Validation of the 575-001 and the ULTRA Series Diffusive Samplers: Long-term Sampling in Indoor and Ambient Air Environments

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Introduction

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 is the migration of volatile chemicals from the subsurface into overlying buildings and 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 for most VI studies. While there are advantages to using canisters, disadvantages include bulky size, expensive cleaning and shipping, extensive training, and unsuitability for sampling semi-volatile compounds (SVOCs). Diffusive samplers are becoming an increasingly popular alternative to canisters for VI studies. These samplers operate by diffusion to collect VOCs and SVOCs onto solid sorbents contained in the sampler housing. Diffusive samplers are small, quiet, easy to use, low cost, and can be placed in any location. An important difference between canisters and diffusive samplers is that canisters do not work well for long-term sampling (3 to 14 days). Diffusive samplers, however, are well suited for long-term studies, especially when sampling indoor air. Recent studies show that when longer sampling periods are employed, temporal variability is reduced.

This report describes the evaluation of the 575-001 Diffusive Sampler (charcoal) and the ULTRA Series Diffusive Samplers (Anasorb® GCB1 and Carbograph 5 TD) for 24-hour to 7-day sampling periods for several VOCs including benzene, methylene chloride, chloroform, trichloroethylene, perchloroethylene, o-xylene, m-xylene, and p-xylene. The data shows that both samplers can work under different situations; however, the ULTRA Series Diffusive Samplers using thermal desorption offer increased sensitivity. The report also includes data from a 30-day field study comparing results from benzene, toluene, methyl-t-butyl ether, xylenes, and ethyl benzene on 575-001 (charcoal) Diffusive Samplers (charcoal) and 226-01 charcoal sorbent tubes (reference method).

Experimental

Laboratory Test Study

A dynamic atmosphere was generated using a syringe pump and filtered airstreams to generate concentrations; the system is shown in Figure 1. The atmosphere was fed into a [PTFE-lined aluminum exposure chamber where 575-001 and ULTRA Series diffusive samplers (SKC Inc, Eighty Four, PA) were exposed. The 575-001 samplers contained activated charcoal and the ULTRA samplers contained either Anasorb GCB1 or Carbograph 5 TD sorbent. The samplers were clipped to a rotating bracket inside the chamber, which simulated different wind velocities and orientations. Test concentrations ranged from 30 to 120 ppb, depending on the analyte. The relative humidity (RH) was set at 60 % at 22 degrees Celsius (◦C). The samplers were exposed to 1, 3, and 7-day time intervals. The test atmospheres were verified using 226-01 charcoal sorbent tubes (SKC Inc, Eighty Four, PA).

Field Study

A field study was conducted in two locations within a lawn mower repair shop. The 575-001 charcoal samplers were in place for 30 days to sample for benzene, toluene, methyl-t-butyl ether, xylenes, and ethyl benzene. The 226-01 sorbent tubes were used as a reference method and were calibrated at 50 ml/min and in place for 7-day intervals. The sorbent tubes were replaced each week during the 30-day sampling event.

Sample Preparation

The ULTRA samplers were desorbed by transferring the sorbent from the sampler housing to an empty Perkin Elmer thermal desorption tube that contained a plug in one end. After the sorbent transfer, the other end of the tube was plugged and then placed on a TurboMatrix ATD (Perkin Elmer, Waltham, MA) and analyzed on a Clarus® 500 gas chromatograph (Perkin Elmer, Waltham, MA) with flame ionization detection (GC/FID). Analytical and desorption conditions are listed in Figure 2.

The 575-001 samplers were desorbed (in-situ) with 2 ml of carbon disulfide and shaken on a flatbed shaker for 30 minutes. The extracts were analyzed by GC/FID.

Each section of the 226-01 charcoal tubes was transferred to a 4-ml glass vial and desorbed with 2 ml of carbon disulfide. Each vial was placed on a sample vibrator for 30 minutes and analyzed by GC/FID.

Results and Discussion

The diffusive sampler data for eight chemicals is shown in Tables 1 through 8. The data for benzene (Table 1) shows that both charcoal and Carbograph 5 TD sorbents can be used for long-term sampling of benzene up to 113 ppb at 60 % RH. Under these same conditions, Anasorb GCB1 shows losses or reverse diffusion of benzene. This is understandable as Anasorb GCB1 has a lower surface area and capacity than either charcoal or Carbograph 5 TD. An important finding in this study is that although both charcoal and Carbograph 5 TD can sample for 7 days, the Carbograph 5 TD, which utilizes thermal desorption, can provide up 25 times lower minimum reporting limits (MRLs) than charcoal, which uses solvent extraction.

The data for toluene and perchloroethylene is shown in Tables 2 and 3. The data indicates that both activated charcoal and Carbograph 5 TD can be used for long-term sampling up to 7 days.

Trichloroethylene, ethyl benzene, o-xylene, and chloroform were sampled using the 575-001 sampler (Tables 4, 5, 6, and 7). The data shows that the 575-001 sampler can be used for up to 7 days with no reverse diffusion effects under the conditions tested. Studies are in progress to test these compounds with Carbograph 5 TD for sampling periods up to 7 days.

