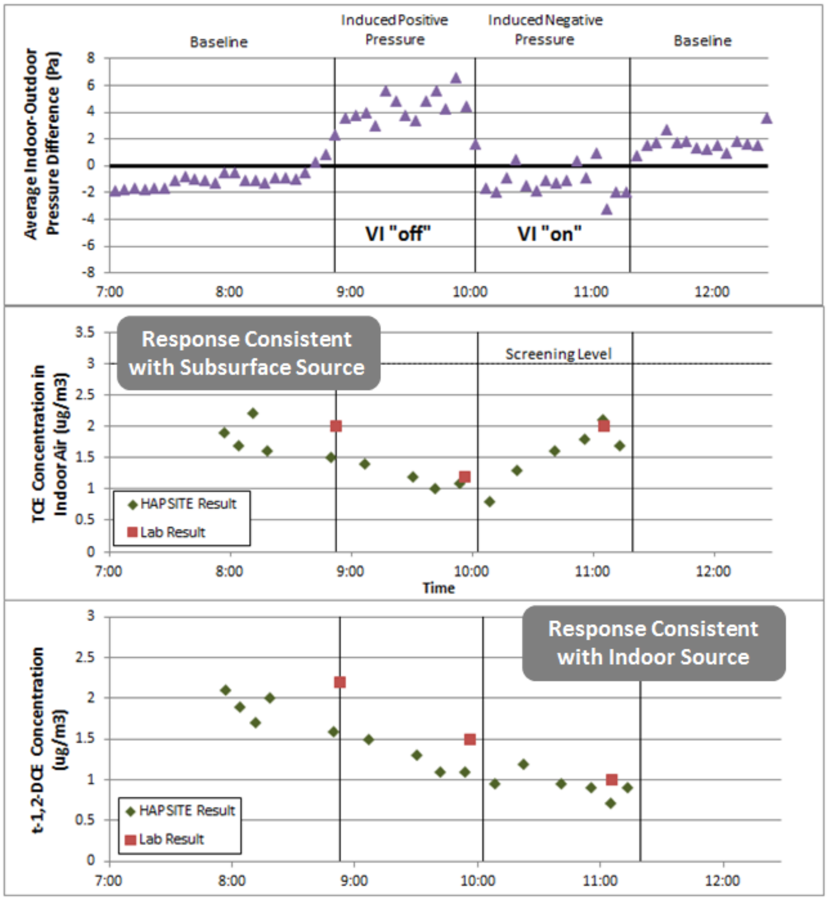
1. Building pressurization: Are target VOC concentrations suppressed by building pressurization? A "Yes" response is consistent with VI.

2. Building depressurization: Are target VOC concentrations enhanced by depressurization? A "Yes" response is consistent with VI.

A positive pressure cycle followed by a negative pressure cycle provides information concerning the source of the target analyte in indoor air (i.e., subsurface source vs. indoor source). If the target analyte concentration is similar under positive and negative pressure (or concentrations decline), an indoor source is indicated. If the target analyte concentration is higher under the negative pressure condition, a subsurface source is indicated.

Note that VOC concentrations in indoor air are likely to decrease somewhat even for VOCs from indoor sources due to the increase in air exchange rate caused by the building pressure control. As a result, the overall interpretation of the building pressure control results depends on the combined responses to building pressurization and depressurization. A decrease in target VOC concentration with building pressurization followed by a rebound with building depressurization is strong evidence of vapor intrusion (Figure 5, middle). A modest decrease in VOC concentration with building pressurization that persists during building depressurization is strong evidence of an indoor source (Figure 5, bottom).

Figure 5: VOC Responses to Building Pressure Manipulation



<u>Pressure Control Procedure</u>

<u>If the target analyte concentration is below the screening level under baseline conditions</u>, then after collecting the baseline samples, negative pressure can be induced in the building by installing a fan in a window or doorway to pull air from inside the building and direct it outside. A differential pressure transducer is used to measure and record the difference between indoors and outdoors and the fan should be set at a speed that maintains at least 1 Pa negative pressure (i.e., vacuum) relative to the outdoors. Larger (e.g., 4-5 Pa, or higher) pressure differentials may be used, but building-specific factors should be considered when setting target levels. For example, increased vacuum (i.e., negative pressure) in the building may increase vapor flow from the subsurface into the building. However, it also may increase the indoor-outdoor air exchange and may result in over-dilution of indoor air with outdoor air.

After the depressurized condition is initiated, the concentration of target VOCs in indoor air should be measured to observe any changes in target VOC concentrations (e.g., every 10 to 15 minutes at the beginning, then less often thereafter (every 15 to 30 minutes) until concentrations stabilize). Concentrations of target VOCs tend to respond quickly to changes in building pressure. Using on-site analysis, the impact of pressure control is often clear within one hour allowing for pressurization and depressurization to be completed in approximately two hours. When concentration changes are small or higher than usual variability is observed, longer times may be required to obtain clear results. Note, however, that for cases where the instrument sensitivity is higher than the applicable indoor air screening level, the instrument may not be able to detect an increase in vapor intrusion through testing of bulk indoor air.

During each pressurization phase, the HAPSITE portable GC/MS, or equivalent, is moved throughout the building, area by area. Indoor air sampling and vapor entry point screening (i.e., Steps 2, 3, and 6 from Section 3.5) should be repeated. Periodic samples are collected from each area of the building until one of the following conditions is observed:

1. The indoor air concentration of the target analyte changes and then stabilizes.

2. No concentration changes are observed (minimum 1 hour observation time).

As with the baseline sampling (Section 3.5, Step 7), a confirmation sample for off-site VOC analysis should be collected at the end of each pressure cycle. If building pressure manipulation is planned, radon samples can optionally be collected at the end of the baseline and pressure cycles. Radon is used as a subsurface tracer. A radon concentration is higher under the negative pressure condition can confirm upward soil gas flow from the subsurface into the building.

Within the context of a regulatory response action, the determination of whether or not target VOC concentrations exceed an applicable screening level typically requires the use of concentration data that meet defined data quality standards. Therefore, the confirmation results from the analytical laboratory should be included in the final data interpretations and used for comparison with regulatory criteria.

4.0 DOCUMENTATION

The results of the on-site analysis program should be documented through field notes and a report that presents the analytical results, interpretation, and overall findings.

4.1 Field Notes

Much of the information to record in field notes is typical of any investigation program (i.e., dates, times, activities, locations, and personnel). Additional information pertinent to the on-site program includes, but is not limited to:

- On-site instrument type, manufacturer, model
- Calibration gas specifications, if applicable
- QA/QC measures
- GC/MS instrument settings (e.g., temperature and other settings, identifying ions for target compounds, predicted elution time as indicated in field notes or instrument reports)
- Detailed sampling location descriptions, including observations of storage conditions in the area/room being sampled

- Detailed descriptions of indoor sources identified (product type, brand name, ingredients listed on labels). Note that the amount of information recorded may be limited by the time allotted for the investigation and the size and contents of the building.
- Photographs. Photographs of specific indoor VOC sources, product labels, and storage areas can be helpful. Photographs of each on-site sampling location are also helpful. The field team, however, should be mindful of privacy or similar concerns.

4.2 Report

The investigation report documenting use of on-site analysis should include the following:

- <u>Introduction</u>: Identify the purpose and context of the investigation program. Provide a description of the site and building(s). Discuss the scope of the investigation. For example, evaluation of current vapor intrusion (baseline sampling) or current and potential vapor intrusion (baseline plus building depressurization).

- <u>Methods</u>: Describe the GC/MS instrument and functions utilized during the investigation (e.g., quantitative sampling, qualitative/survey); describe the investigation process. Instrument calibration and QA procedures and results should be documented in an appendix.

- <u>Results</u>: Tabulate all quantitative results from the on-site analysis. Sample locations should be summarized on a map. Tabulate results for confirmation samples analyzed off-site. Provide a summary of survey mode results that identifies the rooms or areas included in the survey and all locations, products, and buildings features that yielded an instrument response.

