

Passive Samplers for Investigations of Air Quality: Method Description, Implementation, and Comparison to Alternative Sampling Methods

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The U.S. Environmental Protection Agency (EPA) Engineering Issue Papers (EIPs) are a series of technology transfer documents that summarize the latest available information on selected treatment and site remediation technologies and related issues. EIPs are designed to help remedial project managers, on-scene coordinators, contractors, and other site managers understand the type of data and site characteristics needed to evaluate a technology for potential applicability to their specific sites. Each EIP is developed in conjunction with a small group of scientists inside EPA and with outside consultants and relies on peer-reviewed literature, EPA reports, Web sources, current ongoing research, and other pertinent information. As such, this EIP is a technical support document describing the current state of knowledge on passive sampler application and performance and does not represent EPA policy or guidance.

1 PURPOSE AND SUMMARY

The purpose of this EIP is to summarize the “state of the science” regarding the use of passive air samplers for investigating subsurface vapor intrusion (VI) to indoor air. This Paper covers the basics of passive sampler design, compares passive samplers to conventional methods of air sampling, and discusses considerations when implementing a passive sampling program. The Paper also discusses field sampling and sample analysis considerations to ensure data quality is adequate and interpretations based on the passive sample data are supportable. The reader is expected to have a basic technical background on the VI exposure pathway and how to use and interpret indoor air sampling data in the context of a VI investigation. For guidance and policy on VI assessment and technical support documents, please visit:

<http://www.epa.gov/oswer/vaporintrusion/basic.html>
and
http://www.epa.gov/superfund/sites/npl/Vapor_Intrusion_FAQs_Feb2012.pdf.

Passive samplers are capable of measuring a large suite of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in indoor and outdoor air.

Deployment over longer time frames (e.g., weeks or months) than is possible with conventional canister-based methods of air sampling.

One key to successful passive sampling is appropriate calibration of the uptake rate or sampling rate. Uptake rate is usually determined for a particular sampler and chemical of interest in experimental chambers with controls on variables such as the sample duration, temperature, humidity, velocity, and concentration. As with any sampling method, one must also control sources of negative (underestimation) and positive (overestimation) bias. Potential sources of bias for passive samplers include starvation, poor retention, poor recovery, and blank contamination:

- **Starvation** occurs if the passive sampler withdraws target compounds from the surrounding media faster than they are replenished (essentially scrubbing the VOCs from the vicinity of the sampler), causing a negative bias. Starvation can be minimized either by using low uptake rate samplers (tube sampler) or by maintaining an adequate face velocity (i.e., air movement past the sampling surface).
- **Poor retention** occurs if a relatively weak sorbent is used to sample highly volatile compounds, especially for long sample durations. This causes a negative bias, underestimating concentration as VOCs are lost from the sampler media. Poor retention can be managed by selecting stronger sorbents.
- **Poor recovery** can occur when stronger sorbents are used with strongly sorbed compounds. Poor recovery underestimates

Passive samplers can yield reliable, time-averaged sample concentrations with comparable accuracy and precision to established conventional methods (e.g., evacuated canister samples and analysis by U.S. Environmental Protection Agency [EPA] Method TO-15 or pumped sorbent tube samples and analysis by EPA Method TO-17). Passive samplers have the advantage of greater ease of deployment and

concentrations because the sorbed chemical is not completely desorbed from the sorbent during sample analysis. Sorbent selection must balance retention and recovery.

- **Blank contamination** can overestimate concentration and occurs when the sorbents used in passive sampling are inadvertently contaminated during sampler preparation, storage, shipping, or handling. Blank contamination can be minimized with appropriate protocols and verified (or detected) with analysis of trip blanks.

This paper provides information that will be useful in avoiding such biases and getting the best passive sampler results possible. As with any VOC sampling event it is advisable to consult your analytical laboratory when embarking on a passive air sampling effort. An experienced analytical chemist is a great source of information on the most recent passive sampling analytes, uptake rates, sorbents, sampling protocols, and quality assurance procedures necessary to ensure that your passive sampling effort produces high-quality data.

2 INTRODUCTION

Passive sampling techniques have been used to monitor VOC and SVOC concentrations for several decades (e.g., Palmes and Gunnison, 1973). Most of the early applications were for industrial hygiene monitoring, but over the past several years there has been significant progress in using passive sorbent

samplers for measuring VOCs¹ at the lower concentrations needed to assess human health risk at sites regulated under the Resource Conservation and Recovery Act (RCRA); the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); the Brownfields program; and various state environmental programs. Passive samplers have been shown to yield results equivalent to other established methods for many VOCs (Begerow et al., 1999; Oury et al., 2006; Mosley et al., 2008; Cocheo et al., 2009; Lutes et al., 2010; U.S. Navy, 2013).

Passive samplers have several advantages over more traditional indoor air sampling techniques (e.g., U.S. EPA Methods TO-15 and TO-17).

- The sampling protocols are simple, which reduces the risk of inter-operator error, the cost of sampling, and the level of training needed for sampling personnel.
- Passive samplers are small and lightweight compared with the canisters used in Method TO-15, so they are discrete to place and less expensive to ship.
- Passive samplers operate without risk of power loss, clogging, or leaks that may affect canister (Method TO-15) or pumped tube (Method TO-17) samples.
- Passive samplers provide accurate results for a large range of sampling durations, from daily to quarterly sampling periods for certain compounds (U.S. EPA, 2012).

The ability to collect time-weighted average samples over longer durations than the 8 to 72 hours offered by the more traditional methods is advantageous because these longer periods can provide data that are more representative of the long-term average

exposure concentrations needed for cancer risk assessment.

A wide variety of organic and inorganic gases can be monitored using passive samplers, but this paper focuses primarily on the VOCs most commonly of concern at VI sites (i.e., chlorinated solvents and aromatic hydrocarbons).

3 PASSIVE SAMPLER BASICS

A passive sampler is a device that contains a solid sorbent (usually granular) in an inert container with openings of known dimensions that allow VOC vapors to pass through at a fairly constant (and known) rate. The following sections describe the basics of passive sampler theory, summarize the available types of samplers and sorbents, and explain how uptake rate and sampling duration are determined. Section 3.6 describes how to consider these factors when selecting passive sampler/sorbent combinations and includes a list of commercially available passive samplers. Section 3.7 compares passive samplers to other commonly used air sampling methods (i.e., Summa canisters and active sorbent tubes). Appendix A provides a more detailed summary of available research on passive samplers.

3.1 Theory

Passive samplers are deployed for a designated sampling period and then collected and analyzed by extracting the VOCs from the sorbent to measure the total mass of each analyte trapped by the sampler during the sampling period. If the uptake rate of the VOC is known, the average concentration over the sampling period can be calculated as follows:

$$C = M / (UR \times t) \quad 3.1$$

¹ Passive samplers can be used for volatile chemicals including VOCs, SVOCs, and mercury. Reference to “VOCs” in this document includes SVOCs and mercury unless otherwise indicated, although most passive sampling applications are for VOCs. As explained in Section 3, the applicability of specific

passive samplers to specific compounds or substances largely depends on the availability of measured uptake rates for those substances with a particular sampler and sorbent.

where

- C = time-weighted average air concentration ($\mu\text{g}/\text{m}^3$)
- M = mass of VOC retained by passive sampler (pg)
- UR = uptake rate (mL/min, compound-specific); also called “sampling rate”
- T = sampling duration (min)

Mass and sampling duration can be measured with high levels of accuracy; therefore, the uptake rate, or sampling rate, is the most critical variable for accurately determining air concentrations using passive samplers. Uptake rate has units of volume/time, but it is not a flow rate; rather, it is equivalent to the flow rate that would be required for a pumped adsorptive sample to sorb the same mass of a target chemical over the same sample duration when exposed to the same chemical concentration. The uptake rate is dependent on the geometry of the sampling device and the diffusion coefficient of the chemical. The uptake rate is also dependent on the sorbent characteristics of the passive sampler, which determine VOC retention as well as desorption efficiency. Experimentally derived uptake rates for a range of compounds have been published for most passive sampler configurations. The selection of a sampler type for an investigation often is based in part on the availability and reliability of uptake rates. Section 3.4 describes several approaches that can be used to determine uptake rates.

3.2 Passive Sampler Types

Passive samplers can be configured with a porous diffusive barrier or a nonporous membrane to control the rate of VOC collection by the adsorbent media. The porous variety, which allows for movement of air through the sampler, is the most common design, and a wide selection is commercially available. The options of various styles and associated range of uptake rates allow for flexibility in selecting the optimal sampler configuration to meet project-required reporting limits and/or sample durations. In the case of the nonporous membrane type, referred to

as the permeation passive sampler, VOCs dissolve in and diffuse through a membrane and are collected on the adsorbent medium. Although permeation sampler selection is currently limited, the hydrophobic and nonporous nature of the membrane can be advantageous in very high-humidity and high-velocity environments.

Passive samplers with the porous diffusive barrier can be categorized as tube, badge, or radial style. Tube-style (**Figure 1**) and badge-style (**Figure 2**) samplers have a one-dimensional (a.k.a., “axial”) diffusion path to the sorbent bed. The tube style is characterized by a relatively small cross-sectional surface area (A) and long diffusive path length (L) compared with the badge style and therefore has lower uptake rates. Examples of commercially available tube-style samplers are the Dräger ORSA 5 monitor and the standard thermal desorption tubes available from various vendors coupled with a diffusive end cap.

The badge-style passive sampler is characterized by a larger cross-sectional surface area and shorter diffusive path length, resulting in relatively higher uptake rates than tube samplers. The badge face must be covered with a windscreen to minimize uptake by advection. This windscreen can be a perforated cover (e.g., SKC Ultra and 575 and the 521 Organic Vapor Badge from Assay Technologies) or porous plastic (e.g., 3M OVM 3500).

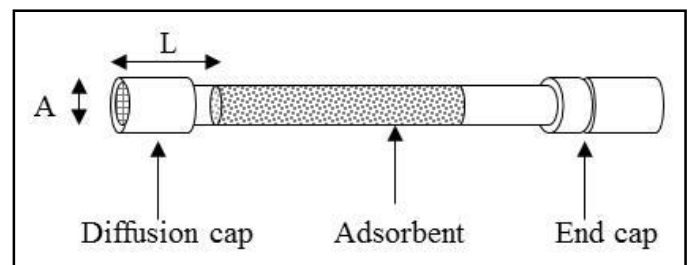


Figure 1. Tube-style passive sampler

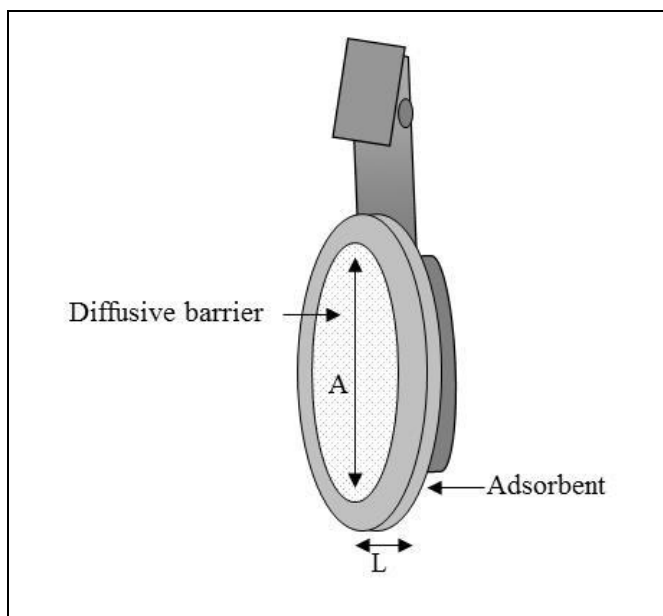


Figure 2. Badge-style passive sampler

The radial-style sampler houses the adsorbent material in a screen mesh tube, and the sorbent tube is housed in a porous cylinder that serves as the windscreen and diffusive barrier (Figure 3). Diffusive sampling occurs parallel to the sampler's radius, providing a very large surface area and a short diffusive path. As a result, radial-style samplers generally exhibit higher uptake rates than tube- or badge-style samplers. The radial-style sampler is patented by Fondazione Salvatore Maugeri as the Radiello sampler.

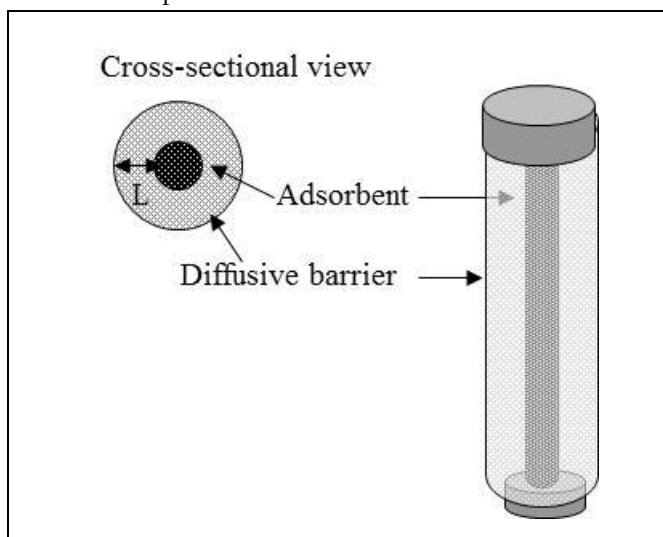


Figure 3. Radial-style sampler

The nonporous permeation passive samplers can be categorized as either the tube or badge style

(Zabiegala and Namieśnik, 2007). The Waterloo Membrane Sampler (WMS) is a commercially available tube-style permeation passive sampler (Figure 4) with uptake rates generally falling between the range of the nonporous tube and badge-style diffusive samplers. At the time of this publication, a commercially available version of the badge type permeation sampler described by Zabiegala and Namieśnik (2007) has not been identified.