Methylene chloride, the lowest boiling compound tested in this study, shows losses or reverse diffusion effects between Day 3 and Day 7 with the 575-001 sampler (Table 8). If sampling periods greater than 3 days are needed, a stronger sorbent will be required to effectively sample this compound. Studies are in progress to determine if this effect is observed at levels less than 1 ppb.

The laboratory studies indicate that charcoal is an excellent sorbent for many of the compounds tested at levels up to 100 ppb. Charcoal has a high surface area and capacity; therefore, it is less prone to reverse diffusion effects during sampling periods longer than 24 hours. However, charcoal uses solvent extraction; therefore, it may not have the sensitivity needed for the 24-hour ambient and indoor air studies specified in EPA methods. Minimum reporting limits for several compounds are listed in Table 9. One of the advantages of thermal desorption is the sensitivity of the technique. Increased sensitivity has to be balanced with the fact that many sorbents commonly used in thermal desorption lack large surface areas or capacities and are more susceptible to reverse diffusion effects, especially for more volatile compounds such as methylene chloride and vinyl chloride.

Data for the field study is shown in Table 10. The sorbent tube data reported is an average of four 226-01 charcoal sorbent tubes taken over a 30-day sampling period. The diffusive sampler result for each compound is an average of two samplers. The data shows very good agreement between the two sampling methods over sampling periods of 30 days.

Conclusion

The data indicates that diffusive samplers are a viable technique for monitoring indoor air and have potential for ambient air studies. Choice of the proper diffusive sampler depends on the compound, the sampling period, and the expected concentration. Diffusive samplers containing activated charcoal (i.e. 575-001) work well for long-term sampling, especially for periods greater than 7 days. Diffusive samplers using thermal desorption, with their increased sensitivity, are better suited for 24-hour to 7-day sampling periods. Some of the more volatile chemicals such as methylene chloride, which tend to have reverse diffusion effects, need further investigation. Stronger sorbents, such as Carbosieve S-III, are being explored for their suitability for sampling the more volatile chemicals.

Table 1. Long-term Sampling with Benzene
Using 575 Series and ULTRA Series Diffusive Samplers

Diffusive Sampler	Days	Test Level (ppb)	Sampling Rate (ml/min)
575-001 (Charcoal)	1	79.0	16.4
	1	113.0	16.4
	3	78.2	15.6
	3	113.0	17.5
	7	45.7	15.9
	7	79.0	15.2
		Mean	**16.2**
ULTRA (Anasorb GCB1)	1	41.0	13.8
	3	41.0	9.83*
		Mean	**11.8**
ULTRA (Carbograph 5 TD)	1	41.0	17.3
	3	41.0	15.5
	7	41.0	15.7
		Mean	**16.2**

** Sampling rate is low due to reverse diffusion effects with Anasorb GCB1 sorbent.*

Table 2. Long-term Sampling for Toluene
Using 575 Series and ULTRA Series Diffusive Samplers

Diffusive Sampler	Days	Test Level (ppb)	Sampling Rate (ml/min)
575-001 (Charcoal)	1	95.1	14.5
	3	95.1	14.9
	7	38.0	14.5
		Mean	**14.6**
ULTRA (Carbograph 5 TD)	1	38.2	14.5
	3	38.2	12.1
	7	38.2	13.3
		Mean	**13.3**

Table 3. Long-term Sampling for Perchloroethylene
Using 575 Series Diffusive Samplers

Diffusive Sampler	Days	Test Level (ppb)	Sampling Rate (ml/min)
575-001 (Charcoal)	1	73.4	13.7
	3	73.4	12.6
	7	73.4	12.6
		Mean	**13.0**

Table 4. Long-term Sampling for Trichloroethylene
Using 575 Series Diffusive Samplers

Diffusive Sampler	Days	Test Level (ppb)	Sampling Rate (ml/min)
575-001 (Charcoal)	1	82.3	14.6
	3	82.3	13.5
	7	82.3	13.2
		Mean	**13.8**

Table 5. Long-term Sampling for Ethyl Benzene
Using 575 Series Diffusive Samplers

Diffusive Sampler	Days	Test Level (ppb)	Sampling Rate (ml/min)
575-001 (Charcoal	1	85.3	12.0
	3	85.3	10.6
	7	85.3	13.7
		Mean	**12.1**

Table 6. Long-term Sampling for o-Xylene
Using 575 Series Diffusive Samplers

Diffusive Sampler	Days	Test Level (ppb)	Sampling Rate (ml/min)
575-001 (Charcoal)	1	58.4	13.1
	3	49.0	13.8
	3	49.7	12.5
	7	28.0	12.7
		Mean	**13.0**

Table 7. Long-term Sampling for Chloroform
Using 575 Series Diffusive Samplers

Diffusive Sampler	Days	Test Level (ppb)	Sampling Rate (ml/min)
575-001 (Charcoal)	1	77.1	14.6
	3	77.1	14.1
	7	77.1	15.0
		Mean	**14.6**

Table 8. Long-term Sampling for Methylene Chloride
Using 575 Series Diffusive Samplers