  If building pressure was manipulated during the investigation, provide pressure transducer readings. Clearly indicate which results were obtained under baseline conditions vs. pressurized/depressurization conditions. Note the initial baseline pressure condition.

- <u>Data Interpretation</u>: Discuss the results from each step in the investigation process and key decision points in the investigation process. Discuss any potential indoor sources that were identified and the basis for identification. If the sources were removed, discuss the impact on the concentration of target VOCs in indoor air. If flux testing was conducted, discuss the findings (i.e., was the tested item a significant source of the target VOC). Discuss any vapor entry points that were identified and the basis for identification. Discuss the overall conclusion regarding the presence or absence of vapor intrusion.

- <u>Supplemental Information</u>: Field notes, laboratory analytical reports, and other investigation details may be provided in appendices, as appropriate.

5.0 HAPSITE USE AND INSTRUCTIONS

The on-site analysis protocol was validated using a HAPSITE GC/MS (i.e., SMART PLUS). Information developed during the validation process is provided below, for reference. Field personnel should familiarize themselves with the protocol before attempting to use it. Additionally, they should have experience with vapor intrusion field investigations and a sound understanding of vapor intrusion processes. This is important because of the dynamic nature of decision-making in the field required by the protocol. It is also recommended that users of the protocol be familiar with operation of the on-site GC/MS analysis instrument so that they have a practical understanding of typical instrument performance and response. This is to better identify and remedy operational issues while in the field.

Sections 5.1 and 5.2 below summarize analytical methods and HAPSITE calibration, respectively. This information was developed during protocol validation and is provided for reference. Specific procedures may be modified depending upon site-specific needs and data quality objectives. Section 5.3 describes approaches to testing potential indoor VOC sources and subsurface vapor entry points. Section 5.4 provides cost estimates for using a HAPSITE in the on-site GC/MS analysis protocol.

5.1 Customized HAPSITE Analytical Methods

The HAPSITE methods described in this section were developed by Erik Dettenmaier (Erik.Dettenmaier@hill.af.mil) and Kyle Gorder (Kyle.Gorder@hill.af.mil) at Hill Air Force Base. Key instrument parameters are discussed below for reference. The user should make adjustments to tailor the method to account for his particular instrument (e.g., retention times on a HAPSITE SMART PLUS (30 m column) will be different than those on an ER (15 m column)) and site-specific requirements (e.g., key target VOCs).

5.1.1 HAPSITE Quantitative Methods

On the HAPSITE, “Analyze” (GC/MS) methods are used to quantify target VOCs. Different methods can be developed to identify specific compounds as well as different concentration ranges. For many indoor air sampling applications where VOC concentrations are low, the selective ion monitoring (SIM) mode can be used to increase the detector sensitivity for the target analytes.

Two customized HAPSITE methods were developed for use with this investigation protocol:

i) **Chlorinated VOCs SIM Method:** a chlorinated VOC method that targets nine common chlorinated VOCs: vinyl chloride (VC), 1,1-dichloroethylene (1,1-DCE), trans-1,2-dichloroethylene (trans-1,2-DCE), 1,1-dichloroethane (1,1-DCA), cis-1,2-dichloroethylene (cis-1,2-DCE), 1,2-dichloroethane (1,2-DCA), carbon tetrachloride (CTCL), trichloroethylene (TCE), and tetrachloroethylene (PCE).

ii) **Petroleum VOCs SIM Method:** a petroleum VOC method that targets methyl tert-butyl ether (MTBE), benzene, toluene, ethylbenzene, and xylenes.

The accuracy, precision, and sensitivity of these methods were documented through a laboratory validation study and field demonstrations (GSI, 2012, 2013). The cVOC method has a sensitivity of 0.5 to 1.0 ug/m^3 and the petroleum VOC method has a sensitivity of 1.0 to 5.0 ug/m^3.

Table 4: Sensitivity of HAPSITE Quantitative Mode

VOC Class	Typical Sensitivity
Chlorinated VOCs	0.5 to 1.0 ug/m^3
Petroleum VOCs	1.0 to 5.0 ug/m^3

Note: Actual instrument sensitivity may vary depending on background ion counts and other field conditions.

The customized methods for the HAPSITE are provided below, including the selected characteristic ions for each compound targeted in the methods, the temperature settings, GC temperature profiles including ramp times and rates, and the timing and mass measurements associated with each scan set in the method. These methods were designed for low concentration samples (i.e., 0 – 10 ppbV range).

For samples anticipated to have high concentrations (e.g., in the 100 – 1000 ppbv range), these methods can be modified simply by reducing the sample volume (i.e., decrease the sampling duration from 1 minute to 10 seconds in Inlet State 2 on Figure 7).

These analytical method specifications are provided as examples. As noted above, adjustments may be needed depending on the particular site target VOCs and instrument model used.

5.1.1.1 Chlorinated VOCs SIM Method

This analytical method was developed for nine cVOCs. The target compounds and characteristic ions used to identify and quantify each compound are summarized in Table 5. TCE and PCE are common drivers for vapor intrusion investigations. Based on the laboratory study and field demonstrations (GSI, 2013), identification of these compounds using this HAPSITE method is reliable. Other compounds such as vinyl chloride and cis-1,2-dichloroethylene may require more effort to identify and quantify accurately. To mitigate this issue, the analytical method can be modified to better measure these compounds at sites where they are the key target VOCs.

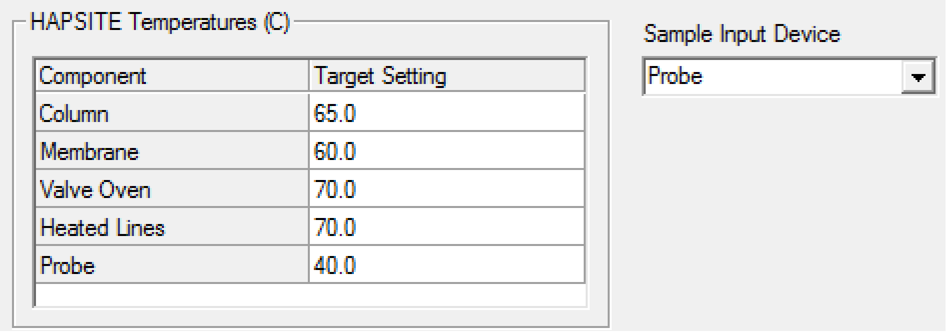
Table 5: Target Compounds in the cVOC Method

Compound	**Selected Characteristic Ions in Order of Decreasing Intensity**
Vinyl Chloride	**62**, 61, 65, 63, 96
1,1-DCE	**61**, 63, 96, 62
Trans-1,2-DCE	**61**, 63, 96, 62, 65
1,1-DCA	**63**, 65, 61, 96, 62
Cis-1,2-DCE	**61**, 96, 63, 62
1,2-DCA	**62**, 64
CTCL	**117**, 119
TCE	**130**, 95, 62
PCE	**166**, 164

Note: Bold font indicates primary identifying ion. Compounds listed in order of elution.

Important instrument settings include startup settings (initial target temperatures [Figure 6]), inlet states and temperature profiles (Figure 7), and compound search parameters (Figure 8). The settings shown were developed for a SMART PLUS.