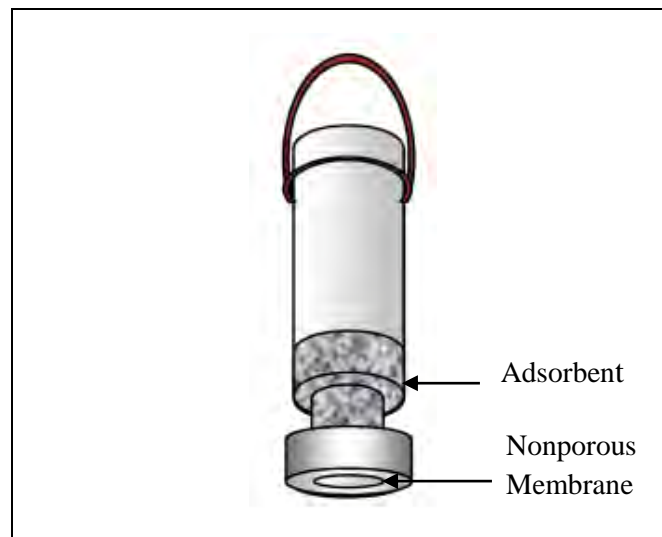


Figure 4. Permeation (tube-style) sampler

3.3 Sorbent Types

Each sampler type must be paired with an appropriate sorbent material for the constituents of interest. There are many different VOCs of interest and many different sorbents, and each compound has a certain affinity for each sorbent. The goal is to select a sorbent that efficiently retains the VOC mass that enters the sampler but also releases the VOC mass efficiently during analysis. A negative bias attributable to poor retention may occur if a sorbent-sorbate interaction is weak, leading to back-diffusion (or reverse diffusion). Weakly sorbed VOCs can also be displaced through competitive adsorption in the presence of high concentrations of other VOCs or water vapor. These effects are magnified when the sample duration is long. Conversely, a negative bias attributable to poor recovery may occur for compounds that are very strongly adsorbed by strong sorbents and are not completely released during

thermal desorption or solvent extraction prior to analysis.

Published studies document the retention of various VOCs by different sorbents (e.g., Brown and Shirey, 2001; American Society of Testing and Materials [ASTM], 2009b; U.S. EPA, 1999b). These data were generated for active (pumped) sampling, but the safe sampling volume and breakthrough volume information can provide useful information for selecting the most appropriate sorbent for passive sampling applications. In some environmental settings, many different chemicals with a wide range of sorptive properties may be present. Therefore, compromises between retention and recovery for some of the measured compounds may be required, along with the advice of an experienced analytical chemist, to select the appropriate sorbent for use in a passive sampler. Otherwise, two or more samplers could be used with sorbents selected for specific compounds of interest.

Sorbents fall into two general categories—very strong sorbents requiring solvent extraction and relatively weaker sorbents amenable to thermal desorption. Activated charcoal is the sorbent routinely used for solvent extraction techniques. The large surface area of activated charcoal allows for efficient adsorption of many VOCs and limited losses due to back-diffusion when applied to extended monitoring applications. The large surface area of charcoal is also beneficial when sampling environments with high total VOC concentrations. Carbon disulfide, the typical extraction solvent in this category, efficiently desorbs a majority of the adsorbed VOCs.

Thermally desorbable sorbents are characterized by smaller surface areas to allow for quantitative VOC recovery at moderate desorption temperatures. A variety of sorbents with varying adsorptive properties exist within this category. The three types of thermally desorbable sorbents commonly used for passive sorbent samplers and examples of each are summarized in Table 1. More detailed listings of

sorbents, their physical properties, and selection considerations are available from sorbent vendors.

Table 1. Thermal Desorbable Sorbents Commonly Used for Passive Sorbent Samplers

Thermal Desorption Sorbent Type	Example Sorbents
Porous Organic Polymers	Tenax TA, Chromosorb 106
Graphitized Carbon Blacks	Carbopack B, Carbograph 1TD, Anasorb GCB1, Carbograph 4TD, Carbopack X, Carbograph 5TD
Carbon Molecular Sieves	Carboxen 1016

The thermal desorption preparation technique generally results in analytical sensitivity much greater than analytical sensitivity using solvent extraction because only a small fraction of the solvent extract is injected onto the instrumentation for analysis, whereas the thermal desorption technique allows for nearly complete transfer of the adsorbed sample onto the analytical equipment. However, the advantage of the improved analytical sensitivity can be offset by the shorter sample collection periods required to avoid sorbent saturation and poor retention when using thermally desorbable sorbents. As sampling periods are extended, the weaker adsorption characteristics of these sorbents can result in poor analyte retention and back-diffusion. Additionally, the lower capacity of these thermally desorbable sorbents means that care must be taken when deploying samplers in environments with potentially high VOC concentrations.

3.4 Uptake Rates

Most passive samplers have a list of published uptake rates for a given number of compounds (see Section 3.7 for typical rates), but this list may not include all of the target compounds needed for a given assessment. Additionally, the rates may not be validated for longer-term environmental monitoring applications. Environmental conditions and sorbent-sorbate interactions are the two primary factors affecting the accuracy and the reproducibility of the uptake rate. As a result, nominal uptake rates are typically determined under a range of environmental

conditions, concentrations, and expected sample exposure periods. Standard methods detailing uptake rate determination can be found in National Institute for Occupational Safety and Health (NIOSH) (Cassinelli et al., 1987), Occupational Safety and Health Administration (OSHA) (2003, 2008), International Standards Organization (ISO, 2000, 2003), and European Committee for Standardization (CEN, 2002a, 2002b, 2004) methods. See Appendix A for further details.

While uptake rates determined experimentally in the laboratory are generally considered to be the most reliable, it is not always practical to conduct these studies, particularly when validating uptake rates over extended sampling periods. In the absence of experimentally determined rates, uptake rates can be estimated based on known or calculated diffusion coefficients. Assuming an ideal diffusive sampler, the uptake rate can be expressed by the following relationship:

$$UR = A/L \times D \quad 3.2$$

where

- UR = uptake rate (mL/min)
- A = passive sampler surface area (cm²)
- L = diffusive path length—distance between diffusive barrier and sorbent bed (cm)
- D = diffusion coefficient (cm²/min)

A discussion of several estimation methods using diffusion coefficients can be found in Namiesnik et al. (1984) and Feigley and Lee (1988). In cases in which VOCs exhibit non-ideal sorbent interaction, the use of calculated uptake rates may vary significantly from experimental rates (Walgraeve et al., 2011), and concentrations generated with calculated rates should be noted by the laboratory. In the case of polydimethylsiloxane-based permeation passive samplers, uptake rates can be estimated from the analyte's linear temperature programmed retention time index (LTPRI) (Seethapathy and Górecki, 2010a). Uptake rates can also be determined in the field using intermethod duplicate samples. Methods such as EPA TO-15 or TO-17 collected concurrently

with a percentage of passive samplers can be used to determine uptake rates based on field conditions (see Section 5.4).

3.5 Sampling Duration

The minimum sampling duration required to provide adequate sensitivity for assessing human health risk can be calculated using a rearranged form of 3.1:

$$t = (M_{\min})/UR \times C_{\text{RBSL}} \quad 3.3$$

where

- t = duration of sampling (min)
- M_{min} = laboratory reporting limit for each individual VOC in the target list (pg)
- UR = the compound-specific uptake rate (mL/min)
- C_{RBSL} = risk-based screening levels (µg/m³)

A longer sample duration may be advisable to provide a reporting limit somewhat lower than the risk-based screening level.

3.6 Passive Sampler Geometry and Sorbent Combinations

A summary of the sampler geometries and sorbent combinations is presented in **Figure 5**. Each sampler geometry can be paired with either a charcoal sorbent requiring solvent extraction or a thermally desorbable sorbent. For a given sampler geometry, the charcoal-type sorbent is most suited for longer sampling durations, which helps offset the lower analytical sensitivity of the solvent extraction preparation technique. Conversely, selecting a high uptake rate sampler geometry coupled with a thermally desorbable sorbent may be most appropriate for a short sampling period.

When selecting the preferred sampler and sorbent combination for a particular set of target analytes and target concentrations, consider the following:

-
- Whether the target analytes all have calibrated uptake rates for the compounds of interest. If calibrated uptake rates are not available, the rate can be estimated as described in Section 3.4. However, estimated rates may not be appropriate for the measurement of key risk drivers at the site without additional verification samples (Section 5.4).
 - The sample duration required to provide reporting limits that meet the target levels given a sampler's uptake rate (see Equation 3.3, Section 3.5). If the calculated duration is longer than the desired sampling period, selecting a passive sampler geometry with a higher uptake rate and/or a TD sorbent to provide a lower analytical reporting limit may be preferred. Alternatively, the calculated duration may result in weakly adsorbed compounds exceeding the estimated safe sampling volumes (Section 4.3), and a stronger sorbent may be required.
 - The suitability of available sorbents for the compounds of interest. In cases where one sorbent is not suitable for all of the compounds

of potential interest, it may be preferable to select the sorbent best suited to the compound(s) considered likely to pose the most significant contribution to risk (present in highest concentrations relative to risk-based target levels). Alternatively, different sorbents can be deployed at the same time if all of the compounds of interest cannot be captured using a single sorbent.

Table 2 provides a list of passive samplers that were available on the commercial market when this document was prepared. The table provides the sampler name, manufacturer, a brief description (with the range of uptake rates), references with published uptake rates and other data, and links to manufacturers' and other web pages where a great deal of additional detail can be found. This information should be helpful to the practitioner who is selecting and applying passive samplers as described in the following section but should be reviewed against current information to ensure that it is up to date in terms of the available samplers and published uptake rates and other information.

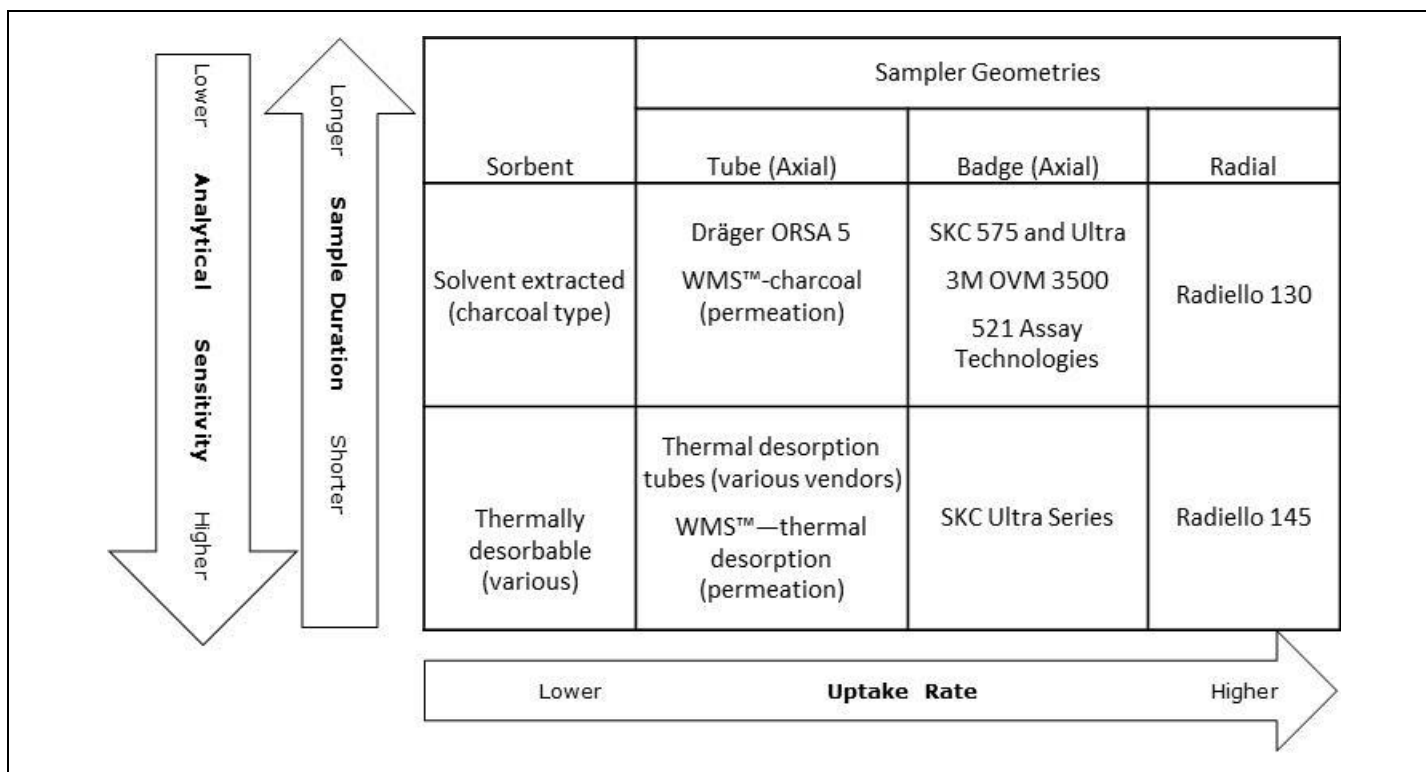


Figure 5. Selection matrix of passive sorbent and sampler types

3.7 Comparison of Passive Sampling to Conventional Air Sampling Methods

Table 3 compares passive sampling to conventional air sampling methods—EPA TO-15 (U.S. EPA, 1999a) and TO-17 (U.S. EPA, 1999b)—in terms of field ease of use, analytical sensitivity, target compounds, typical uptake rates, and sample duration. Each method has advantages and limitations when assessing indoor air quality to support VI investigations.

