USER GUIDE

Demonstration of a Long-Term Sampling and Novel Analysis Approach for Distinguishing Sources of Volatile Organic Compounds in Indoor Air

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Assessing vapor intrusion (VI) from volatile and semi-volatile organic compounds (VOCs and SVOCs) in indoor air environments is challenging, and approaches continue to evolve both within regulatory agencies and by professionals characterizing exposure pathways. At least 2,151 Department of Defense (DoD) sites have costly groundwater plumes where remediation is driven by chlorinated aliphatic hydrocarbons.

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1.0 OVERVIEW

Assessing vapor intrusion (VI) from volatile and semi-volatile organic compounds (VOCs and SVOCs) in indoor air environments is challenging, and approaches continue to evolve both within regulatory agencies and by professionals characterizing exposure pathways. At least 2,151 Department of Defense (DoD) sites have costly groundwater plumes where remediation is driven by chlorinated aliphatic hydrocarbons.

A major challenge in assessing VI is accurately characterizing the airborne VOCs that are representative of occupant exposures. Samples collected in homes and buildings must be representative of long-term human exposures, while also being cost-effective and reproducible. There is a regulatory and stakeholder drive for increasing numbers of sampling rounds driven by the concern with temporal variability.

Routinely over the past decade, 8 to 24-h samples collected in canisters have been the standard to assess if indoor air has been contaminated by VI (US EPA TO-15). To a lesser extent, 1 to 2-week sampling has been conducted using passive sorbent diffusion samplers (US EPA TO-17). A current limitation of traditional canister sampling is that the available controllers only provide reliable sampling for 24 hours, which may not be representative of longer-term exposures without multiple sampling events. **Table 1** presents a summary of the key advantages and disadvantages of each sampling approach. **Table 2** presents key considerations for these approaches.

A new capillary canister sampling method captures the advantages of both canisters and sorbent samplers without their limitation by allowing for longer term (1-3 weeks) sample collection and characterization of average VOCs in buildings at risk for VI. The approach is robust, comparable in cost or less expensive than current methods, allows for long-term sample collection, and requires one sample to capture the full range of analytes and concentrations of interest. Implementation of the capillary flow controller with a canister allows for their use for long durations—weeks as opposed to hours.

The Aura^{TM} personal air sampler is a newly marketed technology that has been designed to meet Occupational Safety and Health Administration (OSHA) and National Institute for Safety and Health (NIOSH) requirements for occupational and environmental sampling. The capillary tube, used to control the flow of air, is a variation on a sharp edge orifice flow controller (**Figure 1**). It essentially controls the velocity of the air as a function of the tube diameter and length. The controller is lightweight, easy to use with a Swagelok miniature quick-connect that starts and stops flow, requires no field calibration, and is quiet because it does not require a pump. Sampling does not require a power source and analysis does not require solvent desorption. This new technology has been researched for well over a decade and was recently commercialized by Restek, Inc.

Table 1. Advantages and Disadvantages of VOC Sampling Approaches

Factor	Canisters	Solid Sorbents
Ease of use in the field	Easy	Easy
Sampling duration	Diaphragm controller - few minutes to 24 hrs Capillary flow controller - minutes to weeks	Hours to 2 Weeks
Ease of analysis	Easy – can analyze multiple samples from single canister; can analyze multiple analytes from single canister	Requires desorption from sorbent; one sample collection may utilize multiple sorbents (chemical-dependent) that are analyzed separately
Range of contaminants	Generally C1 to C12	Limited by type of sorbent used
Impact of environmental conditions	Limited impact of humidity, temperature, face velocity, or concentration	Can be affected by humidity, temperature, face velocity, and concentration
Cost drivers	Shipping due to canister size	Sorbent
Key limitations	Shipping costs Potential to leak in the field	May require multiple sorbents for diverse analytes, reverse diffusion

Table 2. Key Sampling Considerations

Factors	Canisters	Solid Sorbents
Media Type	Whole air	Adsorption
Sensitivity	ppb	ppm
Technique	Passive	Active
Sample Type	Grab or integrated	Integrated
Analyte	Wide range of VOCs	Sorbent specific
Applications	IAQ, emergency response, IH	IAQ, IH
Durability	Reusable	One time use
Inertness	Excellent	Fair
Stability	30-day	Varies by analyte
Sample Volume	0.4-6 L	Varies by analyte
Sampling Time	Minutes to days	Minutes to hours

Adopted from Restek Technical Guide: A Guide to Whole Air Canister Sampling (2010)

Figure 1. Capillary flow controller attached to a 6-L SiloCan.