Figure 6: Initial Temperature Settings in the cVOC Method

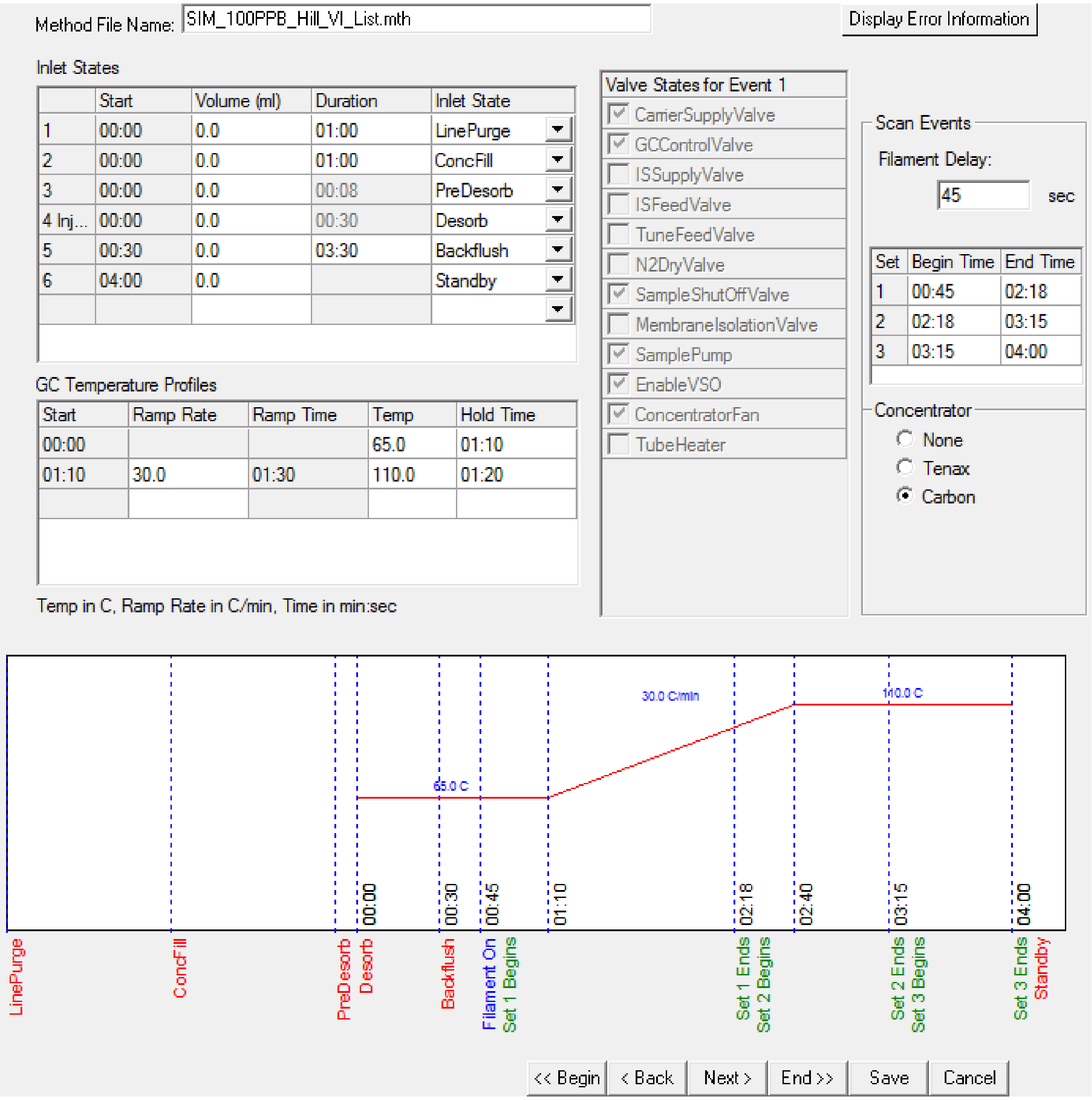


HAPSITE Temperatures (C)

Component	Target Setting
Column	65.0
Membrane	60.0
Valve Oven	70.0
Heated Lines	70.0
Probe	40.0

Sample Input Device: Probe

Figure 7: Volume/duration of inlet states, GC temperature profile, and timing of SIM sets in the cVOC Method



Method File Name: SIM_100PPB_Hill_VI_List.mth

Inlet States

	Start	Volume (ml)	Duration	Inlet State
1	00:00	0.0	01:00	LinePurge
2	00:00	0.0	01:00	ConcFill
3	00:00	0.0	00:08	PreDesorb
4 Inj...	00:00	0.0	00:30	Desorb
5	00:30	0.0	03:30	Backflush
6	04:00	0.0		Standby

GC Temperature Profiles

Start	Ramp Rate	Ramp Time	Temp	Hold Time
00:00			65.0	01:10
01:10	30.0	01:30	110.0	01:20

Temp in C, Ramp Rate in C/min, Time in min:sec

Valve States for Event 1

☑ CarrierSupplyValve
☑ GCControlValve
☐ ISSupplyValve
☐ ISFeedValve
☐ TuneFeedValve
☐ N2DryValve
☑ SampleShutOffValve
☐ MembraneIsolationValve
☑ SamplePump
☑ EnableVSO
☑ ConcentratorFan
☐ TubeHeater

Scan Events

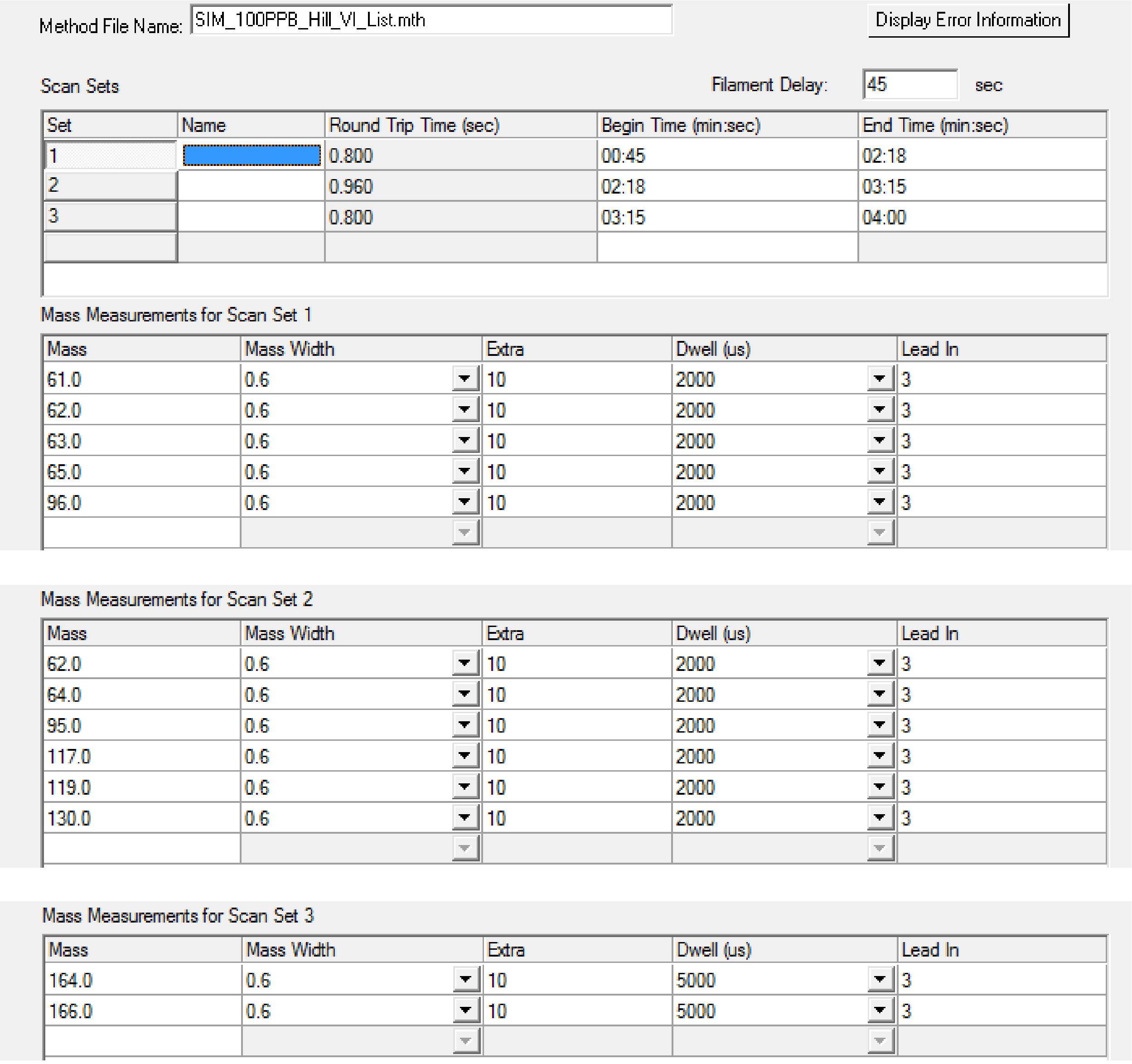
Filament Delay: 45 sec

Set	Begin Time	End Time
1	00:45	02:18
2	02:18	03:15
3	03:15	04:00

Concentrator

○ None
○ Tenax
● Carbon

Figure 8: Specific masses and search parameters in each SIM set in the cVOC Method



