Vapor Intrusion Sampling Options: Performance Data for Canisters, Badges, and Sorbent Tubes for VOCs

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ABSTRACT

The collection of air and soil gas samples containing parts per billion (ppb) levels of volatile organic compounds (VOCs) is becoming more prevalent with the recognition of the human health risks associated with vapor intrusion (VI). Vapor intrusion encompasses many areas including indoor air, ambient air, and sub-slab soil gas. Canister sampling and analysis by EPA Method TO-15 has been the method of choice in most VI studies. While canisters do have advantages, they are bulky, expensive, and require extensive training. Canisters cannot be used for the sampling of semi-volatile compounds. Sorbent tubes with battery-operated pumps have been used for many years for the collection and analysis of VOCs and are described in detail in EPA TO-17. Sorbent tubes are also the basis for multiple OSHA and NIOSH monitoring methods and can be used for gases as well as semi-volatile compounds.

This paper presents the results of two studies: one study conducted in the state of New York, comparing the performance of passive samplers and canisters and a second study conducted in the state of California, comparing the performance of canisters and sorbent tubes. The New York study showed that correlation coefficients between canisters and an ULTRA® sampler packed with Anasorb® GCB1 for benzene and perchloroethylene were 0.9533 and 0.9831, respectively. Toluene and xylenes also showed good correlation coefficients. The California study showed sorbent tube recoveries between 102 and 115% for the target analytes and good correlation coefficients with respect to stainless steel canisters.

The data in this study demonstrate that sorbent-based sampling devices can be used effectively in vapor intrusion studies and are a reliable alternative to canister sampling.

BACKGROUND

The collection of low levels of VOCs has become more prevalent since the recognition of vapor intrusion and other indoor air quality issues.

Canisters have been used for many years and are referenced in detail in EPA TO-14A and 15. The analysis of canisters is accurate, but canisters can be expensive due to high shipping costs, recertification, and extensive training. Simpler alternative methods are desirable. Some of these methods include diffusive samplers and sorbent tubes, which use solid sorbents for collection of the compounds of interest.

Sorbent tubes used with battery-operated pumps have been used since the early 1970s and are considered active samplers. OSHA and NIOSH have developed and validated many methods over the past 30 years using sorbent tubes. Sorbent tubes are primarily used for industrial hygiene air quality monitoring and usually involve solvent extraction to remove the analyte of interest. These methods utilize many different media including activated charcoal, silica gel, XAD-2 resins, and Tenax® TA. Typical tubes employ both a front and a back section so that one can verify that the sample has not been saturated with the analyte of interest. When an analyte is detected in the second section of the tube, it is commonly referred to as “breakthrough.” It is important to verify that the sample is valid and that saturation has not occurred. Typical analysis is by gas chromatography (GC) or high-performance liquid chromatography (HPLC). Sorbent tubes can be used to sample compounds with a wide range of vapor pressures, if the proper collection parameters are selected.

EPA Method TO-17 describes a tube-based monitoring method (active sampling) for VOCs in ambient air. However, instead of solvent extraction, the analyte is removed from the sorbent using thermal desorption (TD). A table presenting information on safe sampling volumes and tube recommendations is provided in EPA TO-17. Thermal desorption provides a dramatic increase in sensitivity, as the whole sample is usually injected into the chromatograph, instead of the very small portion of sample extract typically used with solvent extraction techniques. It is common with thermal desorption tubes to use more than one sorbent in the same tube (referred to as a mixed-bed tube), allowing the user to sample both a gas and a semi-volatile compound simultaneously with one tube. EPA TO-17 requires the use of two tubes at different flow rates to ensure the integrity of the sample. This is simply not necessary because the added sensitivity of thermal desorption (as high as 1000 times more sensitive) requires much smaller flow rates and sample volumes; therefore, there is low probability of breakthrough or saturation occurring. This is further verified in a paper published by the Health and Safety Executive, where they report safe sampling volumes for many compounds.[2]

A diffusive sampler is a device that samples the atmosphere at a rate controlled by the physical process of diffusion. It does not involve the active movement of air through the device, as with a sorbent tube and pump, and is sometimes referred to as a passive sampler or badge. Some of the main concerns with passive sampling are reverse diffusion, low or high wind velocities, and contamination of the sample.