The Aura™ passively collects a whole-air sample over a 14-day period in a cleaned canister. Each Aura™ is manufactured pre-calibrated with a starting flow rate that is approximately 0.11 mL/min. The Aura™ will maintain a near-constant flow (i.e., the ending flow will be within 10% of the starting flow) throughout the sampling duration.

2.0 CANISTER SAMPLING PROCEDURE WITH AURA™ FLOW CONTROLLER

The general procedure for collecting VI exposure assessment samples using canisters and the Aura™ flow controller is as follows:

1. Determine the number of samples to be collected.
2. Contact a commercial laboratory to acquire canisters, flow controllers, connectors, and to plan sample analyses. Assure that canisters have been properly cleaned.
3. Collect additional items needed for field sampling.
4. Identify and label canisters using sample information.
5. Place canisters in pre-determined sampling location.
6. Attach the flow controller to the canister and open the valve (Note: If the canister does not have a valve then the sampling start time begins when the flow controller is attached).
7. Note atmospheric pressure, temperature, humidity, wind direction, and elevation.
8. Collect sample for predetermined sampling duration (**Table 3**).
9. Remove the flow controller from the canister when sampling is complete, and cap the canister or close the canister's valve to prevent sample loss.
10. Ship canisters to lab for analysis.
11. Assure laboratory is following appropriate standard analytical methods.

Table 3. Typical Sample Time Based On Canister Size and Capillary Controller Flow Rate

Canister Size	400 Milliliter	1 Liter	6 Liter	15 Liter
Sample Time	Up to 24 hours	Up to 60 hours	Up to 14 days	Up to 30 days

The following equipment and information is necessary to collect a canister sampler:

- Many canisters will be outfitted with Swagelok stem (male) miniature quick connect (part # SS-QM2-D-400)
    - If a quick connect is not present, two wrenches are needed to attach the flow controller (size of wrenches are typically 9/16 and 7/16)
- Flow controllers: Aura™ flow controller with Swagelok body miniature quick-connect (part # SS-QM2-B-200)
- Chain of Custody forms from the analytical lab must be available to submit with the samples.
- A temperature and relative humidity meter used on site to measure environmental conditions inside the building
- It is important to maintain a detailed field log book (maintaining outdoor records of meteorological data, activity in the building, indoor temperature and % RH, indoor sources of VOCs, etc)

The Aura™ will be attached to the canister in the field. This requires connecting a sample line onto a 1/8-inch Swagelok miniature quick connect, which, in turn, will be connected to the canister stem. Depending on the objective of sampling, the sampler can either be placed on person or as an area sample.

Due to the design of the connection between the canister and the capillary controller, samples will be collected immediately following the attachment of the quick connect or after rotating the valve.

Collecting a Grab Sample:

1. Remove protective cap from the canister.
2. Use field vacuum gauge to record initial pressure of canister (P_o).
3. Turn the valve counter-clockwise to the open position. A hissing sound should ensue as the atmospheric air enters the canister.
4. When the hissing is no longer audible (15 to 30 seconds depending upon the size of the canister), close the canister valve by turning it clockwise. DO NOT OVERTIGHTEN – Snug hand-tight is satisfactory.
5. Replace cap.