Method File Name: SIM_100PPB_Hill_VI_List.mth

Filament Delay: 45 sec

Scan Sets

Set	Name	Round Trip Time (sec)	Begin Time (min:sec)	End Time (min:sec)
1		0.800	00:45	02:18
2		0.960	02:18	03:15
3		0.800	03:15	04:00

Mass Measurements for Scan Set 1

Mass	Mass Width	Extra	Dwell (us)	Lead In
61.0	0.6	10	2000	3
62.0	0.6	10	2000	3
63.0	0.6	10	2000	3
65.0	0.6	10	2000	3
96.0	0.6	10	2000	3

Mass Measurements for Scan Set 2

Mass	Mass Width	Extra	Dwell (us)	Lead In
62.0	0.6	10	2000	3
64.0	0.6	10	2000	3
95.0	0.6	10	2000	3
117.0	0.6	10	2000	3
119.0	0.6	10	2000	3
130.0	0.6	10	2000	3

Mass Measurements for Scan Set 3

Mass	Mass Width	Extra	Dwell (us)	Lead In
164.0	0.6	10	5000	3
166.0	0.6	10	5000	3

Note: Scan Set 1 – VC, 1,1-DCE, trans-1,2-DCE, 1,1-DCA, cis-1,2-DCE; Scan Set 2 – 1,2-DCA, CTCL, TCE; Scan Set 3 – PCE.

5.1.1.2 Petroleum VOCs SIM Method

This analytical method was developed for seven target VOCs. The target compounds and characteristic ions used to identify and quantify each compound are summarized in Table 6. Benzene and ethylbenzene are common drivers for vapor intrusion investigations. Based on the laboratory study and field demonstrations, identification of these compounds using this HAPSITE method is reliable. Compounds such as MTBE may require more effort to identify and quantify accurately. The mitigate this concern, the method can be modified to better measure these compounds at sites where they are the key target VOCs.

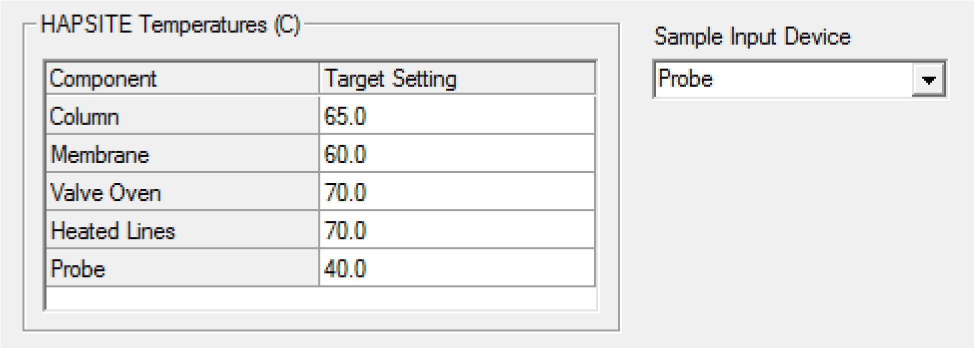
Table 6: Target Compounds in the Petroleum VOCs Method

Compound	Selected Characteristic Ions in Order of Decreasing Intensity
MTBE	**73**, 57
Benzene	**78**, 77, 73
Toluene	**91**, 92, 77
Ethylbenzene	**91**, 106, 77, 92
m,p-xylene	**91**, 106, 77, 92
o-xylene	**91**, 106, 77, 92

Note: Bold font indicates primary identifying ion. Compounds listed in order of elution.

Important instrument settings include startup settings (initial target temperatures [Figure 9]), inlet states and temperature profiles (Figure 10), and compound search parameters (Figure 11). The settings shown were developed for a SMART PLUS.

Figure 9: Initial Temperature Settings in the Petroleum VOCs Method

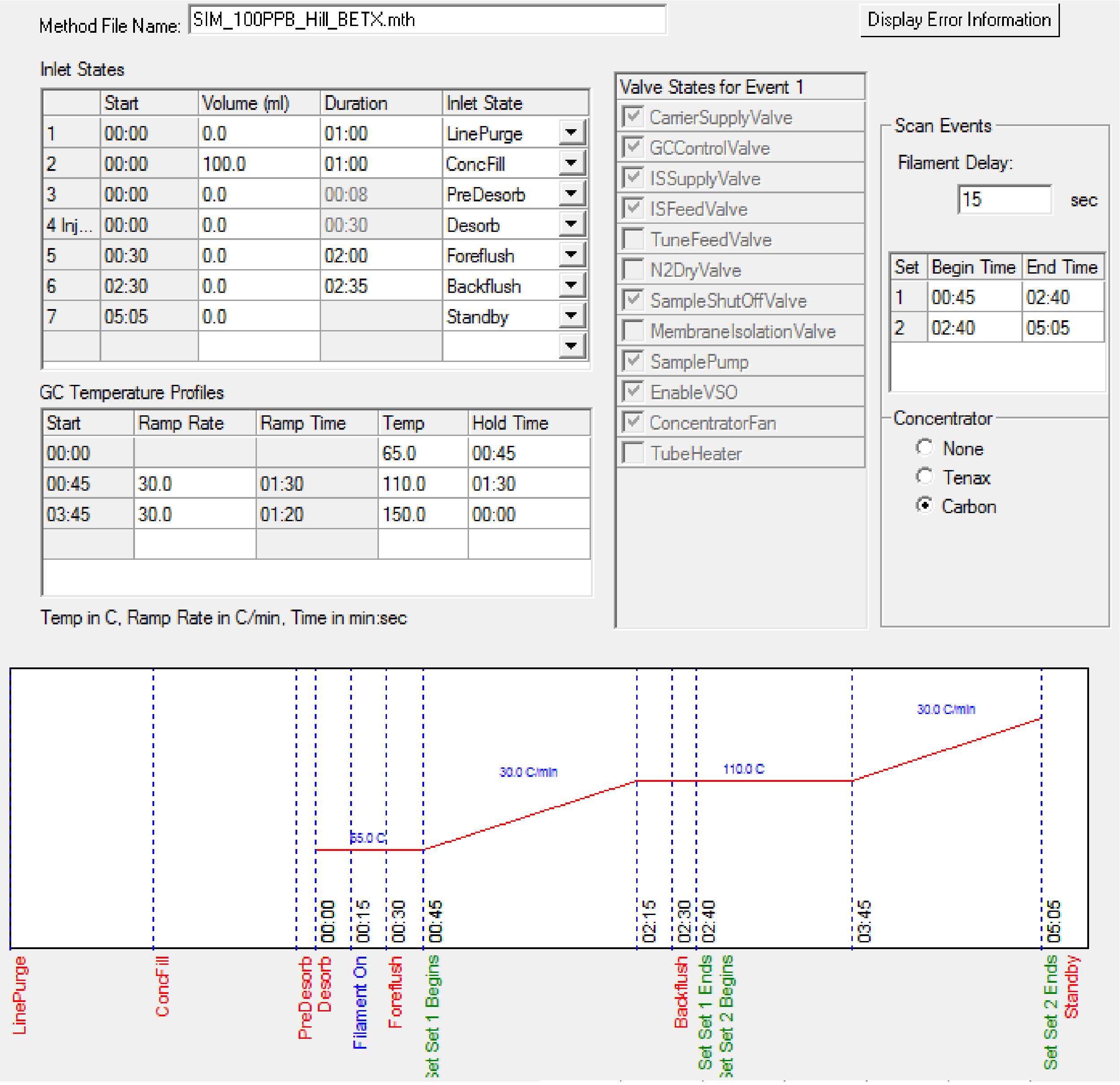


HAPSITE Temperatures (C)

