APPENDIX H

Air Toxics White Paper

Evaluation of Disposable Syringes for the Collection of Soil Gas

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Abstract

Disposable plastic syringes are commonly used to collect soil gas for on-site analysis. While these syringes are inexpensive and convenient, they have not been fully validated for volatile organic compound (VOC) recovery. To evaluate the performance of disposable syringes for soil gas collection, a multi-component NIST-traceable gas phase VOC standard was prepared and stored in plastic syringes from 5 minutes to 30 minutes to model typical field holding times. After the hold-time duration, the contents of the syringe were analyzed by EPA Method TO-15[1] to determine recovery.

Introduction

The potential for chemicals to migrate from contaminated soil or groundwater through the subsurface into nearby or overlying buildings is often determined by measuring the concentration of contaminants in soil vapor. With increased reliance on these soil gas measurements to assess potential health risks from vapor intrusion, soil gas sampling procedures require careful evaluation to insure quality data. Previous work by this author examined the impact of tubing materials used in the soil gas collection probe on VOC recovery.[2] The data indicated that low density polyethylene tubing can result in significant losses when challenged with a sub-ppbv VOC standard even under dynamic conditions of flow through the tubing. These polyethylene tubing results raised concerns regarding the quality of data generated using plastic syringes for soil gas collection. To evaluate the performance of disposable syringes and determine their suitability for soil gas collection, VOC recovery was measured under several hold-time conditions and using two VOC test concentrations.

Experiment

Many types of disposable, plastic syringes are commercially available. This study focused on Norm-Ject®, Air-Tite 60 ml capacity syringes manufactured by Henke Sass and Wolf. These syringes are composed of a polypropylene barrel and a polyethylene plunger and are commonly used for VOC analysis due to their low VOC background contamination.

Two test VOC mixes were prepared from a multi-component NIST-traceable standard. To simulate the soil gas matrix, each mix was prepared at approximately 70% relative humidity (RH). Test mix 1 was prepared at a nominal concentration of 50 ppbv for each VOC. This concentration represented a concentration 1 to 5 times the reporting limit of a typical on-site 8260B analytical system[3]. Test mix 2 was prepared at a nominal concentration of 1000 ppbv with the exception of naphthalene which was spiked at 200 ppbv. Prior to sample collection, each syringe was flushed three times with the VOC test mix. A volume of 50 mL of the test mix was pulled into each syringe, and the luer tip stainless steel needle on the syringe was capped immediately after collection until sample analysis. Recovery of VOCs from the syringes were measured immediately after collection (time 0), as well as 5 minutes, 15 minutes, and 30 minutes after sample collection. Each holding time was evaluated in duplicate using a new syringe.

The analysis was performed by EPA Method TO-15 using a load volume of 50 mL for all analytical runs. Calibration was achieved using a 50 mL load of the test VOC mix analyzed directly from the Summa canister. The calibration sample was loaded onto the TO-15 interface using a mass flow controller. The accuracy of the mass flow controller was verified using a NIST-traceable flow meter. To calculate VOC concentrations, the relative response factors derived from this daily calibration standard were used.

The test mix was analyzed a second time after the daily calibration run to demonstrate precision. In addition, the test VOC mix was analyzed from the canister at the end of the analytical batch to demonstrate instrument stability. After calibration, a laboratory blank and a syringe blank were analyzed. To analyze the syringe blank, zero air was used to flush a new Norm-Ject® syringe three times. After flushing, a 50 mL aliquot of zero air was collected and injected into the TO-15 interface. Following the syringe blank, the syringe test samples were analyzed. The analytical sequence is summarized in Table 1. The sequence was performed using a 50 ppbv VOC test mix and repeated using a 1000 ppbv VOC test mix.