Reverse diffusion, or loss of analyte from the sampler, often occurs when the vapor pressure of the analyte at the sorbent surface is greater than the external concentration, thus creating a situation where the analyte tends to desorb from the media. This can be resolved by selecting the proper sorbent for the analyte of interest.

Ambient air velocity can affect the performance of a diffusive sampler because it can influence the diffusion path length. Under conditions of low external wind speeds, the diffusion path may be increased while under conditions of high external wind speeds, the effective diffusion path may be decreased. Both of these phenomena must be tested prior to usage in the field. Many validation reports are available that demonstrate diffusive samplers can perform well under high and low air velocity conditions and accurately sample volatile organic compounds in the workplace.[3,4,5] Most of these studies were conducted at higher air velocities and also at velocities much higher than those found in indoor air.

Contamination of a passive sample is always a concern. Studies at SKC indicated Tenax TA and Anasorb GCB1 can be stored, in bulk form, for 4 months in the freezer with no change in background. Off-gassing from sampler housings can occur and takes place over time. This can be resolved by simply removing the sorbent from the sampler housing after sampling and storing it in another holding vessel (tube or vial). In a study by the Health and Safety Executive, 20 compounds spiked on Tenax tubes remained stable over an 11-month period at ambient temperatures.[2]

The purpose of this paper is to show side-by-side comparisons between diffusive samplers, tubes, and stainless steel canisters (reference method) and to provide possible alternatives to canisters. We studied the use of samplers for the collection of indoor air samples and thermal desorption tubes for soil gas sampling.

EXPERIMENTAL

A field study was coordinated by SKC and other companies in several homes in the state of New York to investigate the presence of compounds such as perchloroethylene, benzene, xylenes, and toluene at ppb levels. The test sites were being investigated for vapor intrusion by VOCs in ground water from a dry-cleaning establishment and a gas station.

The sampling methods consisted of stainless steel canisters and SKC ULTRA Series diffusive samplers packed with Tenax TA and Anasorb GCB1. The canisters were analyzed by EPA TO-15 for a full-scan VOC list and a method reporting limit of 1 microgram per cubic meter for a 24-hour 6-liter sample. The ULTRA samplers were analyzed using EPA Method TO-17 (thermal desorption) with select ion monitoring. The reporting limits for the samplers ranged from 0.005 to 0.06 micrograms per cubic meter for a 24-hour sample. The ULTRA sampler was designed for easy transfer of sorbent into and out of the sampler housing. This design helps lessen the chance of contamination. Indoor air was sampled at two locations in each home, with one location (usually the basement) selected for the correlation study of the diffusive samplers and canisters attached to a 5-foot sampling stand.

A field study was also conducted by American Analytics in the state of California to investigate the use of sorbent tubes for monitoring soil gas. A preliminary laboratory study was performed initially to validate sampling volumes for the field work for aromatic hydrocarbons and chlorinated compounds. In the laboratory study, samples were prepared in Tedlar® bags by diluting a certified 1 ppm standard to a final concentration of

10 ppbv. To test canisters, a Tedlar bag containing 1 liter of sample was connected to an orifice capable of restricting the flow rate to approximately 150 ml/min, followed by a vacuum gauge fitted with a female quick connect. Sampling was initiated by attaching a canister to the gauge and continued until a gauge pressure of approximately -5 inches of mercury was achieved. To test sorbent tubes, the tube was connected to the bag, followed by the orifice and a vacuum gauge equipped with a quick disconnect fitting. A cleaned canister was then connected to the gauge and was used to pump the sample from the bag onto the sorbent tube. After sample collection, sorbent tubes were thermally desorbed with nitrogen at 300 C and analyzed by EPA TO-15.