Component	Target Setting
Column	65.0
Membrane	60.0
Valve Oven	70.0
Heated Lines	70.0
Probe	40.0

Sample Input Device: Probe

Figure 10: Volume/duration of inlet states, GC temperature profile, and timing of SIM sets in the Petroleum VOCs Method



Method File Name: SIM_100PPB_Hill_BETX.mth

Inlet States

	Start	Volume (ml)	Duration	Inlet State
1	00:00	0.0	01:00	LinePurge
2	00:00	100.0	01:00	ConcFill
3	00:00	0.0	00:08	PreDesorb
4 Inj...	00:00	0.0	00:30	Desorb
5	00:30	0.0	02:00	Foreflush
6	02:30	0.0	02:35	Backflush
7	05:05	0.0		Standby

GC Temperature Profiles

Start	Ramp Rate	Ramp Time	Temp	Hold Time
00:00			65.0	00:45
00:45	30.0	01:30	110.0	01:30
03:45	30.0	01:20	150.0	00:00

Temp in C, Ramp Rate in C/min, Time in min:sec

Valve States for Event 1

- ☑ CarrierSupplyValve
- ☑ GCControlValve
- ☑ ISSupplyValve
- ☑ ISFeedValve
- ☐ TuneFeedValve
- ☐ N2DryValve
- ☑ SampleShutOffValve
- ☐ MembraneIsolationValve
- ☑ SamplePump
- ☑ EnableVSO
- ☑ ConcentratorFan
- ☐ TubeHeater

Scan Events

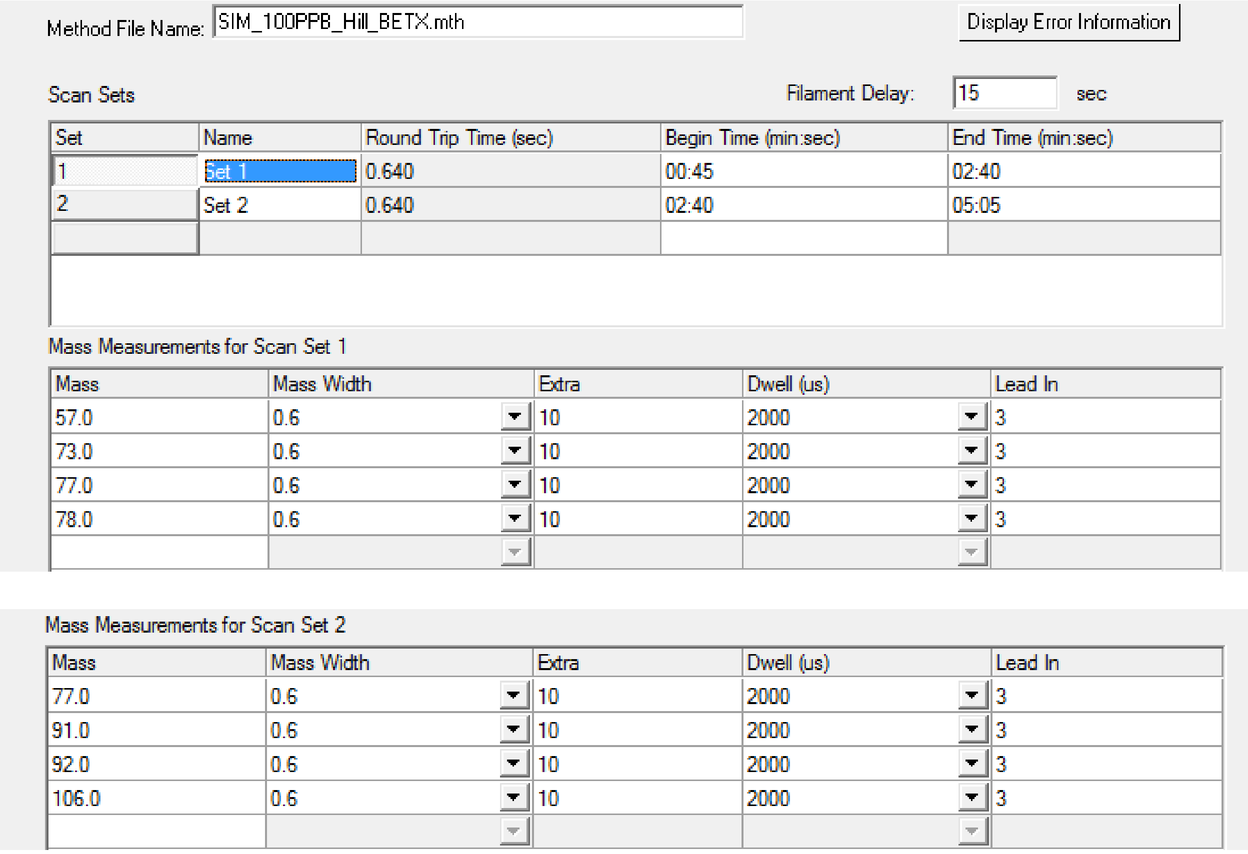
Filament Delay: 15 sec

Set	Begin Time	End Time
1	00:45	02:40
2	02:40	05:05

Concentrator

- ○ None
- ○ Tenax
- ● Carbon

Figure 11: Specific masses and search parameters in each SIM set in the Petroleum VOCs Method



Method File Name: SIM_100PPB_Hill_BETX.mth

Scan Sets

Filament Delay: 15 sec

Set	Name	Round Trip Time (sec)	Begin Time (min:sec)	End Time (min:sec)
1	Set 1	0.640	00:45	02:40
2	Set 2	0.640	02:40	05:05

Mass Measurements for Scan Set 1

Mass	Mass Width	Extra	Dwell (us)	Lead In
57.0	0.6	10	2000	3
73.0	0.6	10	2000	3
77.0	0.6	10	2000	3
78.0	0.6	10	2000	3

Mass Measurements for Scan Set 2

Mass	Mass Width	Extra	Dwell (us)	Lead In
77.0	0.6	10	2000	3
91.0	0.6	10	2000	3
92.0	0.6	10	2000	3
106.0	0.6	10	2000	3

Note: Scan Set 1 - MTBE, benzene; Scan Set 2 – toluene, ethylbenzene, m,p-xylene, o-xylene.

5.1.2 HAPSITE Survey Analytical Methods

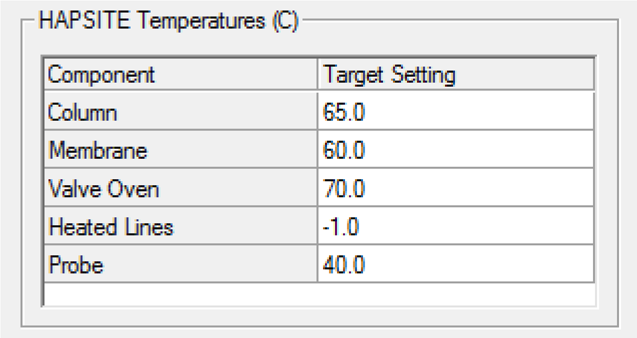
When operated in the continuous-read survey mode, the HAPSITE by-passes the GC column and sends a continous sample directly to the mass spectrometer detector. For vapor intrusion investigations, survey mode is used to detect ions associated with one or two specific target analytes. Three customized HAPSITE survey analytical methods are provided below as examples.

i) a three-ion method for the detection of PCE (Figures 12-13);
ii) a three-ion method for the detection of TCE (Figures 14-15); and
iii) a three-ion method for the detection of Benzene (Figures 16-17).

Details of the survey methods, including the HAPSITE temperature settings and target masses are provided below.