EPA Method T0-15 involves collecting air samples in specially prepared canisters (e.g., Summa canisters) and analyzing aliquots of the samples by gas chromatography/mass spectrometry (GC/MS). EPA Method T0-17 involves collecting VOCs present in air by actively pumping air through multibed sorbents encased in inert tubes, thermally desorbing the VOCs in the laboratory, and analyzing the samples by GC/MS. Appendix B describes other U.S. methods and standards that may be less familiar to American VI practitioners, as well as international and

European standard methods for passive sampling that are applicable to indoor air applications for VOCs at low concentrations.

3.7.1 Ease of Use

Passive samplers generally have fairly simple sampling protocols, and because they do not require power, the sampling process is less subject to battery failure or power failure (as in TO-17) or to the flow controller clogging with dust (as in TO-15). Passive samplers also are smaller, so they are less expensive to ship and can be placed more discretely during the sampling event.

3.7.2 Analytical Sensitivity

Each method can be configured to achieve similar reporting limits. In the case of the active and passive sorbent methods, the reporting limits are a function of sampling parameters. Selection of the proper sample volume pumped through the TO-17 sorbent tube and the appropriate deployment time for passive samplers provides comparable reporting limits to TO-15.

Table 2. Commercially Available Passive Sampling Devices as of June 2014

Name (manufacturer)	Description (typical uptake rates)	References	Weblinks
Automatic Thermal Desorber (ATD) Tubes (Perkin Elmer, Markes, CAMSCO, Supelco)	Open sorbent-filled tube with dust cap over one end during deployment (0.3–0.6 mL/min)	Brown (1999), MDHS 80 (1995), ISO 16017-2 (2003), ASTM D6196-3 (2009b)	http://www.perkinelmer.com/CMSResources/Images/44-74181APP_IndustrialHygieneMonitoringbyTD.pdf ; http://www.markes.com/ ; http://www.camsco.com/ ; http://www.sigmaaldrich.com/analytical-chromatography/air-monitoring.html
OVM 3500 (3M)	Badge with film of activated carbon, film of porous plastic, and air in between (20–40 mL/min)	ISO 16200-2 (2000), Type B sampler; MDHS 88 (1997)	http://www.shop3m.com/70070032142.html http://multimedia.3m.com/mws/mediawebserver?mwsId=SSSSSu7zK1fsxtUMx_U4xmSev7qe17zHvTSevTSeSSSSSS—
Ultra, Ultra II, Ultra III (SKC)	Badge with three different sorbent configurations (indoor: 7–11 mL/min; outdoor: 12–15 mL/min)	Cassinelli et al. (1987), Guild et al. (1992)	http://www.skcinc.com/prod/575-001.asp http://www.skcinc.com/prod/690-101.asp
GABIE (SKC)	Badge	Oury et al. (2006), Langlois (2008)	http://www.skcsouthafrica.co.za/index.php?page=shop_product_details&flypage=&product_id=172&category_id=47&option=com_virtuemart&Itemid=60
575 (SKC)	Badge with screen (9–18 mL/min)	ISO 16200-2 (2000), Type B sampler; MDHS 88 (1997)	http://www.skcinc.com/reports.asp
ORSA (Draeger)	Dual-ended tube (4–8 mL/min)	May (1989); Begerow et al. (1999); ISO 16200-2 (2000), Type A sampler; MDHS 88 (1997)	http://www.afcintl.com/industries-served/industrial.aspx?txtSearch=*%&catpageindex=8&CreatedByUser=1&ProductID=172
Waterloo Membrane Sampler (WMS; SIREM Labs)	PDMS (polydimethylsiloxane) membrane sampler (0.80–19 mL/min)	Seethapathy and Górecki (2010a,b)	http://www.siremlab.com/products/waterloo-membrane-sampler
Radiello (Fondazione Salvatore Maugeri)	Radial porous plastic diffusive barrier with cylinder sorbent insert (40–80 mL/min [solvent extraction diffusive body 120]; 20–30 mL/min [thermal desorption configuration, diffusive body 120-2])	Cocheo et al. (2009); ISO 16200-2 (2000), Type D sampler; MDHS 88 (1997)	http://www.radiello.com/english/index_en.html

Summa canister sampling using TO-15 (U.S. EPA, 1999a) is considered by many to be a “standard” for VI studies. Interlaboratory studies of TO-15 suggest variance in the reported values, ranging from about 30% to 300% (e.g., Lutes et al., 2012; Daugherty et al., 2004; Pearson, 2005). Studies comparing passive sampler results to TO-15 results show good agreement (30% to 90% variance) for chlorinated solvents and volatile aromatics, but poor agreement for polar compounds (e.g., Sweitzer et al., 2006; Odenchantz et al., 2008; Lutes et al., 2010; Allen et al., 2007; and Mukerjee, 2004).

3.7.3 Target Compounds

Passive and conventional air sampling methods differ in the range of chemicals that can be collected and analyzed. The conventional EPA Method TO-15 is limited primarily to compounds that have sufficiently high vapor pressure to minimize condensation on the canister surface. This translates to an upper carbon range limit of approximately C12 or naphthalene. Using a multibed sorbent tube, the conventional method TO-17 can extend the compound range well beyond C12 and can be configured to collect VOCs

Table 3. Comparison of Passive Sampler Method to Conventional Ambient Air Methods

Method	Field Ease of Use	Analytical Sensitivity	Target Compounds	Sample Duration
Passive single sorbent samplers	Excellent	Excellent ^a	Depends on sorbent selected	Hours to weeks
TO-15 (canister samplers)	Good	Excellent	C3–C12	Up to 72 hours
TO-17 (active multibed sorbent samplers)	Fair	Excellent ^b	Depends on sorbents selected (~C3–C26)	Up to 24 hours

^a Depends on sample deployment time, uptake rates, and total VOC levels.

^b Depends on sample volume collected and total VOC levels.

in the approximate carbon range of C3 to C26, providing the greatest level of compositional information for an air sample. In contrast, passive sorbent samplers are limited to a single sorbent bed, thereby limiting the targeted volatility range to the sorbent type selected.

3.7.4 Sample Duration

Passive samplers can be used for longer sampling periods than EPA Methods TO-15 and TO-17. The sample period for a TO-15 6L Summa canister is largely limited by the minimum flow rate that can be set by the flow controller. Flow controllers are available to deliver sampling rates to collect samples over periods up to 72 hours, but beyond that, the flow rates can be unreliable. Most canister samples are collected over 8 to 24 hours. For TO-17, the sample duration is limited by the minimum pump flow rates and the safe sampling volumes of the sorbent tube, based on the published uptake rates for a given number of compounds. Minimum pumped flow rates are constrained not only by mechanical considerations but also by the need to avoid back-diffusion. These limitations translate to a maximum sample period of 8

to 24 hours for TO-17. By contrast, passive samplers can be deployed over periods spanning days to weeks, especially with strong sorbents and/or low uptake rates to avoid exceeding the retention capacity.

It is important to consider the interaction between the selected duration of sampling and the time characteristics of the sources of VOCs detected in the indoor environment (ISO, 2007). Long-term sampling provides a robust measure of mean indoor air concentrations, but long-term sampling leads to a loss of information with respect to the variation with time of the VOC concentrations, which may make it harder to discern the impact of indoor sources. For example:

- Certain building products such as polyvinyl chloride, linoleum, cork, parquets, and wooden furniture containing glues emit VOCs slowly and for a long duration with minimal short-term changes.
- Paints and adhesives are characterized by a continuous, irregular, decaying time profile.
- Intermittent sources such as cooking or smoking often have a spikey and periodic pattern over time.
- Cleaning, maintenance, and hobby products have a spikey, irregular, and variable time pattern over time.
- VI varies in response to changing building pressure and ventilation.

Longer sample durations are more comparable to the exposure durations that are of interest for human health risk assessment. Detailed studies of indoor air quality in buildings where VI occurs (e.g., Johnson et al., 2013; Luo et al., 2012; U.S. EPA, 2012) show that temporal variability can be more than an order of magnitude. Passive samplers allow longer sample durations that provide time-weighted average concentrations that include concentration peaks and valleys and therefore can be more representative of a long-term average concentration than a shorter duration sample. Thus, even if conventional methods

(e.g., TO-15, TO-17) may have a slightly higher accuracy, passive samplers can provide more representative data for long-term indoor air exposure assessment.

4 DESIGNING AND IMPLEMENTING A PASSIVE SAMPLING PROGRAM

This section describes how to design and implement a passive sampling program that will provide reliable results. Selecting and deploying passive samplers involve technical decisions on sampler design and placement. It is important to establish a good relationship with your analytical chemist early in the process to select the correct sampler and method properly.

4.1 Selecting a Passive Sampler Suited to Your Investigation

4.1.1 Target Chemicals—What are your compounds of interest?

Passive sampling requires selecting the appropriate sampler, sorbent, and sampling duration to meet a preliminary data quality objective (DQO) and project-specific goals. The first consideration is to determine the compounds of interest. For most VI investigations, a list of compounds most likely to contribute to inhalation risks can usually be developed by comparing soil gas or groundwater sample concentrations to risk-based screening levels (RBSLs) available from EPA or state regulatory programs (e.g., EPA Regional Screening Levels²). The compounds that exceed the RBSL by the greatest margin will dominate the risk at a site and should be the primary focus of sampler selection.

4.1.2 Sampler Selection—How many of the target compounds have known uptake rates?

It is advantageous to select a passive sampler that has vendor-supplied uptake rates supported by controlled chamber tests or at least a considerable body of field-calibrated uptake rates for as many of the target

compounds as possible. (Table 2 has references for uptake rates available from passive sampler suppliers.) For compounds without published uptake rates, an estimate can be made (Section 3.4) and/or verified by field calibration (side-by-side sampling using both passive and active methods in a certain percentage of locations). If diffusion through air is the uptake mechanism (as it is for indoor and outdoor sampling), the diffusion coefficient depends primarily on the molecular weight

(<http://www.epa.gov/athens/learn2model/part-two/onsite/estdiffusion.html>). If permeation through a membrane is the uptake mechanism, the uptake rate may be proportional to the partitioning and permeation constants (Seethapathy and Górecki, 2010a, 2010b).

4.1.3 Reporting Limits and Sampling Duration—What target reporting limits are needed and how does that influence the duration of passive sampling?

Once the target compounds and uptake rates are known, the sample duration needed to provide a reporting limit as low or lower than the risk-based target concentration or screening level can be calculated for each compound using Equation 3.2. The sample duration will usually be dictated by the chemical with the lowest target concentration or lowest uptake rate. At this stage, two checks should be applied:

1. The sample duration should be compared with project goals and practical constraints. For example, if the sample duration is calculated to be relatively short (e.g., less than 24 hours), it may be appropriate to extend the duration to achieve a more representative time-weighted average concentration for each analyte. Alternatively, if the sample duration is relatively long (e.g., many weeks or months), it may be preferable to use a higher uptake rate sampler to achieve a shorter sample duration. A shorter sample duration can also potentially be

² <http://www.epa.gov/region9/superfund/prg/>; contact your state regulatory office for state-specific RBSLs

achieved using thermal desorption instead of solvent extraction because the thermal desorption process results in better sensitivity.

2. The product of the sample duration and the sampling rate ($UR \times t$) for each compound should be compared with the recommended safe sample volume (SSV) for each chemical on the sorbent typically used with the passive sampler. If $(UR \times t)$ is greater than the SSV, it may be prudent to select a stronger sorbent instead. Before a final selection is made, the target compound list should be reviewed to assess whether the most strongly adsorbed compounds will be recovered well during thermal desorption or solvent extraction prior to analysis. This step is similar to the design considerations for TO-17 sampling and should be performed with the assistance of an experienced analytical chemist.

Overlapping deployment periods (e.g., Johnson et al., 2013; Johnston, 2013) can be used as a precaution against sorbent media overloading or underloading. U.S. EPA (2012) has information on the performance of passive samplers over different sampling durations for tetrachloroethylene (PCE), toluene, chloroform, and benzene.