Diffusive Sampler	Days	Test Level (ppb)	Sampling Rate (ml/min)
575-001 (Charcoal)	1	83.3	16.9
	3	76.6	16.7
	7	76.6	9.09†
		Mean	**14.2**

† *Sampling rate is low due to reverse diffusion effects with charcoal sorbent.*

Table 9. 24-hour Sampling for VOCs
Minimum Reporting Limits (MRLs)

Compound	Carbograph 5 TD (thermal desorption) µg/m³ (ppb)	Activated charcoal (solvent extraction) µg/m³ (ppb)
Benzene	2.18 (0.68)	8.68 (2.71)
Toluene	0.19 (0.05)	4.83 (1.27)
Trichloroethylene	0.12 (0.03)	6.10 (1.52)
o-Xylene	0.13 (0.03)	5.81 (1.34)

Table 10. 30-day Sampling for Six VOCs
Using Charcoal Sorbent in 575-001 Diffusive Samplers
and 226-01 Sorbent Tubes

Compound	Diffusive Sampler (ppb)	Sorbent Tube (ppb)
Benzene	95.0	87.8
Ethyl benzene	70.0	53.0
MTBE	48.0	59.0
Toluene	570.0	540.0
o-Xylene	92.0	79.8
p-Xylene	59.0	52.0

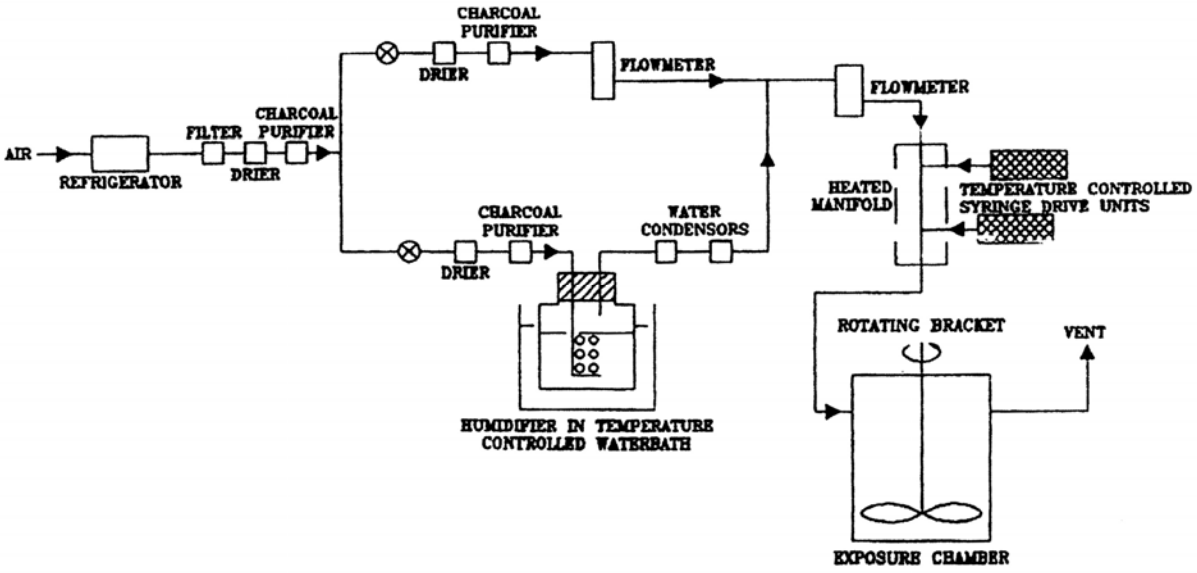

Figure 1. Test System

TD METHOD REPORT

Created: 26/05/2011 09:41
Modified: 26/05/2011 09:41
Method Filename: Carbograph 350.tdm
TD Mode: Two Stage Desorbtion

Temperatures (C)		Times (min.)		Options	
Tube:	350.0	Tube Desorb:	20.0	Inlet Split:	Off
Transfer Line:	250.0	Trap Hold:	10.0	Outlet Split:	On
Valve:	200.0	Standard Inj.:	0.1	Internal Std.:	Off
Trap Low:	-30.0	Cycle:	35.0	Injections:	1
Trap High:	300.0	Purge:	1.0	Heated Purge:	Off
Trap Rate (C/s):	40				

Pneumatics

Inlet Split (ccm):	50.0
Outlet Split (ccm):	50.0
Desorb (ccm):	50.0

Event Relays

Column: 60 m x 0.32 mm 1.0 micron film Stabilwax®
GC: Perkin Elmer Clarus 500 with TotalChrom® Software
Oven Program:
Initial Temp: 45 ◦C
Initial hold: 3.0 minutes
Ramp 1: 10 c/min to 125 ◦C for 3.0 min
Ramp 2: 10 c/min to 230 ◦C for 1.0 min
Total Run time: 25.5 minutes
Injection Temp: 250 ◦C
Detector Temp: 250 ◦C
Carrier Gas: Nitrogen
Flow: N_2: 2.5 ml/min
Air: 450 ml/min
H_2: 45 ml/min

Figure 2. Analytical and Thermal Desorption Conditions for ULTRA