5.1.2.1 PCE 3-ion Survey Method

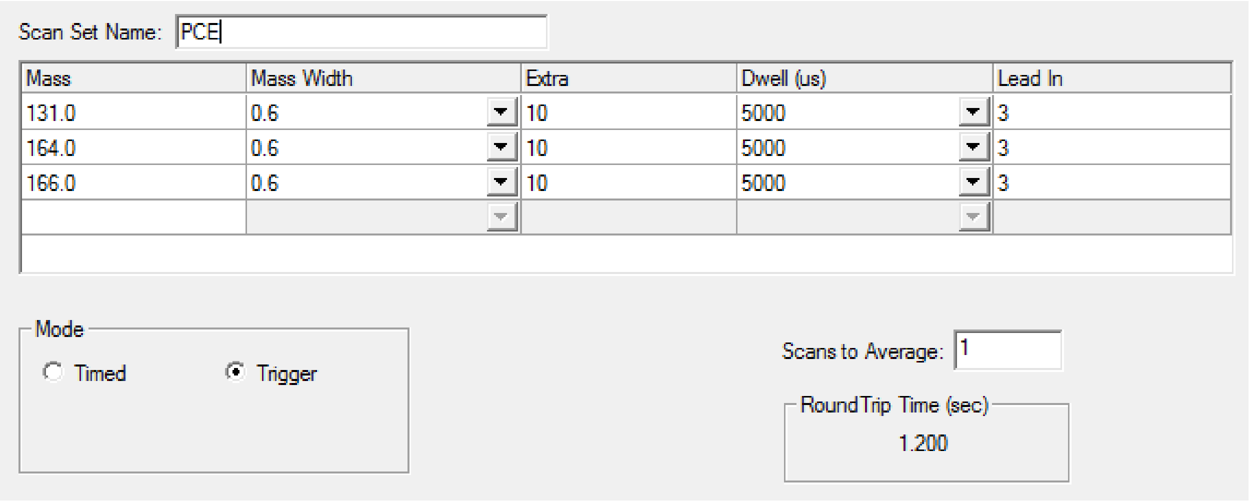
Figure 12: Temperature Settings in the PCE 3-ion Survey Method



HAPSITE Temperatures (C)

Component	Target Setting
Column	65.0
Membrane	60.0
Valve Oven	70.0
Heated Lines	-1.0
Probe	40.0

Figure 13: Specific Masses and Search Parameters in the PCE 3-ion Survey Method



Scan Set Name: PCE

Mass	Mass Width	Extra	Dwell (us)	Lead In
131.0	0.6	10	5000	3
164.0	0.6	10	5000	3
166.0	0.6	10	5000	3

Mode

○ Timed ● Trigger

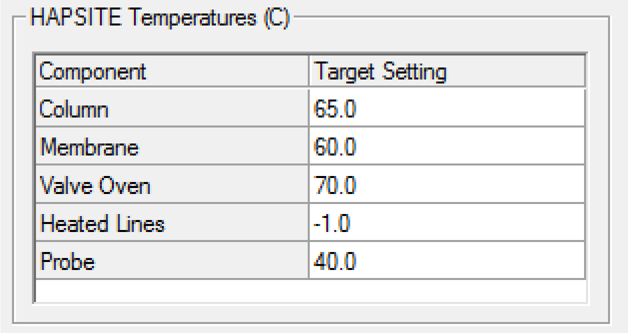
Scans to Average: 1

RoundTrip Time (sec)

1.200

5.1.2.2 TCE 3-ion Survey Method

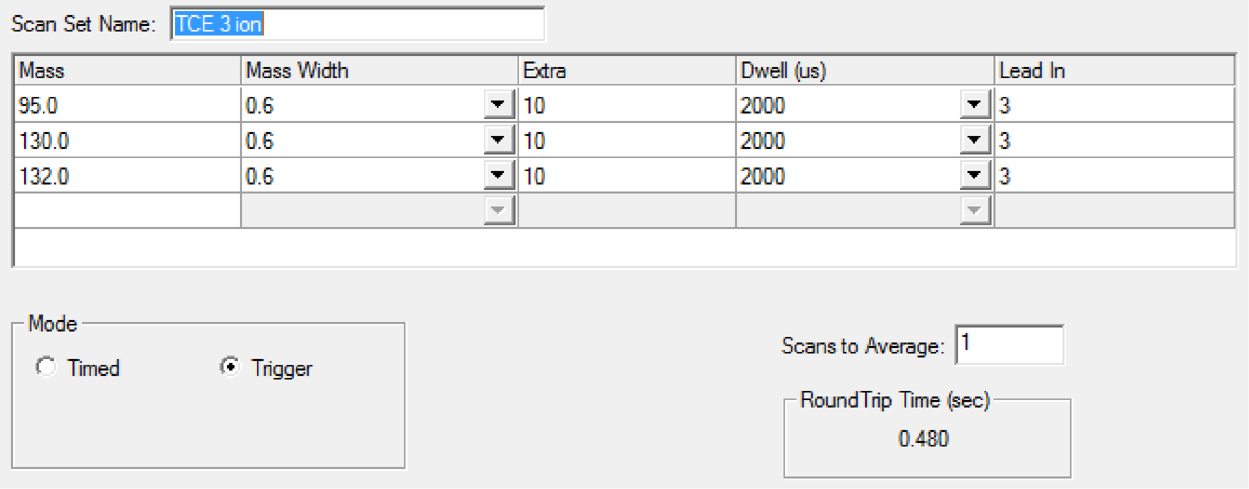
Figure 14: Temperature Settings in the TCE Survey Method



HAPSITE Temperatures (C)

Component	Target Setting
Column	65.0
Membrane	60.0
Valve Oven	70.0
Heated Lines	-1.0
Probe	40.0

Figure 15: Specific Masses and Search Parameters in the TCE Survey Method



Scan Set Name: TCE 3 ion

Mass	Mass Width	Extra	Dwell (us)	Lead In
95.0	0.6	10	2000	3
130.0	0.6	10	2000	3
132.0	0.6	10	2000	3

Mode

○ Timed ● Trigger

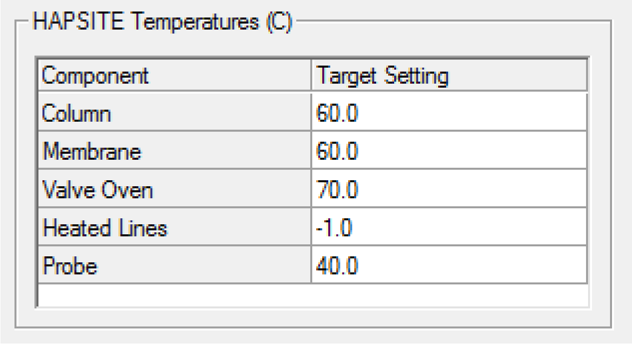
Scans to Average: 1

RoundTrip Time (sec)

0.480

5.1.2.3 Benzene 3-ion Survey Method

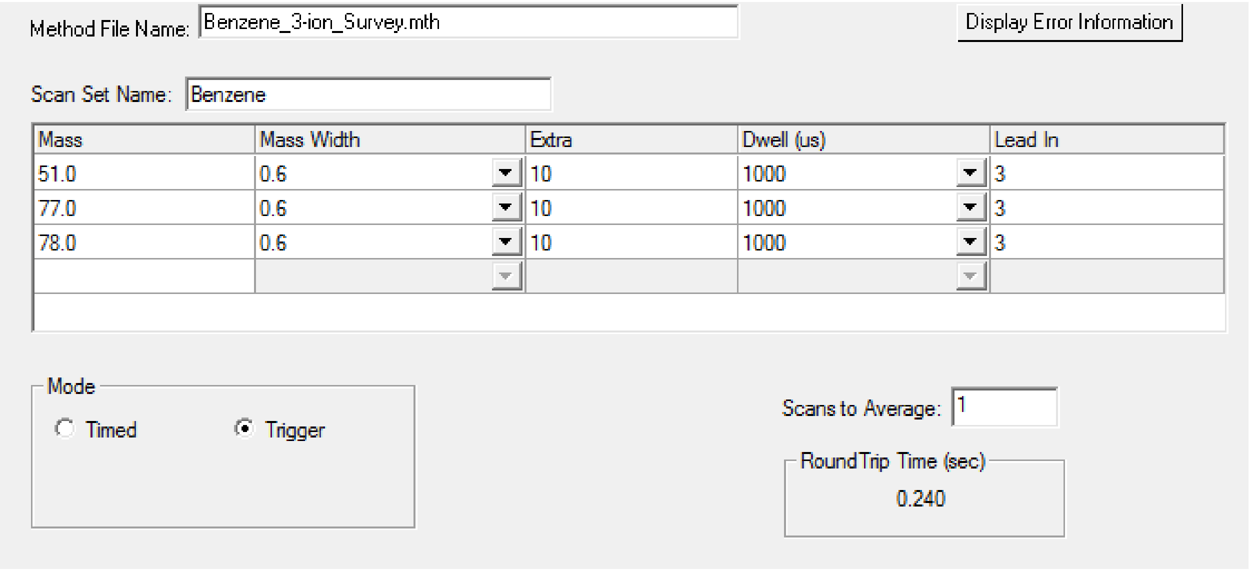
Figure 16: Temperature Settings in the Benzene Survey Method