4.2 Placing Passive Samplers Indoors

Three technical factors should be considered in deploying passive samplers indoors:

- **Air velocity:** The rate of air flow past passive sampler devices can result in high bias via turbulent uptake for most samplers, so sampler devices should not be placed near areas prone to high air flow such as areas near windows, doors, chimneys, and air vents. Areas with insufficient air circulation, which can result in low bias via starvation, also should be avoided to provide a representative atmosphere to the sampler.
- **Humidity:** Humidity can affect the uptake rate of some passive samplers, so high humidity areas such as laundry rooms and bathrooms should be avoided.

- **Security:** The samplers should be placed to minimize the risk of accidental or unauthorized physical intervention (e.g., from children and pets).

4.3 Placing Passive Samplers Outdoors

Six technical factors should be considered when deploying passive samplers outdoors:

- **Air velocity:** Windy locations as well as very protected locations should be avoided for the reasons described above. A shelter may be used to avoid excessive wind-speeds, precipitation, and direct sunlight.
- **Precipitation:** Moisture can affect the uptake rate or retention of some passive samplers, so the samplers should be protected from rain and snow.
- **Temperature:** The samplers should be protected from temperature extremes (e.g., avoid direct sunlight) that can speed degradation of sorbed chemicals or release of sorbed chemicals.
- **Security:** The samplers should be placed to minimize the risk of accidental or unauthorized physical intervention (e.g., from children and pets or from vandalism).
- **Plant transpiration:** Avoid placing samplers under or in trees that can evapotranspire VOCs from the subsurface and create a high bias for ambient samples (Johnson et al., 2003).
- **Location relative to building:** Avoid placing outdoor samplers near windows, doors, or exhaust fans to minimize the influence of indoor air concentrations on the outdoor samplers. For commercial buildings, it can be instructive to position outdoor air samplers near the building air intake(s) to assess the outdoor air quality as it enters the building.

4.4 Instructions for Occupants for Passive Indoor Air Sampling Events

Controlling the use of or removing consumer products containing VOCs is common practice when

sampling indoor air over the typical 8- to 24-hour sampling periods. It is harder and often impracticable to control or eliminate the use of consumer products containing VOCs when using passive sampling methods for longer sampling durations (days to weeks). Similarly, it should be expected that building occupants will continue with normal ventilation, heating, and other occupancy activities (U.S. EPA, 1990). The Massachusetts Department of Environmental Protection provides detailed discussions of the pros and cons of opening and closing windows and doors, operating mechanical ventilation systems, and isolating certain parts of the building during indoor air sampling (MADEP, 2002).

It is important to document the presence of household chemicals or other potential sources of VOCs to assist with data interpretation (ISO, 2007). Certain consumer products that contain VOCs (e.g., paints, glues, aerosols) are often used very infrequently and can be stored in plastic bins outside the residence for an extended sampling duration. Additionally, it is helpful if the occupant keeps a log of the types and dates of operation of heating systems, air conditioners, and ventilation devices like window and attic fans. This information will be useful for interpreting the results (CEN, 2004), particularly when evaluating sequential sampling events in a particular building or concurrent sampling events in adjacent areas.

4.5 Considerations for Other Applications

Several past studies have demonstrated novel ways that passive samplers can be used in a VI investigation. Some examples include the following:

- Passive samplers can be used in a quantitative or semiquantitative manner to measure VOC vapors in subslab and deeper soil gas. During subslab or soil deployments, passive samplers should be protected from direct contact with soil, and the sampler should be sealed in place with a seal that is at a depth just above the sampler, not just at ground surface (McAlary et al., 2014a,b,c; Hodny et al., 2009; Odencrantz and O'Neill, 2009).
- Zencak et al. (2007) and Johnson and Dawson (1999) used passive sampling to collect atmospheric samples suitable for stable isotopic analysis.
- Researchers have used overlapping deployment periods as a precaution against media overloading or underloading, as a method to determine the stability of uptake rates and evaluate back-diffusion over time (U.S. EPA, 2012) and as a method to facilitate temporal analysis of meteorological factors in VI (Johnston and Gibson, 2013).

Other studies have combined long-term passive sampling with triggered sampling. Yao (2007) combined long-term passive sampling with event-triggered active sampling for meteorological conditions when atmospheric pollutant transport was expected. Crump et al. (2011) tested a strategy in which a photoionization detector monitoring device was used to trigger a sorbent-based VOC sample in an aircraft cabin.

5 DATA QUALITY OBJECTIVES

As with any environmental measurement, DQOs for passive samplers are an important consideration. To meet the DQOs, the investigation should include both field and laboratory quality assurance/quality control (QA/QC) procedures to ensure that sampling and analysis procedures do not bias the sample results (i.e., results do not consistently under- or over-estimate actual concentrations), results are reproducible and comparable (i.e., *precision*—results can be replicated by following the same procedures), and results are sufficiently *accurate* to support environmental decisions to be made with the data. Passive samplers typically have similar DQOs as other indoor air measurement techniques (such as TO-15 and TO-17). This section provides an overview of the important DQOs and QA/QC procedures for indoor air sampling with a focus on what is different for

passive samplers. Laboratory QA/QC for passive sampler analysis is discussed in **Appendix C**.

5.1 Media Preparation for Field Deployment

Passive samplers require similar preparation as active samplers used in Method TO-17. Reusable sorbent cartridges require cleaning and certification to prevent chemical carryover from previous sampling events. Samplers can be “batch-certified” (5 to 10% of a batch is analyzed without being deployed) or individually certified (every sampler is analyzed before and after use). Many of the single-use samplers are pre-certified by the manufacturer without the need for additional laboratory or field preparation steps. After manufacture or cleaning/certification, the storage time before use is usually limited to a few months, and shelf-life studies are typically conducted to establish expiration or “use-by” dates. Recertification and recleaning should be considered for any samplers used after their expiration date.

Samplers should be stored and transported to and from the field protected from heat and in well-sealed, inert containers to protect from the ingress of VOCs. The recommended storage condition for various charcoal and thermal desorption-type axial and radial samples is generally room temperature (EN 13528-3; CEN, 2003), but polar compounds (e.g., 2-butanone) have been reported to exhibit poor stability on charcoal, so transport on ice is recommended if quantitative results are required (ISO, 2000; 3M, 1996).

5.2 Passive Sampler Deployment—Field Handling Protocols

Passive sampling is relatively simple: the sampler is removed from protective packaging, positioned in the sampling location, and left for a specified interval, after which it is returned to the protective packaging. The date and time of deployment and retrieval must be recorded, along with the sample identification number and location. Some samplers such as the WMS, 3M OVM badge, and SKC 575 badge are

preassembled, and deployment simply requires removing the outer packaging. Other samplers, such as Radiello, require transferring sorbent resin or cartridge to the diffusive body. The SKC Ultra III is available in both the prepacked or user-filled version. The Automatic Thermal Desorber (ATD) tube requires removing the end cap and replacing it with a diffusion cap. All of these procedures are easily learned, so training is minimal. In fact, building owners and occupants can be trained to perform sample deployment and retrieval (e.g., Jaward et al., 2004a,b; Johnston, 2013; Johnston and Gibson, 2013). A chain of custody should be completed to document the transfer of samples from the field to the laboratory.

5.2.1 Recording Field Conditions

Monitoring of ancillary parameters such as temperature, relative humidity, and barometric pressure can improve the accuracy of the reported concentrations and assist in the interpretation of passive sampler data. Temperature has weak or negligible impact on membrane samplers (Zabiegała and Namieśnik, 2007; Seethapathy and Górecki, 2010b) but can affect the uptake rates of diffusion-controlled samplers. The uptake rates of diffusion samplers can be corrected using the relationship of mass adsorbed to temperature derived using Maxwell’s equation and the ideal gas law as described in ISO 16017-2 (ISO, 2003). Assuming an ideal diffusive sampler, the mass adsorbed varies with the square root of the absolute temperature, translating into approximately a 0.2% increase per degree Celsius. Indoor air temperature is usually controlled in occupied buildings to a relatively narrow range for comfort, however, so the potential bias in most cases is negligible.

If the reported concentrations are required to be expressed as standard ambient temperature and pressure, both the average barometric pressure and temperatures are required. These adjustments may not be necessary or significant in buildings where temperature, humidity, and air flow are well

controlled, but ancillary measurements may have other beneficial uses. For example, U.S. EPA (2012) highlighted the usefulness of differential temperature as a predictor of the stack effect, which has an effect on the differential pressures between the building and the subsurface. It is particularly useful to record the temperature, relative humidity, and air velocity when sampling outdoor air, because of the wider range of values for these parameters.

A sketch of the site should be prepared, noting the location of key building features and the locations of the samplers.

5.3.2 Storage and Transport Requirements to Laboratory

General requirements for passive sampler storage and return transport to the laboratory are outlined in standard EN 13528-3 and include packing in inert, closed shipping containers and avoiding exposure to high temperatures. Cold storage is not necessary in most cases, but some methods recommend or require it. For example, EPA TO-17 requires transporting ATD sample tubes back to the laboratory at $<4^{\circ}\text{C}$, but ISO 16017-2, EN 13528-2, and ASTM D6196-03 methods describe shipping of thermal desorption samples to the laboratory at ambient temperatures. Also, as previously mentioned, transport on ice is recommended for charcoal-based samplers and polar compounds.

5.3 Field Quality Control Samples

Field QC samples are used to evaluate potential sources of measurement error during sample collection and handling.

5.3.1 Trip Blanks

Trip blanks are a critical requirement for all adsorptive sampling programs and are used to quantify any potential blank contamination arising from sample transport, handling, and storage. These are samplers that travel to and from the field sampling site without being opened. An adequate number of field blanks is usually one per shipment but may vary

with the size of the sampling program (e.g., 1 per 10 or 20 investigative samples).

5.3.2 Field Duplicates

Field duplicates are routine QC samples to assess overall precision by evaluating effects of field conditions on precision. In the case of passive samplers, care should be taken to place the duplicate samplers with sufficient distance (air space) between them to ensure that they do not influence each other's uptake rates.

5.4 Intermethod Duplicates

A certain percentage of collocated duplicate samples using alternative methods (e.g., TO-15 or TO-17) can assist in evaluating passive sampler measurement accuracy. Passive sampler uptake rates can vary in response to changes in field conditions (temperature, humidity, pressure, wind speed, and sample duration). Intermethod duplicates collected using methods that are less sensitive to environmental parameters can be valuable in identifying and evaluating the significance of any bias inherent in the passive measurement (Tolnai et al., 2000). Additionally, these concurrent measurements can be used to calculate site-specific uptake rates, which is especially useful for situations in which either the uptake rate is undetermined or when field conditions are outside the ranges for which the uptake rates were validated. The reproducibility of passive samplers is quite good, so the number of collocated intermethod duplicate samples need not be excessive to provide a high degree of confidence in the accuracy of all passive samplers collected in similar conditions.

Methods TO-15 and TO-17 samples are not designed for long sample durations that can be achieved with passive samplers. To extend the sample collection period to align with the passive samplers, either multiple successive sorbent tubes or canisters are required or modifications to the conventional sampling protocols must be made.

One approach to extend pumped sorbent tubes or canister sampling times is to collect intermittent

samples over the desired collection period. Programmable sample pumps have been used to cycle the pumps on and off at scheduled times, allowing for pump operation at reliable flow rates without exceeding safe sampling volumes for the sorbent tube (Gordon et al., 1999; Jia et al., 2007). To conduct intermittent canister sampling, a programmable solenoid/timer device such as the Nutech 2701 can be attached to the canister flow controller, turning the Summa canisters on and off for short periods over the sampling event (U.S. EPA, 2009a, 2009b). Canister sampling periods can also be extended by attaching a set of 6L canisters to a manifold connected to a single flow controller. This approach increases the effective collection volume of the canister, thereby extending the sampling duration while operating the mass flow controller in the range of reliable flow rates. Although the laboratory only needs to analyze one of the set of canisters, this approach requires preparation and delivery of a set of 6L cans per selected collocated site (U.S. Navy, 2013; ESTCP, in press; Johnston and Gibson, 2013; Johnston, 2013). Some studies have deployed canisters at the beginning, middle, and end of the sampling period. This approach is most appropriate under controlled conditions where temporal variability is expected to be moderate (Lutes et al., 2010).

Another approach to verifying performance of passive samplers is to deploy concurrent passive samplers at subintervals (U.S. EPA, 2012). This may require using an alternative passive sampler geometry/sorbent combination to achieve the targeted sensitivity. Comparing the average of the subinterval concentration to the measured average provides information about the stability of the uptake rate for the long-term passive sampler. This can be important if the sampler has not been validated for prolonged exposures or if the selected sorbent is not ideal for one or more of the target compounds.

6 INTERPRETATION OF PASSIVE SAMPLING RESULTS

6.1 Measurement Uncertainty and Implications to Data User

All results reported by a laboratory have the potential for bias (high or low) and variability, both of which contribute to measurement uncertainty, regardless of the analytical method. Any measurement affected by bias and variability may still be fit for its intended purpose as long as the uncertainty is considered in the interpretation. For example, if a particular compound has a risk-based screening level of $1 \mu\text{g}/\text{m}^3$ and the measured concentration is $0.1 \mu\text{g}/\text{m}^3$, then the measured concentration could be interpreted as lower than the screening level even if the uncertainty in the measurement was up to an order of magnitude. The impact of temporal variability decreases as the sample duration increases (Steck, 2013), so a passive sampler deployed over longer durations is likely to exhibit lower overall measurement uncertainty associated with temporal variability than conventional methods deployed over shorter durations.