Collecting a Time-Weighted Average Sample:

1. Remove protective cap from canister quick-connect.
2. Use field vacuum gauge to record initial pressure of canister (Pi).
3. If the canister is not fitted with a quick-connect, use 7/16-inch wrenches to attach flow of the capillary controller. If a quick-connect is on the canister, attach the flow controller by placing the Swagelok female quick connect (on the Aura), on the Swagelok male quick-connect (on the canister) (**Figure 2a**), while applying moderate pressure, pull up on the Swagelok female quick-connect (**Figure 2b**). The two should snap together (**Figure 2c**).
4. Place the canister in the desired location and turn the valve counter-clockwise until the valve is fully open. The canister pressure gauge should read approximately -30” Hg.
5. Record start time and necessary meteorological data (atmospheric pressure, temperature, humidity, wind direction, and elevation).
6. After the end of the sampling period, if the canister has a shut off valve, turn the valve clockwise to close. DO NOT OVERTIGHTEN. Snug hand-tight is satisfactory. Once the valve is closed, then disconnect the Aura™ from the canister.
7. Record the sample pressure (P_s), and record the end time.
8. Complete the Chain of Custody form for the laboratory where the samples will be analyzed.

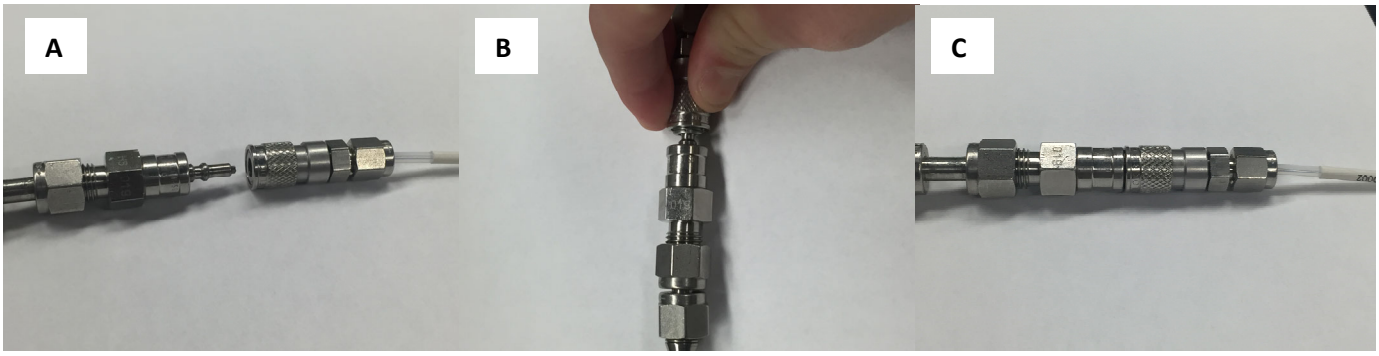

Figure 2. (a) Swagelok female quick-connect (on the Aura (right)) and the Swagelok male quick-connect (on the canister (left)); (b) Swagelok being pulled open for connection; (c) Connected Aura flow controller to a canister.

At the end of the sampling period, the Aura™ is disconnected from the canister. The sample pressure and end time are recorded. The valve is turned clockwise to close. It is critical to NOT OVER TIGHTEN. Snug hand-tight is satisfactory. The canister should be capped, or the valve should be closed, to prevent sample mishandling. The OPEN/CLOSE valve ensures sample preservation and almost eliminates sample mishandling.

Once air samples are collected, they can be stored for up to 30 days without significantly decaying (USEPA TO15), although, this is compound-specific and should not be the rule of thumb. Samples should be sent to the lab for analysis immediately. Compounds may react with another in the canister and produce daughter/intermediate compounds. Becoming familiar with the analytes of concern is important for proper sample handling and storage.

The shipping container(s) that the lab supplied to transport the canisters can also be used to return the canisters and supplies. The canisters are robust; however, the valves can be damaged if the canisters are not packaged properly.

A cardboard box with bubble wrap around each canister or foam is sufficient for shipping through the U.S. mail (or UPS or Fed Ex). If possible, reuse the shipping container(s) from the laboratory to return for analysis. The canisters do not need to be refrigerated. The shipment should be insured for the value of the canisters.

3.0 FREQUENTLY ASKED QUESTIONS

1. **Will the capillary-controlled system meet regulatory requirements for vapor intrusion investigations?**

   - From a regulatory perspective, canister samplers have been the gold standard for VI sampling. The capillary flow controller now simply provides for a longer-term canister sample.

2. **What if the pressure when starting is not at -30" Hg?**

   - The canister is not fit to sample and should be returned to the laboratory.