The field study with stainless steel canisters (0.4 and 1.6 liter) and sorbent tubes was conducted in an area with a known historical soil gas concentration of chlorinated compounds and petroleum hydrocarbons. A canister and a sorbent tube sampling train were connected to the same soil gas probe through a manifold assembly. The canister was equipped with a pressure gauge and flow control restrictor set for 150 ml/min. The sorbent tube sampling train consisted of two tubes in series, a flow restrictor, a pressure gauge, and a second canister. This canister served as a pump for the sorbent tube. After sample collection, the sorbent tubes were thermally desorbed with nitrogen and analyzed by EPA TO-15.

RESULTS

Diffusive Samplers and Canisters

Correlation data for benzene, toluene, xylene, and perchloroethylene are shown in Figures 1 through 4. Results for trichloroethylene and dichloroethenes yielded mostly non-detectable results, which made it difficult to show side-by-side comparisons. The correlation data for perchloroethylene with canisters and diffusive samplers is shown in Figure 1.

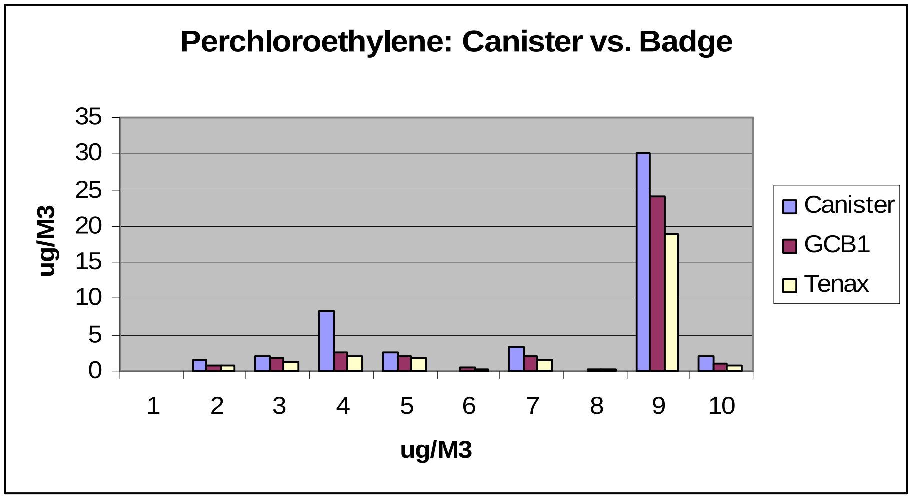

Figure 1. Concentration Results for Perchloroethylene

The correlation coefficients for perchloroethylene were 0.9831 and 0.9837 for passive samplers containing Anasorb GCB1 and Tenax TA, respectively. The field data using an Alnor® velocity meter indicated that the highest velocity reading in the homes was 2 feet per minute, with many readings indicating zero velocity. Additional laboratory work was performed to study sampling rates for the diffusive samplers in stagnant air or at zero velocity. The data indicated that sampling rates for the samplers read approximately 60% on average of the sampling rate listed in the original validation studies. These rates are in Table 1. The sampling rate at the lower velocity was used to calculate the results in the field study.

Table 1. Sampling Rates for ULTRA Diffusive Samplers

Compound	Sampling Rate (ml/min) 10 to 200 cm/sec	Sampling Rate (ml/min) < 5 cm/sec*
Acetone	20.3	5.79
Benzene	16.0	10.1
1,1-Dichloroethene	12.3	9.74
cis-1,2-Dichloroethene	14.8	10.67
trans-1,2-Dichloroethene	14.8	10.2
Ethyl benzene	12.9	7.83
Hexafluorobenzene	12.99	7.77
Hexane	14.3	9.59
Methyl ethyl ketone	16.88	6.27
Methylene chloride	14.7	9.61
Perchloroethylene	13.1	9.4
Toluene	14.5	8.58
p-Xylene	12.8	7.57
Trichloroethylene	14.9	10.2

**Low air velocities, typically found in indoor air, result in lower uptake rates in diffusive samplers.*

Correlation coefficients and concentrations results for benzene, toluene, and m- and p-xylene are shown in Figures 2, 3, and 4. The benzene data in Figure 2 showed correlation coefficients of 0.953 and 0.944 for Anasorb GCB1 and Tenax TA, respectively.