Intermethod sample results should be reviewed to assess whether any environmental parameters are skewing the passive sampler results. As described above, passive sampler uptake rates vary with wind speed, humidity, temperature, and other environmental factors, so when these parameters are unusual or highly variable, the accuracy of passive samplers may be influenced (Tolnai et al., 2000). Where sampling conditions are typical of indoor air (temperature near 21°C , moderate humidity, and gentle air circulation) and manufacturers have published uptake rates for a particular compound, sampler/sorbent, and sample duration, the accuracy of the passive sampler results is probably comparable to other indoor air quality monitoring protocols.

Trip blanks and certification blanks should be reviewed to assess whether any chemicals are present in the passive samplers from sources other than the media being monitored. A blank correction may be worthwhile, depending on the DQO. Retention and

recovery should be considered for the weakly and strongly sorbed compounds, respectively. Several factors may contribute to the overall uncertainty, but the dominating factor can often be used to estimate the total measurement uncertainty. Accuracy and precision can be tested and documented with an appropriate number of QA/QC samples, and it also is valuable to include the professional judgment of an analytical chemist experienced with passive sampler use and analysis.

6.2 Other Lines of Evidence

In designing and conducting air quality studies, collecting multiple lines of evidence simultaneously, rather than sequentially, offers benefits. Multiple simultaneous lines of evidence can provide greater power to evaluate interpretative questions such as “Were the samples collected under near worst case conditions for VI?” or “Why did the concentration vary between sampling period A and sampling period B?” Matching the durations of sampling or observations of multiple variables facilitates time series data analysis. In this section, we briefly describe other lines of evidence that can be collected over the same sampling durations as passive samplers to assist with interpreting the passive sampling data.

6.2.1 Radon

Radon has been suggested as a potential gauge of the spatial and temporal variability of VI (Schuver and Mosley, 2009; U.S. EPA, 2012; Schuver, 2013). Many well-tested and cost-effective passive radon sampling devices are available with durations available that can be matched to passive samplers for VOCs. These include Alphatrack detectors for 90- to 365-day deployments, various types of electret ion chambers for 2- to 365-day periods, and activated charcoal adsorption canisters for 2 to 7 days. Continuous radon monitors are also available. See U.S. EPA (1992, 2012) for details on these passive and continuous instrumental measurements.

6.2.2 Passive Air Exchange Rate Measurements

Passive air exchange rate measurements can be made with a technique that combines a small passive emitter of perfluorocarbon tracers with a passive sampler (EPA Method IP-4A; U.S. EPA, 1989). By varying the number of emitters, experiments can be designed for a wide variety of durations from 1 day to several months. Air exchange data can assist with the interpretation of temporal variability in indoor air measurements. Indoor air concentrations are strongly influenced by air exchange rate, exhibiting higher concentrations with lower air exchange rates (all other factors being equal).

6.2.3 Differential Pressure Measurements

Differential pressure across the floor slab can be useful to determine the driving force behind VI, especially if it is supported by wind speed and barometric pressure monitoring (U.S. EPA, 2012). Instructions for differential pressure monitoring in structures can be found in U.S. EPA (1993), and procedures for calibrating differential pressure measurement devices are in U.S. EPA (1998). Although this technique is still normally only applied in research contexts to unmitigated structures (e.g., U.S. EPA, 2012), it is a routine technique in VI mitigation design and monitoring.

7 CURRENT CHALLENGES, LIMITATIONS, AND RESEARCH AND DEVELOPMENT NEEDS

Although at the time of the publication of this document there was substantial research available on passive samplers for VOCs in air focused on industrial hygiene, ambient outdoor air quality, and compliant building investigations (see **Appendix A**). However, several current challenges and limitations to using passive samplers remain. Some of the more important challenges for applying passive samplers in VI investigations are discussed below. Readers encountering such challenges are encouraged to identify and consult more recent studies for advancements addressing these limitations.

7.1 Intermethod Comparisons

A compilation of the results of intermethod duplicate sampling studies would be helpful for identifying field-validated uptake rates for a wider range of chemicals. If measurements of the environmental conditions (e.g., temperature, pressure, humidity, wind speed) also were compiled, a statistical analysis could be conducted to determine whether and how much these effects bias the results and whether these biases are significant compared with spatial and temporal variability. It should also be recognized that the primary alternative, TO-15, is only suitable for a portion of the over 100 compounds of potential concern for VI and shows interlaboratory variability that may be significant compared with the intermethod differences (see Section 3.7).

7.2 Longer-Term Sample Durations

Questions remain regarding the limits of applicability of passive samplers to longer-term sampling durations. For example, sampling over very long durations (e.g., 3 months, 6 months, 1 year) may be desirable to provide time-weighted average samples inclusive of the short-duration, infrequent intervals of enhanced VI that can significantly contribute to long-term average exposure. However, less strongly sorbed compounds may not be well retained on passive samplers over such long intervals. In addition, longer sampling durations provide more time for the uptake of water to influence performance through competition for adsorptive sites for some sorbents (e.g., activated carbon), hydrolytic degradation of some chemicals (e.g., methyl ethyl ketone, 1,1,1-trichloroethane), or reactions with ground-level ozone.

Long-term controlled chamber tests and field studies would be beneficial to verify sampler performance over time and could be designed to address these and other long-term sampling concerns. In addition, demonstration and validation studies may be needed as novel sampling strategies are developed for using passive samplers in VI investigations. For example, one could represent long-term exposure in

commercial, industrial, or other occupational settings by collecting samples over multiple workdays and opening samplers during business hours and closing them over nights and weekends.

7.3 Additional Compounds

Most of the studies of passive sampler performance include a specific list of target analytes or provide data for compounds present at a particular location. As a result, some of the more common compounds of interest for VI (e.g., chlorinated ethanes, ethenes, and methanes and aromatic compounds such as benzene, toluene, ethylbenzene, and xylenes [BTEX], trimethyl benzenes [TMBs], and naphthalene) have been studied much more extensively than others. Controlled chamber tests for multiple samplers and a broad list of chemicals of concern for VI would be very valuable. Field tests of the passive samplers provide a useful supplement to chamber tests in that they challenge the samplers with realistically varying concentration and temperature profiles that are difficult to produce in chamber tests.

7.4 Challenging Compounds

Some compounds are particularly challenging to measure using passive samplers, and additional research is needed to demonstrate the capabilities and limitations of various passive sampler/sorbent combinations in measuring such compounds. For example, vinyl chloride, chloromethane, and possibly other low boiling point, low molecular weight compounds tend to be weakly sorbed and poorly retained, especially with long sample durations, high uptake rate samplers, or thermally desorbable sorbents. Vinyl chloride is retained well by Unicarb™ (Wolfenden, 2010), but other VOCs (e.g., naphthalene and SVOCs) may be too strongly sorbed to allow adequate recovery. Thus, in some cases, it may be necessary to use parallel samplers with strong and weaker sorbents to cover the range of target analytes.

Compounds with relatively low risk-based screening levels (e.g., 1,3-butadiene, chloroform, 1,2-

dichloroethane [1,2-DCA], hexachlorobenzene, hexachlorobutadiene, all of the polycyclic aromatic hydrocarbons [PAHs] and polychlorinated biphenyls, 1,1,2,2-tetrachloroethane [1,1,2,2-PCA], 1,1,2-trichloroethane [1,1,2-TCA], and vinyl chloride) may require long sample durations to achieve reporting limits comparable to the screening levels. In some cases, that could result in oversaturation of the sorbent with compounds that may be more abundant (e.g., limonene, pinene, and other fragrances; hydrocarbons; aerosols; and other chemicals from background sources). Controlled chamber tests including a variety of sorbents and a range of challenging compounds would help assess the capabilities and limitations of using longer-term passive sampler deployments to meet the reporting limits needed for VI assessments.

7.5 Application to Soil Gas

Passive sampling has been used to assess soil gas quality for decades, but until recently, the relationship between the mass sorbed on the sampler and the concentration in the soil gas has been poorly understood. Recent advances indicated that quantitative passive sampling is possible as long as the uptake rate of the sampler is the rate-limiting step (i.e., the rate of diffusive delivery of vapors from the surrounding soil or fill materials is not the rate-limiting step) (McAlary et al., 2014a, 2014b, 2014c). The rate of diffusive delivery from the soil depends on the porosity and moisture content of the soil. More field testing is needed to better define the range of soil types and moisture contents that are conducive to quantitative passive soil vapor concentration measurements.

7.6 Sample Duration for Different Exposure Periods

For some compounds of interest for VI, short- or medium-term average exposure concentrations may be important for assessing acute or subchronic health effects, while long-term average concentrations are important for assessing the risk of chronic health effects such as cancer. If the chronic and subchronic

screening levels are similar, it would be cost-effective to have a set of sampling tools that could combine a long-term average concentration estimate with a measurement of short- or medium-term peak concentrations. Additional research is needed on how to best employ passive samplers in conjunction with traditional (i.e., TO-15, TO-17) methods and specific field techniques (e.g., electromechanical timers, sensor controlled sampling) in a sampling system to achieve such goals.

7.7 Triggering Methods for Intermittent Passive Sampling

Passive samplers generally have a long shelf life if stored in the protective containers provided by the manufacturers, which creates an opportunity to monitor during selected intervals of suspected high potential for VI based on meteorological events (e.g., rapid decreases in barometric pressure allow soil gas to expand and can cause a short-term increase in the volumetric flow of soil gas into overlying buildings). Research is needed to assess whether this strategy is effective and, if so, what special design considerations are necessary (e.g., high uptake rate samplers may be needed to achieve low enough reporting limits within a limited sampling period).

8 ACRONYMS AND ABBREVIATIONS

ANSI	American National Standards Institute Inc.
ASTM	American Society for Testing and Materials
ATD	Automated Thermal Desorber
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CEN	European Committee for Standardization
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DQO	Data Quality Objective
EIP	Engineering Issue Paper
EPA	Environmental Protection Agency

ESTCP	Environmental Security Technology Certification Program
FID	Flame Ionization Detector
GC	Gas Chromatography
ISEA	International Safety Equipment Association
ISO	International Standards Organization
LCS	Laboratory Control Spike
LTPRI	Linear Temperature Programmed Retention Time Index
MADEP	Massachusetts Department of Environmental Protection
MDHS	Methods for the Determination of Hazardous Substances
MS	Mass Spectrometry/Spectrometer
NIOSH	National Institute for Occupational Safety and Health
ORD	Office of Research and Development
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic Aromatic Hydrocarbon
PCE	Tetrachloroethene
PDMS	Polydimethylsiloxane Membrane Sampler
QA	Quality Assurance
QC	Quality Control
RBSL	Risk-Based Screening Level
RCRA	Resource Conservation and Recovery Act
RSD	Relative Standard Deviation
SD	Standard Deviation
SOP	Standard Operating Procedure
SSV	Safe Sample Volume
SVOC	Semi-volatile Organic Compound
TCE	Trichloroethene
TIC	Tentatively Identified Compound
TMB	Trimethyl Benzene
UR	Uptake Rate
VI	Vapor Intrusion
VOC	Volatile Organic Compound

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As the technology and science advances, interested parties should further consult the body of literature and experience that constitutes the state of the art for passive samplers. For additional information, interested parties may also contact EPA ORD/NRMRL/ETSC:

Dr. John McKernan, Director
 U.S. EPA Engineering Technical Support Center
 26 W. Martin Luther King Drive, Mail Code-190
 Cincinnati, OH 45268
 513-569-7415

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APPENDIX A: RESEARCH ON PASSIVE SAMPLERS

A.1 Introduction

Passive samplers have been used extensively for industrial hygiene monitoring (ASTM, 2009a) and a variety of environmental sampling applications (Górecki and Namieśnik, 2002; Seethapathy et al., 2008), but the use of passive sampling for vapor intrusion (VI) investigations involves lower concentrations (ppb instead of ppm), a wider range of conditions (e.g., wind, temperature and humidity for outdoor air samples, which are important for assessing background vapor concentrations), and media that have been less extensively tested (e.g., soil gas monitoring). The application of passive samplers to conditions not normally encountered in industrial hygiene monitoring involves some uncertainties, particularly the accuracy of the uptake rate (Tolnai et al., 2000; Bohlin et al., 2007). To address these uncertainties, recent research has been conducted specifically to address the testing conditions relevant to VI investigations and compare passive sampler performance to methods (e.g., TO-15) that are considered more conventional for VI investigations.