HAPSITE Temperatures (C)

Component	Target Setting
Column	60.0
Membrane	60.0
Valve Oven	70.0
Heated Lines	-1.0
Probe	40.0

Figure 17: Specific Masses and Search Parameters in the Benzene Survey Method



Method File Name: Benzene_3-ion_Survey.mth

Scan Set Name: Benzene

Mass	Mass Width	Extra	Dwell (us)	Lead In
51.0	0.6	10	1000	3
77.0	0.6	10	1000	3
78.0	0.6	10	1000	3

Mode

○ Timed ● Trigger

Scans to Average: 1

RoundTrip Time (sec)

0.240

5.2 Calibration Procedures for Quantitative Analytical Methods

Instrument performance goals should be established during workplan development, and the on-site instrument should be checked prior to fieldwork to verify that it is operating properly. The initial equipment checks and QA analyses can be done using an existing method and calibration library. If the QA results fall outside of the desired performance goals, the instrument should be recalibrated. Example QA samples and data quality objectives (DQOs) include:

- Method blanks (i.e., outdoor air or a sample of VOC-free nitrogen). Example DQO: result for key target VOC less than lower calibration limit; and
- CCV sample(s). Example DQO: RPD < 100% for key target VOC.

A calibration curve with a minimum of five points is recommended for quantification of air samples. Because sample results will be used to distinguish between vapor intrusion and indoor sources of VOCs, the calibration range should span VOC concentrations expected in typical indoor air (i.e., 0 to 10 ppbv).

Standard mixes at different concentrations within the calibration range are created by diluting a standard gas with blank air. Standard gases containing known quantities of the target VOCs can be obtained from specialty gas vendors. Laboratory-grade nitrogen to dilute the standard can also be obtained from specialty gas vendors. Note that if ambient (e.g., outdoor) air is sufficiently "clean", it may be used to dilute the standard gas in lieu of lab grade nitrogen.

An example series of dilutions is provided in Table 7. The proportions shown in Table 7 have been found to minimize dilution errors (GSI, 2013). However, specific proportions of blank vs. parent/standard gas may vary and should be tailored to project-specific needs and data quality requirements. The example below assumes a pure standard gas with 1 ppm (1000 ppb) of each target VOC as a starting point. We also assume that the standard mixes are prepared in 1-L Tedlar bags. Additional recommendations to minimize errors during the calibration process include i) adding the appropriate quantity of blank air to each Tedlar bag first, then adding the appropriate quantity from the VOC parent bag; ii) reusing Tedlar bags a maximum of 10 times; and iii) analyzing the dilution bag samples within 1-2 days of preparation.

Table 7: Example Concentrations Utilized in the cVOC and Petroleum VOC Calibration Curves

Tedlar Bag No.	Standard Mix Goal (ppb)	Blank Air for Dilution	+	Volume / Parent Bag Concentration	Total Volume Available for Analysis (mL)
1	Pure Standard	n/a		Need at least 90 mL	
2	100	810 mL Blank Air	+	90 mL of pure standard (1000 ppb)	900
3	30	525 mL Blank Air	+	225 mL from 100 ppb bag	750
4	10	810 mL Blank Air	+	90 mL from 100 ppb bag	900
5	5	750 mL Blank Air	+	150 mL from 30 ppb bag	900
6	3	525 mL Blank Air	+	225 mL from 10 ppb bag	750
7	1	810 mL Blank Air	+	90 mL from 10 ppb bag	900
8	0.5	855 mL Blank Air	+	45 mL from 10 ppb bag	900

Note: Blank air is either laboratory-grade nitrogen or "clean" outdoor air.

Standard mixes of the desired dilutions are made in order of high to low concentrations (i.e., Bag Nos. 1 though 8, in order).

These mixes are analyzed in order from low to high concentrations (e.g., Bag No. 8, 7, 6, 5, 4, 3, in that order). The results are used to build the calibration curve using the instrument software. Each calibration curve may be forced through the origin (zero concentration). This curve fitting method is often helpful to quantify VOCs at low concentrations. For certain compounds such as vinyl chloride and MTBE, analysis of the lowest (i.e., 0.5 ppbv) standard may result in a non-linear response. This lowest point may be removed from the calibration curve for those specific compounds.

Criteria Utilized to Assess the Quality of Each Calibration Curve

The basic procedure for developing the calibration curves is described above. QA criteria for calibration curve acceptability are project-specific. However, criteria demonstrated to be suitable for implementation of the on-site analysis protocol (GSI, 2013) include: i) RSD <20%, ii) RSD of RF < 30% , and iii) curve fit $R^2 \geq 0.98$, where

a) Relative Standard Deviation (RSD %) is the measure of the linearity of the concentration levels (ion counts) in the calibration curve for each compound.

b) Relative Standard Deviation of the Response Factor (RSD of RF %) is the measure of the linearity of the response factors for each compound in the calibration curve, where the response factor is a measure of the relative response (ion count) of an analyte compared to that of an internal standard.

5.3 Testing Specific VOC Sources with the HAPSITE and Isolation Device

Specific indoor sources (i.e., consumer products) and potential vapor entry points can be isolated and tested to determine the degree to which they may be impacting indoor air quality. This section describes different options for construction, use, data analysis, and interpretation of results.

5.3.1 Indoor VOC Sources

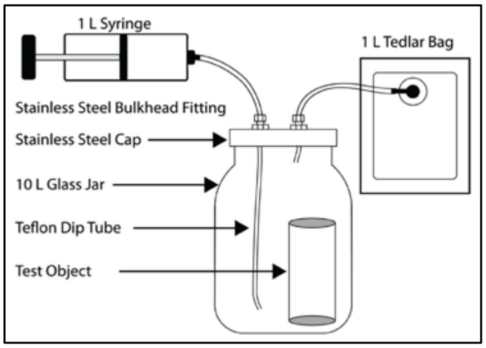
"Flux" or "emission" chambers can be used to isolate potential VOC sources and test the degree to which they may be impacting indoor air quality. Items can be identified for testing based on results of a HAPSITE survey or other method such as product type or information on the label. The testing process includes isolating the item(s) in a sealed container, allowing the items to off-gas for several minutes, and then collecting a quantitative sample of the air in the container.

Construction

The container or chamber should be large enough to contain one or two typical consumer products (e.g., aerosol cans). The chamber can simply be a tote used to isolate the items. The chambers can also be constructed to be air-tight, with two ports and tubing installed through the cap. A syringe and a Tedlar bag can be attached to mix air in the system and collect a sample, respectively (Figure 18). Non-reactive materials (e.g., glass jar, Teflon tubing) may be used to minimize adsorptive loss of VOCs and allow the chamber to be re-used with minimal carry-over. The components of such a chamber are shown in Figure 19.

Figure 18: Testing a Potential Indoor VOC Source

Figure 19: Indoor Source Flux Chamber Construction



Use: Step-by-Step

Emission chambers can be used to simply evaluate whether the indoor source is significant or not. In this case, the chamber is closed for several minutes to allow the items to off-gas. Then, the HAPSITE probe is inserted to collect the sample from within the chamber. If the concentrations in the chamber are significantly (i.e., 10x) higher than the air at the testing location, then the items are likely significant sources of the target VOCs. Note that, because of the potentially high concentrations in the chambers, it is advisable to switch to an analytical method suitable for high concentrations prior to doing the testing.