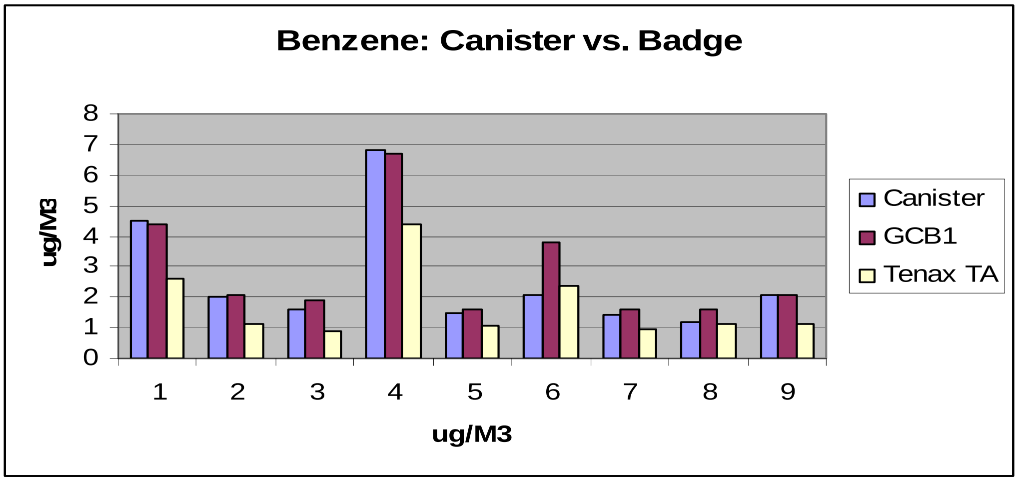

Figure 2. Concentration Results for Benzene

The toluene data in Figure 3 showed correlation coefficients of 0.9863 for Anasorb GCB1 and 0.9798 for Tenax TA, respectively. Similar results were observed for m, p-xylene. In almost all cases, diffusive samplers containing Anasorb GCB1 gave higher results than those containing Tenax TA. This could be attributed to better adsorptive properties for Anasorb GCB1 compared to Tenax TA. Anasorb GCB1 is comparable to Carbopack B.