A.2 ESTCP Passive Sampling Research

The Department of Defense Environmental Security Technology Certification Program (ESTCP) and the U.S. Navy sponsored passive sampler testing that included laboratory tests in controlled chambers with a range of temperature, humidity, velocity, concentration, and duration for 10 VOCs spanning a range of properties (vapor pressure, solubility, Henry's Constant, and sorptive affinity), as well as field testing of indoor, outdoor, and soil gas samples (ESTCP, in press, ER0830). This laboratory showed that the uptake rates often change by statistically significant (5% level of significance) amounts in response to the factors tested in the chambers, but not in a consistent or readily predictable way for all combinations of different samplers and chemicals. The indoor air field testing showed that passive samplers can provide similar accuracy and precision

to Summa canisters and TO-15 up to a week's duration for many compound/sampler combinations; however, a low bias was typically observed when the product of the uptake rate and sample duration was greater than the safe sample volume for a particular chemical/sorbent combination, which appeared to be attributable to poor retention. Outdoor air field testing showed mostly results below the detection limit. A breakthrough was achieved in passive soil gas sampling because mathematical modeling and field sampling both showed that passive samplers can be used to quantify soil vapor concentrations provided the uptake rate of the sampler is less than the supply rate of vapors from the surrounding materials to avoid low bias from the starvation effect (McAlary et al., 2014a, 2014b, 2014c). This finding contradicts recent documents (ASTM, 2011a; CalEPA, 2012) that state that passive sampling cannot be used to quantify soil vapor concentrations.

A.3 U.S. EPA (2012) Passive Sampler Research

U.S. EPA (2012) evaluated the performance of Radiello charcoal passive samplers for various VOCs at a range of sampling durations in a test house with chloroform and tetrachloroethene (PCE) VI in Indianapolis. Indoor air VOC concentrations during the test are provided in Table A-1 for chloroform and PCE along with trichloroethene (TCE) and petroleum-related chemicals that were predominantly from outdoor air. Radiello charcoal samplers were selected for the study because the high sampling rates of the radial style sampler provided good sensitivity at these concentrations for the weekly samples. Additionally, the charcoal sorbent cartridge was selected over the thermally desorbable cartridge because of its stronger retention characteristics for the target VOCs and its higher VOC loading capacity, both beneficial attributes for long-term sample exposure. Daily, 2-week, 4-week, 3-month, 6-month, and 1-year sample durations were compared against

concentrations for the same periods built up from weekly measurements, with an accuracy (percent bias) goal of $\pm 30\%$.

Table A-1. VOC Concentration Ranges for U.S. EPA (2012) Based on 371 Weekly Radiellos

Compound	Min.	Mean	Max.	SD
Benzene	0.36	0.80	2.3	0.30
Chloroform	0.06	0.33	4.0	0.42
Hexane	0.23	0.68	2.6	0.38
PCE	0.08	1.10	22.0	2.40
Toluene	0.50	1.80	6.0	1.10
TCE	0.01	0.12	2.7	0.26

Table A-2 and Figure A-1 show the percent bias by duration and VOC detected in indoor air. Percent bias varied by chemical with a general increase with increasing VOC volatility and increasing sample duration. Toluene and PCE met the performance criteria for all durations tested, with mean biases well below 7% except for 21% for PCE at the 1-year sample duration. Hexane performed within bias limits for up to 3 months (with 23% bias), and TCE and benzene performed well up to 1 month (with 19% and 13% bias, respectively). Chloroform, the most volatile chemical tested, did not perform well for sample durations 1 month or longer. Percent biases were positive for all sampling durations significantly different from the 1-week measurements, indicating that the longer duration samples consistently underpredicted results built up from weekly samples, although in many cases this consistent bias was under 30%.

A.4 Research Comparing Passive Samplers with Other Methods

Summa canister sampling using TO-15 (U.S. EPA, 1999a) is considered by many to be a “standard” for VI studies; therefore research comparing the performance of TO-15 to passive sampling methods is of interest in this document. With respect to TO-15, the method defines the single laboratory performance criterion for method TO-15 as a replicate precision within 25% and an audit accuracy “*within 30 percent for concentrations normally expected in contaminated ambient air.*” In contrast, results of interlaboratory comparison tests with method TO-15 suggest that the standard for accuracy is not achieved in practice. A recent TO-15 interlaboratory comparison administered by the commercial standard company, ERA, found the following acceptance ranges for PCE results: 33% to 168% (for a July to September 2009 study) and 56% to 131% (for an October to November 2007 study) (Lutes et al., 2012).

In 2007, a TO-14/TO-15 study conducted by Scott Specialty Gasses noted that values for toluene reported by 12 labs varied from 51 to 290% (Lutes et al., 2012). In a study by Daugherty et al. (2004) comparing four laboratories, one under contract to EPA and three typically used by the Colorado Department of Health, the results for 1,1-DCE in one of the laboratories were more than double the results of the three remaining laboratories.

Results for an intercomparison of 10 laboratories have been presented by Pearson (2005) of the California Air Resources Board. This test was conducted with a real-world ambient air sample collected using a specially designed apparatus that allowed 14 Summa canisters to be sampled in parallel. The results show approximately a 2-times variation across the set of 10 labs for the compounds of interest to this project. It is also interesting to note that the apparent outlier labs were not the same for each compound.

Table A-2. Average Percent Bias from 1-Week Sample Results for Various Radiello Sample Durations (U.S. EPA, 2012)

VOC	Vapor Pressure (mm Hg)	Average Percent Bias (Standard Error) by Sample Duration and Chemical				
		2 Week	1 Month	3 Month	6 Month	1 Year
Chloroform	197	12 (2.0)	31 (6.3)	88 (23)	150 (31)	NA
Benzene	95	8.0 (1.9)	13 (3.0)	33 (5.5)	40 (5.5)	NA
TCE	69	11 (2.0)	19 (3.4)	34 (6.7)	42 (8.4)	NA
Hexane	151	3.1 (1.4)	11 (2.2)	23 (3.7)	32 (4.5)	67 (2.4)
PCE	19	-0.10 (0.84)	-0.50 (1.2)	5.9 (2.0)	2.9 (3.3)	21 (0.77)
Toluene	28	0.40 (0.84)	0.0 (1.2)	2.4 (2.3)	-4.8 (3.1)	0.80 (0.05)

Based on comparison with weekly results, positive numbers indicate negative bias (compared sampler underestimates concentration derived from weekly samples). Highlights indicate cases where average percent bias is ≥ 30 .

Italics indicate statistically significant differences ($P \leq 0.05$) between weekly samples and tested durations.

NA—not enough data for analysis

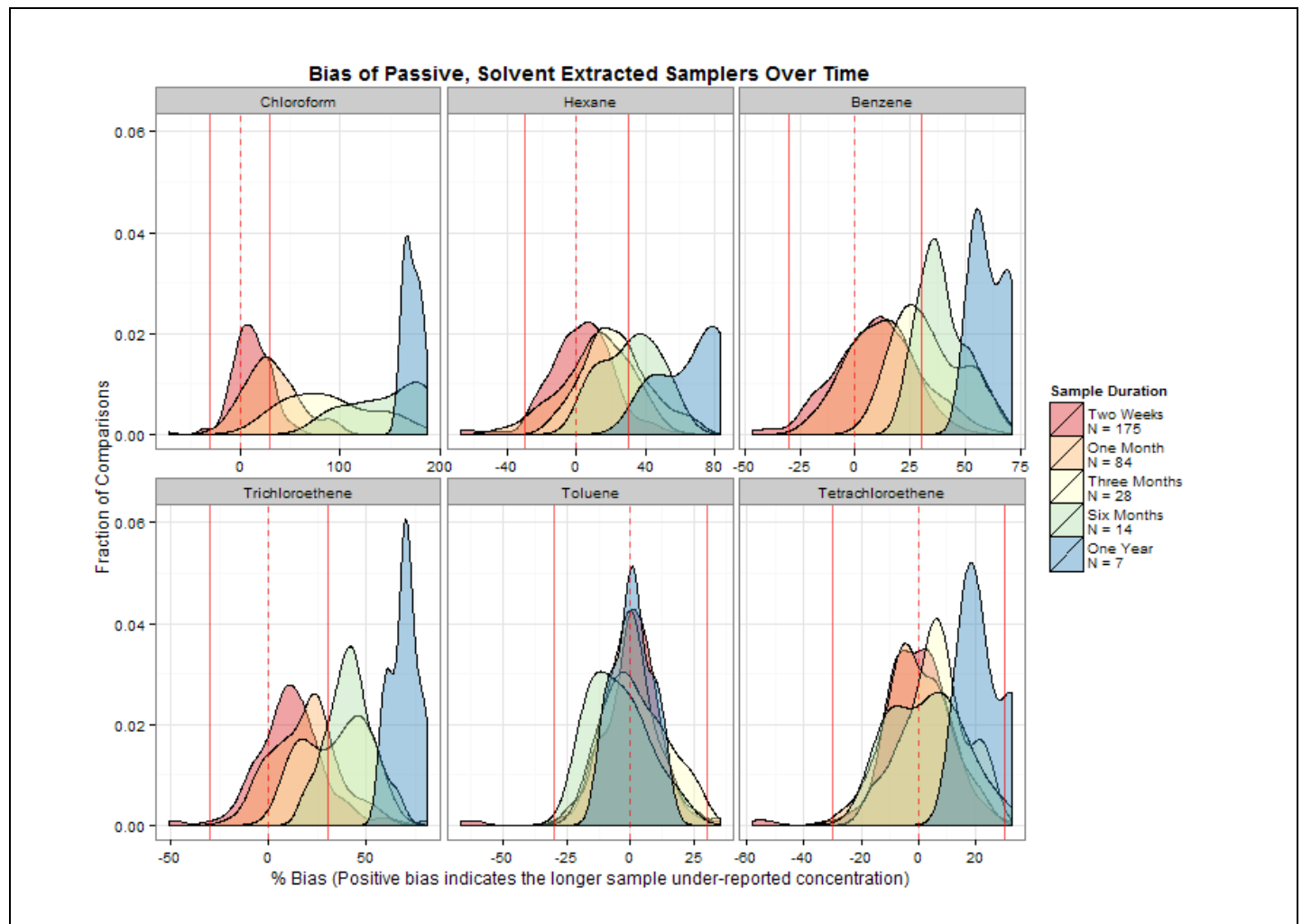


Figure A-1. Percent bias of VOCs by sample duration (U.S. EPA, 2012)

Sweitzer et al. (2006) compared Perkin Elmer passive samplers to TO-15 and on-site GC in ambient sampling. Agreement for BTEX was within 30% of the Summa canister result. Odencrantz et al. (2008) reported comparison between tube-style passive samplers and found that the results were always within two times and that the tube-type samplers were generally lower than the TO-15. Lutes et al. (2010) reported two field studies comparing thermally and solvent extracted Radiello samplers with TO-15 samples collected at the beginning, middle, and end of 2-week-long passive sampling periods. The TO-15 results were generally slightly higher. Good agreement was found for chlorinated solvents and volatile aromatics but poor for polar compounds.

Thoma et al. (2011) compared Perkin-Elmer tube-style samplers with reasonable agreement with an automated GC with $r^2 = 0.86$ for benzene in ambient air. Allen et al. (2007) compared a tube-type passive sampler to an automated field GC and generally found good correlation and the passive concentrations averaging 55 to 90% of the GC values. Mukerjee (2004) compared a 3M OVM 3520 badge sampler with a field GC and found good agreement with the passive sampler 5 to 10% above the field GC values.

Because intermethod results can't be expected to compare better than interlaboratory variability of the single methods compared (general $\pm 30\%$), most of these TO-15 to passive and GC to passive comparisons are considered to be acceptable.

APPENDIX B: AVAILABLE PASSIVE SAMPLING METHODS AND APPLICABILITY

B.1 Introduction

The purpose of this section is to provide an overview of the available international and U.S. methods and standards that may be less familiar to American vapor intrusion (VI) practitioners. International and European standard methods are available for passive sampling that are applicable to indoor air applications for VOCs at low concentrations. The ASTM also has developed passive sampler standard methods. EPA has written that the “*Use of ASTM and ISO (International Standards Organization) standards in lieu of EPA methods is consistent with Public Law 104-113, which mandates that federal agencies use private consensus standards organizations whenever possible to develop standardized methods*” (Lewis, 2000) Note also that method TO-17 is largely developed from and cites United Kingdom (MDHS) methods.

B.2 International Methods and Standards

The available international methods that may be pertinent to VI investigations include the following.

B.2.1 ISO³ Method ISO 16017-2

ISO 16017-2 (ISO, 2003) is applicable “*to a wide range of VOCs including hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, ketones and alcohols ... applicable to the measurement of airborne vapours of VOCs in a mass concentration range of approximately 0.002 mg/m³ to 100 mg/m³ individual organic for an exposure time of 8h or 0.3 µg/m³ to 300 µg/m³ individual organic for an exposure time of four weeks.*” The method is designed for thermal desorption with GC/flame ionization detector (FID) “*or other suitable detector*” analysis. The method provides detailed directions for sampling and analysis. The method is primarily focused on tube-type geometries

and provides uptake rates for a number of single sorbents in tube-type samplers. However, the method is open to other sorbents: “*Equivalent products may be used if they can be shown to lead to the same result.*” Tabulated QC data are provided for recoveries from spiked tubes, precision of analysis, and storage recovery for durations up to 11 months. The precision and accuracy estimates compare quite favorably with those of EPA air sampling methods with overall uncertainty being better than 30%. Table C1 in the standard provides a detailed cross reference between sorbent and suitable analytes.