If a more quantitative result is desired, we recommend the following steps using the equipment illustrated in Figures 18 and 19 above.

1. Place the item for testing in the chamber and close the lid. Attach the syringe and Tedlar bag, and check that the connections are secure.

2. Record the time the item was sealed in the chamber. Allow the item to flux (i.e., off-gas) within the chamber for approximately 2 minutes. Pump the syringe to mix air in the system during this time.

3. Select an appropriate quantitative analytical method for low ppm concentrations of target VOC. For the HAPSITE, use either the Chlorinated VOCs PPM Method or Petroleum VOCs PPM Method (Section 5.1.1). Expel the air from the syringe and then detach the Tedlar bag. Using the HAPSITE in quantitative mode, measure the concentration of the target VOC from the air sample in the Tedlar bag.

4. Record the time the sample was collected (i.e., elapsed time), and concentrations of the target VOCs. If the VOC concentration is non-detect, a more sensitive analytical method can be used. For example, use either the Chlorinated VOCs SIM Method or Petroleum VOCs SIM Method (Section 5.1.1). If the VOC concentration is above the linear range of the instrument, the sample can be diluted to obtain a more accurate concentration measurement.

5. Calculate the Emission Rate:

   $E = (C \times V_t)/t$

   Where:

Parameter	Description	Units
E	Emission Rate	ug/min
C	Concentration of Target VOC in Chamber	ug/m^3
V_t	Volume of Emission Chamber (total flux volume)	m^3
t	Emission time (flux sampling time)	min

Note: Concentration (ug/m^3) = Concentration (ppbV) x Molecular Weight / 24.45

6. Estimate the predicted indoor air concentration corresponding to the measured emission rate.

   $C_{air} = E/(I \times V)$

   Where:

Parameter	Description	Units
C_{air}	Predicted Concentration in Indoor Air	ug/m^3
E	Emission Rate	ug/min
V	Volume of Building (or part of building with higher VOC concentration)	m^3
I	Estimated Building Air Exchange Rate*	min^{-1}

   Note: Air exchange rate for a residence is typically 6 to 20 day^{-1} (0.004 to 0.014 min^{-1}). An assumption of 12 day^{-1} is generally acceptable (0.5 per hour, or approximately 0.01 per minute).

7. Compare the measured concentration of the target VOC in indoor air to the predicted concentration based on the flux measurement. Note that the predicted concentration will have significant uncertainty due to the semi-quantitative nature of the flux testing and the uncertainty associated with the air exchange rate. However, if the measured and predicted concentrations are within a factor of 2 to 3, then the tested item is likely the primary source of the target VOC in indoor air.

5.3.2 Subsurface Source Isolation and Testing

Floor cracks or other areas can be isolated to test the degree to which vapors may be migrating into the building from beneath the slab. Floor cracks or penetrations (e.g., expansion joints, plumbing penetrations) can be identified for testing based on results of a HAPSITE survey. Areas for testing can also be identified by noting rooms with anomalously high target VOC concentrations in which no indoor sources are found.

The overall process involves isolating a section of the floor under a cover and collecting air samples from the isolated space for quantitative analysis.

Construction

Materials used to isolate cracks in slabs, floor drains, and other features can be made of plastic (e.g., polyethylene) sheeting (Figure 20, left) or can be a device specifically designed for this testing (Figure 20, right). Use of plastic to isolate the crack is acceptable, but a metal isolation device is more reliable because VOCs can diffuse through plastic.

Figure 20: Examples of Vapor Entry Point Isolation and Testing

Use: Step-by-Step

If the area is a significant source of VOCs to indoor air, the vapor entry rate will be high enough to result in high ppb or low ppm VOC concentrations in the trapped air.

If possible, conduct the testing during the baseline (i.e., unmanipulated) or the depressurized building pressure conditions. Sufficient indoor air measurements should be available so that the indoor VOC concentration range is established prior to floor testing.

If plastic sheeting is used to isolate the area, testing can be done by simply sealing the area, waiting several minutes, inserting the HAPSITE probe through the plastic, and collecting the sample. Note that the appropriate quantitative method (e.g., low ppm method) should be selected commensurate with the anticipated level of target VOCs.

Depending on project goals and on-site findings, different variations of the sampling may be helpful (e.g., sampling when the covering is first placed and resampling after some time (e.g., 20 minutes) to determine if VOCs are building up in the isolated space).

If more quantitative evaluations are desired, the following steps can be taken:

1. Place the chamber on the floor, sealing it to the floor with VOC-free modeling clay, plumber's putty, or similar. Attach a 1-L syringe and an empty Tedlar bag to each of the ports, and check that the connections are secure.

2. Record the time the floor area is isolated. Allow additional time (e.g., 5 minutes) for potential vapor flux into the chamber. At the end of this period, slowly pull air from beneath the chamber into the syringe, open the Tedlar bag, and then push the plunger of the syringe so that air fills the Tedlar bag. Collect at least 300 mL into the Tedlar bag to ensure that sufficient air is available for HAPSITE analysis.

3. Select an appropriate quantitative analytical method for low ppm concentrations of target VOCs. For the HAPSITE, use either the Chlorinated VOCs PPM Method or Petroleum VOCs PPM Method, as appropriate for the building target VOCs. Using the HAPSITE in quantitative mode, measure the concentration of the target VOCs from the air sample in the Tedlar bag.

4. Record the time the sample was collected (i.e., elapsed time), and concentrations of the target VOCs. If no target VOCs are detected, a more sensitive analytical method can be used. For example, use either the Chlorinated VOCs SIM Method or Petroleum VOCs SIM Method. If the VOC concentration is above the linear range of the instrument, the sample can be diluted to obtain a more accurate concentration measurement.

Compare the measured concentration of the target VOCs from the floor sample to concentrations in indoor air. Note that the former concentration will have significant uncertainty due to the semi-quantitative nature of the testing. However, if the result is more than 2-3 times the indoor air concentration, the tested area is likely to contribute to VOC concentrations in indoor air. Additional evaluation may be required to determine if this location is the primary entry point for VOCs.

5.3.3 Estimated Costs

Costs for conducting the on-site analysis protocol are marginally higher than implementing a conventional vapor intrusion investigation. Additional analysis can be found in the ER-201119 Final Report (GSI, 2013); costs are summarized in Table 8. However, in summary, additional effort and expense can be expected for project preparation (e.g., equipment rental, calibration/QA steps, etc.) and data management (e.g., differential pressure and HAPSITE data files, collecting detailed field notes to document sampling conditions/locations/times, etc). Because of the data volume collected, one can also expect additional effort during project reporting, to allow for reconciling all the different types of data.

Table 8: Estimated Costs for Implementing the On-Site Analysis Protocol at Four Buildings

Cost Element	Category				Unit Cost	Unit	Cost	TOTALS
1. Project planning and preparation	Labor	Senior Project Scientist/Engineer	16	hours	$150	$/hr	$2,400	$6,000
	Labor	Project Scientist / Engineer	36	hours	$100	$/hr	$3,600	
2. On-site analysis field program	Labor	Senior Project Scientist/Engineer	24	hours	$150	$/hr	$3,600	$10,605
	Labor	Project Scientist / Engineer	24	hours	$100	$/hr	$2,400	
	Equipment Rental	HAPSITE, Floor fan, differential pressure recorder	3	days	$575	$/day	$1,725	
	Off-site Sample Analysis	VOCs (3 samples x 4 buildings)	12	samples	$240	$/spl	$2,880	
	Off-site Sample Analysis	Radon (3 samples x 4 buildings)	0	samples	$110	$/spl	0	
3. Data evaluation and reporting	Labor	Senior Project Scientist/Engineer	15	hours	$150	$/hr	$2,250	$5,750
	Labor	Project Scientist / Engineer	35	hours	$100	$/hr	$3,500	
							Project Total:	**$22,355**
							Cost Per Building	**$5,589**

Note: 1) Estimates assume application of the procedure at four buildings during a single field program, assuming 2 buildings per day. Project planning and preparation includes pre-mobilization and on-location tasks (equipment prep/QA). 2) Cost estimates do not include travel to the site or shipping.

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