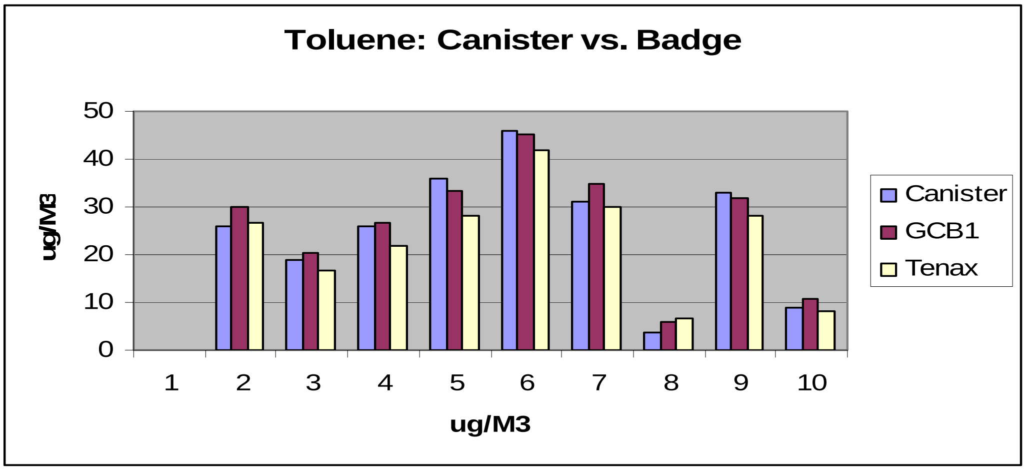

Figure 3. Concentration Results for Toluene

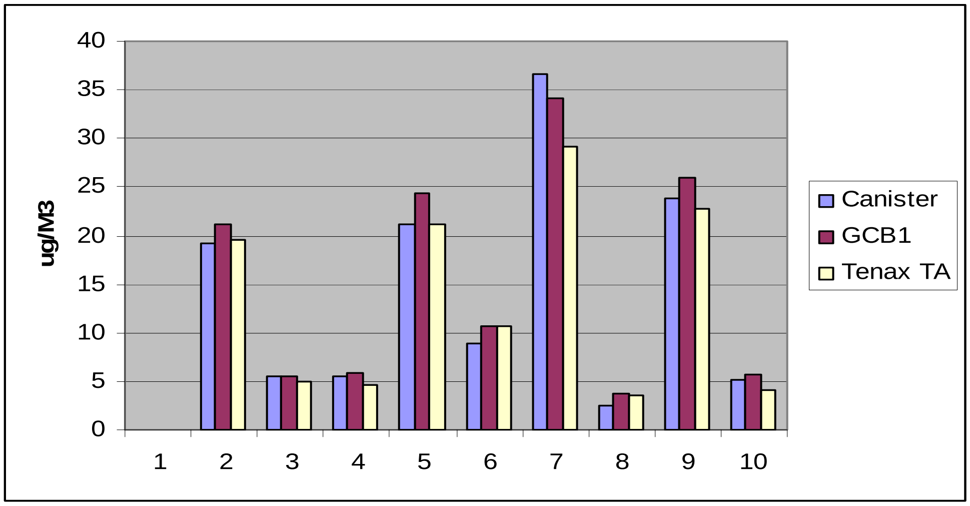

Figure 4. Concentration Results for m- and p-Xylene

This field study indicates that diffusive samplers can be used as a screening tool and a potential predictor of concentrations inside homes involved in vapor intrusion studies. This is just one field study and more studies need to be completed to further substantiate these findings. The small size and ease of operation of diffusive samplers make them a cost-effective tool for this type of study.

Sorbent Tubes and Canisters

This field study used a multi-bed sorbent tube (SKC Inc., Cat. No. 226-349) containing both Anasorb GCB1 and Carbon Molecular Sieve and stainless steel canisters for soil gas sampling.

A preliminary laboratory study was conducted to evaluate the performance of the sorbent tubes under humid sample conditions, as this was anticipated at the field location. Some of the laboratory results are shown in Table 2.

Table 2. Recovery Comparisons Between Canisters and Sorbent Tubes

	Tedlar Bag	Canister 2-70		Sorbent Tube 2-70	
Compounds	Conc. (ppbv)	Conc. (ppbv)	Recovery (%)	Conc. (ppbv)	Recovery (%)
Dichlorofluoromethane	8.21	7.87	96	9.14	111
Trichlorofluoromethane	7.67	7.33	96	8.48	111
1,1-Dichloroethylene	7.7	7.56	98	8.55	111
1,2-Dichloroethane	7.7	7.4	96	8.82	115
Vinyl chloride	6.99	6.09	87	7.44	106
Benzene	8.05	7.03	87	8.51	106
Trichloroethylene	7.83	7.6	97	9.0	115
Toluene	7.92	6.74	85	8.27	104
Tetrachloroethylene	8.24	7.69	93	9.06	110
Ethyl benzene	7.75	5.63	73	7.89	102
m, p-Xylene	7.45	5.31	71	7.58	102
o-Xylene	7.55	5.36	71	7.73	102

The results suggest comparable recovery values from the multi-bed sorbent tube and the canister, with slightly higher values observed for the tube. More studies are needed, however, to confirm this observation.

The field study for the soil gas determination was conducted in Southern California where the soil has been impacted by both chlorinated volatile organic compounds and petroleum hydrocarbons. Two soil gas monitoring wells, SG23 and SG13, were selected for this study. The wells had been installed onsite during a previous site assessment. The wells consist of ¼-inch high-density polyethylene perforated near the bottom to facilitate the flow of gases. The data from the field studies are shown in Figures 5 and 6.