B.2.2 European Standard⁴ EN 14412 (2004)

EN 14412 (CEN, 2004) provides guidelines for the selection, use, and maintenance of diffusive samplers used to “*analyse gaseous pollutants in indoor air including measurement and planning.*” It covers use of passive media both for indoor air quality sampling and as a personal sampler (defined as “*a device attached to a person that samples air in the breathing zone*”). The standard provides specific provisions for sampler deployment (location, etc.) that are discussed in Section 4 of this EIP and provides an annex table describing the characteristics of various tube, badge, and radial diffusion samplers for benzene and other VOCs as well as formaldehyde.

B.2.3 United Kingdom Method MDHS⁵ 80

MDHS 80 (MDHS, 1995) is designed for passive sampling and analysis for a wide variety of volatile organics (depending on the selected sorbent) and is primarily focused on tube-type samplers that are thermally desorbed. MDHS 80 is designed for concentrations from 1 to 1,000 mg/m³ and relatively shorter exposure times of 30 min to 8 hours. The

³ ISO is a network of national standards bodies. For example, in the United States, ANSI, the American National Standards Institute, is a member.

⁴ European standards are published by the European Committee for Standardization, an international nonprofit that works under a framework from the European Union.

⁵ MDHS = Methods for the Determination of Hazardous Substances. Unlike the ISO and EN methods that must be purchased, the MDHS methods are available for free at <http://www.hse.gov.uk/pubns/mdhs/>.

method refers to published method validation with a Perkin-Elmer diffusive tube. They report a laboratory determination of precision of 12% for benzene, toluene, heptane, xylene, and decane. Storage stability to 11 months is reported. Diffusive uptake rates are provided for the Perkin-Elmer sorbent tubes for a variety of sorbents for 14 hydrocarbons, 19 halogenated hydrocarbons, 11 esters and ethers, and 11 other compounds. A temperature correction of the uptake rate is provided for benzene.

B.2.4 United Kingdom Method MDHS 88

MDHS 88 (MDHS, 1997) is designed for diffusive sampling, followed by solvent extraction and gas chromatography analysis. The method does not specify one sampler geometry, referring instead to “*sorbent separated from ambient air by some form of diffusion resistance.*” The method mentions badge, tube, and radial geometries. Uptake rates are tabulated for four different major manufacturer samplers covering tube, badge, and radial geometries. Uptake rates for the tube and badge samplers are provided for 39 hydrocarbons, 39 halocarbons, 28 esters, 30 alcohols and glycol ethers, 20 ketones, 13 ethers, and 15 miscellaneous compounds. For the radial geometry uptake, rates are provided for 12 hydrocarbons, 6 halocarbons, 4 esters, 11 alcohols/glycol ethers, four ketones, 2 ethers, and one miscellaneous compound. Specific sampling instructions are provided for each of these four types of samplers. An extensive discussion of the various levels of quality for uptake rate determinations is provided. Carbon disulfide desorption is emphasized for nonpolar compounds, and a variety of solvents are discussed for polar compounds. Both GC-FID and GC-MS analytical methods are discussed.

B.2.5 European Standards EN13528

EN13528 is a general standards designation comprising several standards documents. EN13528-1 (CEN, 2002a) is introductory material, primarily definitions of terms and DQOs that will be used in the other parts of EN 13528. The German standard DIN EN 13528-3 (CEN, 2003) has considerable

overlap in content with the other European standards discussed above. Tube, badge, and radial samplers are mentioned with both thermal desorption and solvent extraction. This document does, however, provide some useful additional guidance on outdoor sample placement and operator training. EN13528-2 (CEN, 2002b) focuses on ambient air but also is intended to be relevant to indoor air. This document includes procedures to qualify passive sampling devices based on laboratory or field tests. As such, it is not in and of itself a field sampling method. It notes: “*This standard can encourage the development of new types of diffusive sampler*” in that it provides procedures for sampler evaluation. Detailed instructions are included on how to evaluate passive sampler characteristics including desorption efficiency, effect of air velocity/sampler orientation, storage after sampling, shelf life before sampling, blank values, uncertainty, and uptake rate.

B.2.6 European Standards EN 14662-4, EN 14662-5

EN 14662-4 (CEN, 2005a) is specific to benzene by diffusive sampling with thermal desorption analysis. The target concentration range is 0.5 to 50 $\mu\text{g}/\text{m}^3$ with a typical sampling period of 14 days. Uptake rates are provided for three sorbents in tube-type geometries with varying exposure times and estimates of standard deviation in uptake rate. An extremely detailed uncertainty propagation analysis is developed in an appendix leading to a conclusion that the combined relative uncertainty, including both sampling and analysis, will be 6.7%. An interlaboratory comparison of five laboratories is provided using six different test atmospheres, including two derived from ambient air. The resulting interlaboratory uncertainty for these measurements ranged from 3.1 to 9.0%. It should be noted that these interlaboratory results are better than those commonly reported for Summa canister methods, which typically show a range of a factor of 2 to 5 between the minimum and maximum of the study acceptance window, or between the lowest and highest lab in the study (Lutes et al., 2012; Pearson, 2005, Daugherty et al., 2004). EN14662-5 (CEN, 2005b) is also specific to benzene but is relatively

unique among the EN methods in that it specifies a charcoal passive sampler with solvent desorption for longer-term sampling.

B.3 U.S. Methods and Standards

In the United States, the most comprehensive guidance published for diffusive sampling is from ASTM, although EPA has also developed some methods documents.

B.3.1 ASTM Method D6196-03

ASTM D6196-3 (ASTM, 2009b) covers ambient and indoor VOC sampling using *either* pumped or diffusive methods. Both tube and radial geometries of passive sampling are specifically discussed. A large range of VOCs with boiling points from 0 to 400°C is encompassed. The method, however, suggests that radial samplers should only be used for compounds with an equal or lower volatility than benzene. For axial samplers, it states a range of 0.3 mg/m³ to 300 mg/m³ for exposure times of 4 weeks. Typical background artifact levels are provided for various sorbent types. The method discusses the use of two sorbents in separate devices used in parallel to extend the range of compounds monitored. Analysis under this method is by thermal desorption with GC-ECD (electron capture detector), GC-FID, or GC/MS. Humidity up to 95% in the sampling area can be handled with hydrophobic sorbents, but the method advises caution for humidity greater than 65% with less hydrophobic, strong sorbents. Options specified to manage this problem include dry purging, use of a membrane that excludes water from the diffusive sampler, or reduction of the time of diffusive sampling. Diffusive sampling rates (uptake rates) are tabulated with a number of different sorbents in axial diffusion tubes for 29 hydrocarbons, 23 halogenated hydrocarbons, 22 esters/glycol ethers, 9 ethers, 7 alcohols, and 13 miscellaneous compounds based on an 8-hour exposure period. Sampling rates for axial tube samplers and 2- and 4-week exposures are provided for benzene, toluene, ethylbenzene, and xylenes (BTEX) and a few other hydrocarbons. The method provides sampling rates for radial diffusive

samplers for 22 compounds and 1-week exposures. Sampling periods from 1 to 4 weeks are recommended for indoor and ambient monitoring.

B.3.2 ASTM Method D6306-10

ASTM D6306-10 (ASTM, 2010) focuses on placing and using diffusive samplers in the indoor environment. However, information is provided about practical matters such as how to label samples without contaminating them and recording site-specific information about the sample. Monitoring placements are specified for both personal and area sampling.

B.3.3 ASTM Method D6246-08

ASTM D6246-08 (ASTM, 2013) provides procedures for evaluating the performance of diffusive samplers through chamber experiments. It is focused on short-duration exposure periods of 4 to 12 hours and thus appears to be primarily focused on samplers used in workplace applications.

B.3.4 ANSI/ISEA Standard 104-1998 (R2009)

A passive sampler standard is also available from the American National Standards Institute Inc./International Safety Equipment Association (ANSI/ISEA 104-1998 [R2009]; ANSI/ISEA, 1998). This standard was developed for occupational exposures and covers both direct on-site reading devices and samplers and laboratory analysis. It focuses on chamber tests of passive sampler performance over durations of 15 min to 8 hours. It describes multifactorial tests that can be done to evaluate sampler performance at various temperatures, humidities, face velocities, orientations, and contaminant concentrations (both constant and transient peaks). Evaluation approaches for storage time, shelf life, sorbent reuse, and interferences are also provided.

There are also several U.S. government (and state) methods available, including U.S. EPA's Procedure for Placement of Stationary Passive Samplers in Indoor Environments (Appendix C-2 in U.S. EPA's *Compendium of Methods for the Determination of Air*

Pollutants in Indoor Air [U.S. EPA, 1990]). This document refers to sampling durations from 3 days to 1 year. Through a cooperative agreement, Arizona State University and EPA's Office of Research and Development prepared a standard operating procedure (SOP) for passive sampling for VOCs at indoor and outdoor sites for benzene, toluene, and TCE (U.S. EPA, 1997). The SOP is specific to activated charcoal with the 3M OVM 3500 sampler. It provides some detailed guidance for sampler location and how to screen for and evaluate problems such as fallen samplers. U.S. EPA Region 4 has also developed passive sampling SOPs for the analysis of VOCs for the EPA School Air Toxics Program (U.S. EPA, 2009a, 2009b).

B.3.5 Massachusetts Department of Environmental Protection Indoor Air Sampling and Evaluation Guide

This MADEP guidance (MADEP, 2002) discusses applications of passive badges for up to 3 weeks using a charcoal adsorbent. They indicate that *“In general, MADEP has found good agreement between results from badges and pumped samples, and good precision.”* They discuss use of passive sampling as part of a *“two-component sampling period involving sub-chronic and chronic sampling durations”* with the passive samplers used for the chronic sampling component.

B.4 Other Applications

Passive samplers have been applied not only to the VOCs commonly measured by methods TO-15 and TO-17 (U.S. EPA, 1999a, 1999b) at VI sites, but also to a wider range of other volatile and semi-volatile chemicals:

- formaldehyde and other aldehydes in indoor air (EPA Method IP-6C; U.S. EPA, 1990; SKC, 2004)
- vapor-phase mercury in workplace atmospheres, OSHA method ID-140⁶ and

longer duration sampling applications up to months (Brumbaugh et al., 2000)

- pesticides (Jaward et al., 2004a), polycyclic **aromatic hydrocarbons** (PAHs), and other semi-volatiles (Jaward et al., 2004b, Bartkow et al., 2004) in ambient air
- nicotine as a marker for tobacco smoking (see <http://www.epa.gov/ncea/ets/pdfs/etsch3.pdf>)
- tracers used for determining air exchange rates (Dietz and Cote, 1982; EPA Method IP-4A, U.S. EPA, 1989)

Passive samplers have also been used to measure VOC vapors in soil gas in both a semiquantitative (EMFLUX, Petrex, Gore, and Beacon) and quantitative (McAlary et al., 2014a, 2014b, 2014c) fashion. These studies have tried to tie in the relationship between mass and concentration (Odencrantz and O'Neil, 2009) or calculate starvation (Hodny et al., 2009). McAlary et al. (2014a, 2014b, 2014c) showed that the key is to use a sampler with an uptake rate similar to or lower than the diffusive supply rate of vapors to the face of the sampler so that the sampler uptake is the rate-limiting step. In cases where the uptake rate is not the rate-limiting step, a low bias from the starvation effect is likely. A detailed description of subsurface applications of passive sampling technology is beyond the scope of this paper, but some important aspects of using passive samplers for soil gas are discussed in ESTCP (in press).

⁶ <http://www.osha.gov/dts/sltc/methods/inorganic/id140/id140.html>

APPENDIX C: ANALYTICAL LABORATORY QA/QC

Analytical test methods and performance requirements for a variety of passive samplers and VOCs are detailed in ASTM D6196-3 (2009b), EN 13528-2 (CEN, 2002a, 2002b), ISO 16017-2 (2003), ISO 16200-2 (2000),⁷ EN 14662-4 (CEN, 2005a) and EN 14662-5 (CEN, 2005b). These standards provide a comprehensive overview of the sampling and analytical performance requirements for passive samplers; however, the laboratory may determine specific analytical parameters, detailed protocols for QC samples, and corresponding QC acceptance criteria. Therefore, it is important to select a laboratory that is knowledgeable and experienced with passive sampling. This appendix provides a comprehensive summary of analytical and laboratory quality considerations unique to the analysis and data interpretation of passive samplers for long-term environmental measurements, including possible enhancements to conventional industrial hygiene methods to meet DQOs of vapor intrusion investigations.

C.1 Selectivity—Analytical Instrumentation: GC/FID vs. GC/MS

Although the ISO and EN standards do not specify instrument configuration details, the U.S. industrial hygiene methods for workplace monitoring using passive charcoal samplers rely on an FID for compound detection. These OSHA methods are tailored for a single chemical or a limited set of chemicals based on the solvents or materials used in the workplace. In these circumstances, in which the target compound list is limited with little concern for interfering compounds present at similar levels, a nonspecific detector like the FID meets the DQO. However, when deploying charcoal samplers in indoor or outdoor environments, the samplers are exposed to a complex mixture of chemicals of which the target compounds are typically present at low

concentrations. In this situation, the identification and quantification of the target compounds benefit from the selectivity of the mass spectrometer (MS). Although the extraction solvent for charcoal samplers, carbon disulfide, can interfere with the detection of compounds during its elution, negative impacts can be minimized through proper configuration of the GC/MS parameters. In the case of thermally desorbable sorbents, the MS is routinely applied for environmental analysis following EPA Method TO-17 (U.S. EPA, 1999b). The MS also provides additional sample characterization by allowing for tentative compound identification and concentration estimation of uncalibrated peaks.