3. **Should the canister hiss when I start to sample?**

   - No. The canister should only hiss when you are taking a grab sample, not a longer-term sample using the capillary flow controller. If the canister starts to hiss after opening the valve, and has a flow controller attached, please contact your laboratory.

4. **What if I don't have access to a barometer or thermometer in the field?**

   If you do not have physical access to a barometer or thermometer in the field, do not worry. You may obtain temperature and barometric pressure from the nearest National Weather Service station via a smart device. Adjustments might need to be made in barometric pressure if there is an elevation difference between the Nation Weather Service station and the sampling point.

5. **Do I need to record environmental parameters during the entire sample collection period, or just at the beginning and end of the 14-day sample period?**

   - Environmental parameters, such as pressure, temperature, and humidity, should be measured directly in the field for the duration of the sampling. In addition, outdoor meteorological conditions should be measured or obtained from a local weather station. Typically weather underground is used (https://www.wunderground.com/).

6. **How far should I fill the canister when using a capillary flow controller before I stop sampling?**

   - Canisters should only be filled to 50% of the MAXIMUM volume. However, filling to 35% is preferred.

7. Why did my canister fill completely during the allotted amount of time?

- A number of problems could cause this, such as damage to the flow controller or how the flow controller was connected to the canister. Contact the laboratory which supplied you the canister and flow controller.

8. Why didn't my canister fill during the allotted amount of time?

- The valve was not opened at the start of the sampling.
- Debris could have clogged the flow controller.
- The flow controller may be crushed or otherwise damaged.

9. Do I have to refrigerate my samples after I take them?

- No, samples are preserved at room temperature. Pressurizing your sample after collection preserves them and is recommended before shipping.

10. What happens if I return my canister to the laboratory under vacuum?

- This is not a problem. It is expected to be under some vacuum because it should not be filled more than 50%. The laboratory will check the vacuum upon receipt of the canisters.

11. Can I modify the laboratory's analyte list?

- Yes. You can modify the list as needed; shorten or even add to the compound list. Before modifying the compound list, please contact the laboratory to ensure the chosen compounds can be reported.

12. Why do my reporting limits vary from sample to sample?

- Analytical sensitivity varies for compound to compound. In addition, if the dilution factor can vary significantly from sample to sample.

4.0 RESOURCES

There are a number of technical documents and resources provided by the US EPA, DoD, NIOSH, US states, and manufacturing companies for conducting a proper VI investigation. These agencies and the technical documents are but not limited to:

- US EPA (https://www.epa.gov/vaporintrusion/vapor-intrusion-resources)
  - Background VOC concentrations
  - Vapor Intrusion databases
  - Conceptual Model Scenarios
  - Mitigation Approaches
  - TO-15
  - TO-17
- DoD (https://clu-in.org/download/char/dodvihdbk200901.pdf)
  - DoD Vapor Intrusion Handbook (2009)
- Interstate Technology & Regulatory Council (ITRC)
  - Vapor Intrusion Pathway: A Practical Guideline (http://www.itrcweb.org/GuidanceDocuments/VI-1.pdf)
  - Vapor Intrusion Pathway: Investigative Approaches for Typical Scenarios (http://www.itrcweb.org/GuidanceDocuments/VI-1A.pdf)
- NIOSH Manual of Analytical Methods (NMAM 5th Edition)
  - Method 3900 (https://www.cdc.gov/niosh/nmam/default.html)
- Vapor Intrusion – Guidance Documents By State
  - http://www.envirogroup.com/links.php
- Minnesota Pollution Control Agency (https://www.pca.state.mn.us/sites/default/files/c-rem3-01.pdf)
  - VI Technical Support Guide
- New Jersey Department of Environmental Protection
  - NJDEP Vapor Intrusion Technical Guidance (August 2016) http://www.nj.gov/dep/srp/guidance/vaporintrusion/vig_main.pdf?version_4
- World Health Organization
  - Guidelines for Indoor Air Quality: Selected Pollutants http://www.euro.who.int/__data/assets/pdf_file/0009/128169/e94535.pdf?ua=1
- Wisconsin Department of Natural Resources
  - Addressing Vapor Intrusion at Remediation & Redevelopment Sites (2010) http://dnr.wi.gov/files/pdf/pubs/rr/RR800.pdf

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