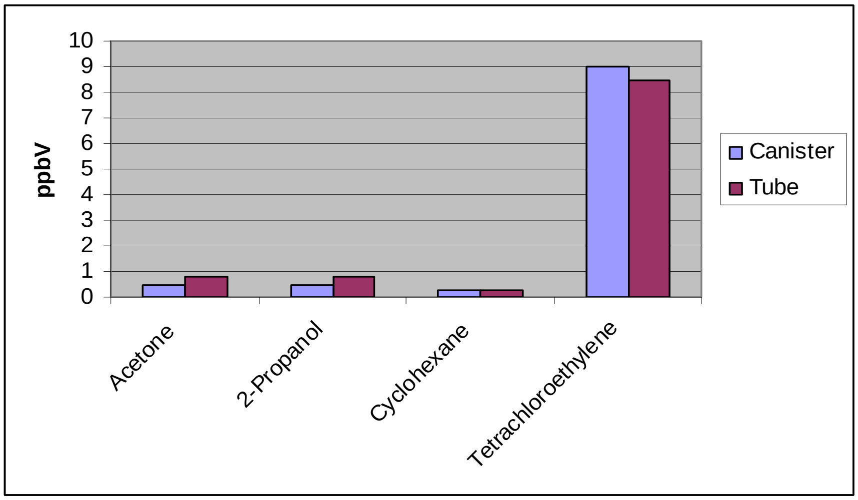

Figure 5. Canister and Tube Results for SG 23

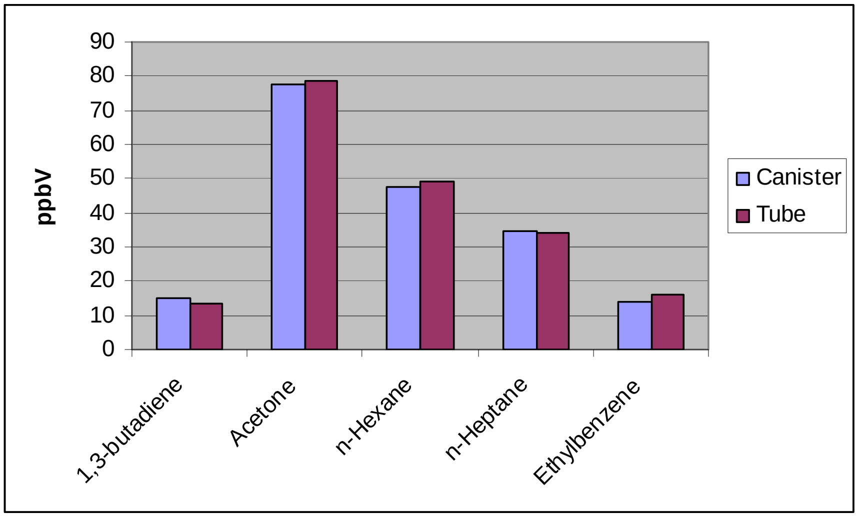

Figure 6. Canister and Tube Results for SG13

Good agreement was observed between the concentrations measured in the samples collected with the canisters and the multi-bed sorbent tubes. The correlation coefficients between the tubes and the canisters for the SG23 and SG13 field studies were 0.9992 and 0.9987, respectively. The data indicate good correlation between the two sampling methods. Additional studies are in progress.

CONCLUSION

The results of the New York field study indicate that diffusive samplers packed with Anasorb GCB1 or Tenax TA correlate well with stainless steel canisters. Data also demonstrate that ULTRA diffusive samplers have adequate sensitivity to detect low ppb levels of VOCs and can be used as a screening tool and a potential predictor of concentration inside homes in vapor intrusion studies. Field studies with thermal desorption tubes indicate their potential for monitoring VOCs in soil gas studies. They also correlated well with canisters. Both sampling techniques, diffusive samplers and sorbent tubes, are simple to operate and require the same analytical methods employed with stainless steel canisters.

REFERENCES

[1] U.S. Department of Labor, OSHA, *Index of Sampling and Analytical Methods*, Washington, D.C.

[2] Health and Safety Executive, *MDHS 72 Volatile Organic Compounds in air*, March, 1993

[3] Eide, M., *OSHA Analytical Methods Manual:* Benzene, Method 1005, Sept., 2002

[4] Elskamp, C., *OSHA Analytical Methods Manual:* Toluene, Method 111, April, 1998

[5] Elskamp, C., *OSHA Analytical Methods Manual:* Trichloroethylene and Tetrachloroethylene, OSHA 1001, May, 1999