C.2 Measurement Range

The useful VOC concentration range measured with a passive sorbent sampler is determined by both the sorbent characteristics and the analytical method. The upper limit is determined by the sorptive capacity of the sorbent and the linear range of the analytical instrumentation. Dilution of the sample can extend the analytical measurement range. For charcoal-based samples, the solvent extract can be diluted prior to injection. In the case of thermally desorbed samplers, dilution is achieved by adjusting instrument split flows to reduce the mass injected onto the GC/MS. The lower measurement limit is set by the blank levels of VOCs from the sampler and/or preparation steps (C.3) as well as the analytical sensitivity of the laboratory equipment. Detector noise levels typically define the lowest possible calibration level.

C.3 Method Background—Sorbent Artifacts, Solvent Impurities, and Common Lab Contaminants

The blank values originating from the sorbent material and laboratory handling and preparation can be significant for passive sorbent samplers, and it is

⁷ Although ISO 16200-2 is written for 8-hour workplace monitoring, this standard provides detail on solvent-extracted

passive samplers, including detail on the various types available and sampling rates.

critical for the laboratory to minimize and monitor these blank levels to ensure DQOs are met. Prior to using any sorbent or solvent, the batch should be verified as clean to the required levels. Carbon disulfide, the extraction solvent routinely used for charcoal extraction, commonly contains benzene as an impurity. Although this solvent can be purchased with a “low benzene” specification, each lot should be verified prior to use. Additionally, the handling of sorbents during preparation can also result in elevated blank levels. To minimize exposure to lab contaminants, the sorbent transfer from the sampler or storage vial to a thermal desorption tube or extraction vial should be conducted in a solvent-free environment away from any source of VOCs.

C.4 Laboratory QC Elements

Development of laboratory methods requires defining analytical measurement objectives, frequency, and measurement performance criteria. NIOSH and OSHA charcoal sorbent methods, EPA SW-846 8000 series, and EPA Method TO-17 are resources for applicable quality elements and acceptance criteria for passive sampler analysis. Laboratory SOPs should address the minimum QC elements listed below including not only the frequency and acceptance criteria, but also corrective action for noncompliance as well.

C.4.1 Initial Calibration

During initial calibration the analyst determines the relationship between concentration and detector response and defines the range in which relationship is linear. Internal standard calibration techniques are recommended for solvent extraction and thermal desorption GC/MS techniques to adjust for variations in the sample injection volume as well as variations in the instrument response. Linearity can be established by generating relative response factors at each level and evaluating % relative standard deviation (RSD) against an acceptance criterion (EPA TO-17) or by evaluating the fit of the response curve as described in the NIOSH and OSHA methods. General guidelines for initial calibrations are described

in detail in EPA SW-846 Method 8000C (U.S. EPA, 2003).

C.4.2 Reporting Limit

The generic term *reporting limit* is used to denote the lowest concentration that can be reliably measured by the method. A detailed discussion of the technical approaches to determine reporting limits is outside the scope of this discussion and can be found elsewhere (e.g., OSHA, 2008). Regardless of the specific procedure used to establish the reporting limit, in each case, the reporting limit must be supported by the lowest concentration of the calibration curve and also must take into account method background factors (C.3). Artifacts from the sorbent material, reagents, and preparation steps may translate into a reporting limit several times higher than the lowest calibration level.

C.4.3 Sample Preparation QC Samples

A laboratory blank and laboratory control spike (LCS) should be prepared with each preparation batch to monitor blank levels and recoveries. As part of the initial method validation, desorption efficiencies should be determined for each target compound. Desorption efficiencies can be verified with each preparation batch by preparing an LCS spiked with representative target compounds. Details regarding desorption efficiency studies and recommended frequency are outlined in the ISO and EN standards listed in **Appendix B** as well as in the NIOSH and OSHA reference methods.

C.4.4 Sample Duplicates and/or LCS Duplicates

With sorbent samples, duplicate samples cannot easily be prepared because the entire sorbent bed is consumed in the preparation step. As such, sample duplicates are typically a replicate injection of the sample extract or analysis or the recollected thermal desorption sample. Although these replicate injections provide instrument precision, method precision that measures both preparation and analysis steps can be measured by preparing and analyzing two LCS samples in each preparation batch.

C.4.5 Sample Preparation Surrogate Spikes

Although surrogates are not routinely described in NIOSH or OSHA charcoal sorbent methods, the addition of surrogates to the sorbent bed prior to the extraction step provides verification of the extraction efficiency and can identify factors affecting measurement accuracy. For example, the commonly used solvent for extraction, carbon disulfide, can evaporate during extract storage, thereby concentrating the sample and altering the target compound concentration. In lieu of a surrogate or in addition to a surrogate, an internal standard can be added to the charcoal bed prior to extraction. This internal standard procedure is described in the Radiello user manual (Radiello, 2013) and EN 14662-5 (CEN, 2005b). Any change in extract volume due to evaporation affects both the internal standard and target compound concentration similarly, minimizing any bias in the measured compound concentration.

C.5 Laboratory Identification and Documentation of Analytical Interferences

The identification and documentation of analytical interferences can be critical to properly interpret the reported concentrations for passive sorbent samplers. Although efforts can be made in the project planning stage to properly select samplers and parameters for anticipated field conditions, the conditions of high humidity and the presence of high VOC concentrations should be noted in the report.

C.5.1 Water (High Humidity)

High mass loading of water on sorbents can occur in cases when samplers are exposed to prolonged periods of high humidity. Strong sorbents such as charcoal or molecular sieve resins are most susceptible to adsorbing large amounts of water, affecting both the analytical and sampler performance. In terms of analytical performance, excess water is evident in the solvent extraction step as a separate layer in the carbon disulfide extract, which can result in partitioning of polar compounds to the water phase. In the case of thermal desorption,

excess moisture can affect both the chromatography and the MS detector response. Retention times of the early eluting peak may shift, the baseline of the total ion chromatogram may be elevated in the initial stages of the GC run, and the internal standard responses may show low recovery.

To some degree, the laboratory can employ measures to mitigate the effects of moisture during preparation, thereby minimizing the impact on data quality. In the case of charcoal sorbents, a desorption solvent modifier such as dimethylformamide can be added to carbon disulfide to dissolve the water layer (ISO, 2000). When samplers are prepared using thermal desorption, the laboratory can use dry-purge techniques to remove excess water prior to analysis (ISO, 2003). To assist in the evaluation and interpretation of the test results (Section 5.2.8), the laboratory should document if the effects of water are observed during sample preparation and analysis.

C.5.2 High Concentration Target or Non-target VOC on Trace-Level Measurements

High mass loadings of VOCs measured on passive sorbent samplers can affect both sampler performance (C.8) and analytical reporting limits. Diluting the sample extract or increasing the split of the thermal desorption unit will keep target VOCs within the calibration range and/or minimize the impact of interfering non-target peaks on the analytical system. Although, in theory, undiluted or lesser dilutions can be analyzed to provide the lowest reporting limits for each target VOC, in practice, contamination of the analytical unit and subsequent issues with carryover limit the effectiveness of this approach. High mass loadings of target and non-target VOCs measured on the samplers should be documented in the test report.

C.6 Reporting Tentatively Identified Compounds—Mass Adsorbed on Sorbent Bed vs. Calculated Air Concentrations

Using an MS for sample analysis allows the lab to report tentative identifications and semiquantitative

mass concentrations for uncalibrated, non-target compounds. Although tentatively identified compounds (TICs) can be important for site characterization and also provide the data user direct information regarding total mass adsorbed on the sampler, calculating corresponding air concentrations can be difficult. In the absence of published uptake rates for TIC compounds, estimated rates can be applied to calculate an approximate air concentration. However, this would exacerbate the uncertainty in TIC quantitation, which is already approximate because of the use of generic response factors.

C.7 Concentration Correction Calculations

C.7.1 Adjustments for Field Conditions—Temperature, Pressure, and Face Velocity

The diffusive uptake rate in the field can vary as a function of site temperature and pressure. To report mass concentrations at specified conditions, such as normal ambient temperature and pressure, the following equation can be used (ASTM, 2009b):

$$Q_T = Q_{298} \times (T/298)^{1.5} \times (101/P)$$

where

Q_T = uptake rate at the field temperature T (in Kelvin)

Q_{298} = reference uptake rate at 25°C (298 K) and 101 kPa

T = average field temperature in Kelvin

P = average barometric pressure at field site (kPa)

The laboratory should document whether uptake rates have been corrected for temperature and pressure in the test report.

In addition to temperature and pressure adjustments, conditions of low face velocity commonly encountered in indoor air environments can require correction of the sampling rate. In the case of SKC badges, sampling rates have been determined in the laboratory under face velocity conditions of <5 cm/s

to apply to samplers deployed in homes. These indoor air rates are significantly lower than uptake rates generated under the standard validation conditions of 10 to 200 cm/s (SKC, 2008).

C.7.2 Blank Correction

The European and ISO standards, as well as the U.S. industrial hygiene methods, generally require subtraction of the blank tube analyte mass from the sample analyte mass to calculate the concentration in the sampled air. Because blank subtraction is not allowed in EPA environmental monitoring methods as stated in EPA SW-846 8000C (U.S. EPA, 2003), labs applying EPA method QC criteria to the analysis of passive samplers may report sample concentrations without blank correction. The test report should clearly outline the procedure followed by the laboratory.

C.8 Data Qualifiers

1. Denote Level of Validation Associated with Uptake Rate—Estimated vs. Validated.

Several levels of evaluation of uptake rates are used to determine sample analyte concentrations that are outlined in EN 838 (CEN, 1995), MDHS 27 (MDHS, 1994), and NIOSH (Harper and Guild, 1996; Cassinelli et al., 1987). Uptake rates calibrated by controlled chamber tests or by an independent validated method in the field are assigned a partial or full evaluation level. If calibrated rates are not available, sampling rates can be calculated using published or estimated diffusion coefficients and the geometric constant of the diffusive sampler. In the case of permeation samplers, uptake rates can be calculated using the retention time of the VOC on a nonpolar phase column (Seethapathy and Gorecki, 2010a). If concentrations are determined using calculated uptake rates, the associated results should be flagged with an appropriate data qualifier.

2. Denote Sample Duration Exceeding Manufacturer's Recommended Maximum and/or Situations in Which the Uptake Rate Times the Sample Duration Exceed the Safe Sampling Volume for a Given Chemical

Weakly adsorbed chemicals can reverse diffusion under prolonged exposure. If the manufacturer's recommended maximum sampling duration is exceeded for specific sampler/sorbent combination, then data should be used with caution. In general, low bias due to back-diffusion can only be confirmed and quantified by comparing to field verification samples. If a low bias is indicated, either the passive sampler result is flagged as an estimated value or the uptake rate is adjusted for the associated samples to account for field-specific conditions. This adjustment should be documented in the test report.

3. Flag Affected Data in Which Interferences Result in Low Bias

Evidence of excess water adsorption on the sorbent sampler noted by the laboratory and/or documented in the field should alert the data user to potential low bias for specific compounds depending on the sorbent used and the sampler storage conditions. For example, polar compounds such as acetone and methyl ethyl ketone can exhibit low recovery from charcoal sorbents exacerbated by sample storage at room temperature (3M, 1996; Harper, 2000).

In addition, interferences noted by the laboratory and also identified by inspection of the chromatogram can result in low bias for weakly retained VOCs when using non-ideal sorbents. Common indoor air contaminants from household products and activities such as limonene and pinene can compete for sorption sites and displace more weakly adsorbed target VOCs. Additionally, high concentrations of target VOCs can saturate the sampler and exceed the capacity of the media. This oversampling is most common when using thermal desorbable sorbents due to their relatively low surface area as compared with charcoal-based sorbents. Comparison of the total mass adsorbed to the sorptive capacity of the media can assist in evaluating and interpreting the results.

Although suspect results can be flagged, field verification samples are useful to quantify the impact of the interference on the reported concentration. Corrections for water and coexisting chemicals may be possible if the passive samples collected for the study exhibit similar interferences. Corrections are not recommended if the sampler was overloaded and exceeded the sorptive capacity. However, in many such cases a flagging convention (e.g., "J" flags) can be used to convey to the decision maker the likely direction of any bias. For example, sampler overloading will lead to underestimation of target compounds, and in many cases this will not affect site management because overloaded samples also tend to be well above risk-based screening levels.

4. Flag Results in Which Measured Adsorbed Mass is Less than a Defined Factor Above the Field Blank

Detections of VOCs in the trip blank are not unexpected when evaluating down to nanogram levels on the thermal desorption sorbent samplers. The general guideline listed in ISO 16017-2 and ASTM D6196 is that the analyte peak in the field blank should be less than 10% of the target peak area measured in the sample. If this criterion is not met, the associated sample data should be flagged to indicate high bias in the test report.



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