Table 1. Analytical sequence for syringe study

Day 1 = 50 ppbv Test Mix	**Day 2 = 1000 ppbv Test Mix**
BFB Tune Check	BFB Tune Check
Daily Calibration – Canister VOC test mix	Daily Calibration – Canister VOC test mix
Calibration check – Canister VOC test mix	Calibration check – Canister VOC test mix
Lab Blank	Lab Blank
Syringe 1: Syringe Blank	Syringe 10: Syringe Blank
Syringe 2 : Time = 0 min	Syringe 11 : Time = 0 min
Syringe 3: Time = 0 min	Syringe 12: Time = 0 min
Syringe 4: Time = 5 min	Syringe 13: Time = 5 min
Syringe 5: Time = 5 min	Syringe 14: Time = 5 min
Syringe 6: Time = 15 min	Syringe 15: Time = 15 min
Syringe 7: Time = 15 min	Syringe 16: Time = 15 min
Syringe 8: Time = 30 min	Syringe 17: Time = 30 min
Syringe 9: Time = 30 min	Syringe 18: Time = 30 min
End Check – Canister VOC test mix – Not Analyzed	End Check – Canister VOC test mix

Results and Discussion

The VOC recoveries for the syringe samples were calculated and summarized in Tables 2a and 2b. The precision for each duplicate syringe sample was expressed as a relative percent difference (%RPD). The associated quality control samples are summarized in Table 3. The end check was not analyzed on Day 1 for the 50 ppbv test. The average recovery of Day 1 calibration check was 104% with 5.8% RSD. The respective average recoveries of Day 2 calibration check and Day 2 end check were 101% and 94% with 1.7% and 1.3% RSD.

In general, the precision for the sample duplicate analysis was less than 5% RPD for most target VOCs. The notable precision outliers were six VOCs in the 50 ppbv study that demonstrated recoveries much greater than 100%. Evaluation of the total ion chromatogram showed that three of the eight 50 ppbv test runs, Run 1 at time 0 and Runs 1 and 2 at time 5 minutes, showed a pattern of light hydrocarbons interfering with several of the target compounds. These hydrocarbons were primarily in the C3 to C7 range and resulted in high recoveries and poor precision for propylene, chloromethane, 1,3-butadiene, acetone, 2-propanol, hexane, and heptane. Chloromethane and 1,3-butadiene exhibited a high bias due to interfering peaks contributing to the area of their quantitation mass ion.

While the interfering hydrocarbon pattern was not evident in the syringe blanks, the affected syringe samples showed varying degrees of this background contamination even after flushing the syringes three times with sample prior to analysis. The source of the hydrocarbons may be a result of out-gassing of the polyethylene and polypropylene material or residual from the manufacturing and packaging process. The syringes used for the study were from the same shipment from the distributor. However, the lot number was not recorded at the time of analysis.

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Table 2a. Syringe VOC recovery performance - 50 ppbv

Compound	Spiked Conc. (ppbv)	Time = 0 min % Recovery Run 1	Run 2	%RPD	Time = 5 min % Recovery Run 1	Run 2	%RPD	Time = 15 min % Recovery Run 1	Run 2	%RPD	Time = 30 min % Recovery Run 1	Run 2	%RPD
Propylene	50	1302.0	82.9	176.1%	587.8	535.9	9.2%	84.1	99.0	16.2%	103.3	83.8	20.8%
Dichlorodifluoromethane	50	87.5	78.6	10.7%	85.4	77.6	9.6%	81.5	87.7	7.3%	75.1	79.4	5.5%
Freon 114	50	83.1	81.5	1.9%	80.8	79.5	1.5%	85.9	92.7	7.6%	80.4	80.7	0.3%
Chloromethane	50	323.3	81.7	119.3%	179.8	79.8	77.0%	87.7	96.4	9.4%	89.2	84.4	5.4%
Vinyl Chloride	50	105.0	91.1	14.1%	97.7	92.9	5.0%	94.2	99.1	5.1%	86.9	89.8	3.2%
1,3-Butadiene	50	351.0	99.1	111.9%	202.1	192.4	4.9%	102.3	107.6	5.0%	104.1	97.3	6.7%
Bromomethane	50	74.6	78.0	4.5%	73.9	78.1	5.5%	75.4	96.8	24.9%	73.1	70.3	3.8%
Chloroethane	50	71.2	67.9	4.7%	71.2	67.4	5.4%	65.7	68.9	4.7%	65.5	66.2	1.1%
Trichlorofluoromethane	50	86.1	81.5	5.5%	80.5	78.0	3.1%	82.4	89.7	8.5%	79.0	79.7	0.8%
Ethanol	50	104.7	90.1	15.0%	101.1	102.2	1.1%	98.1	86.9	12.1%	92.1	100.1	8.3%
Freon 113	50	84.7	81.8	3.4%	80.1	80.5	0.6%	86.6	89.7	3.5%	81.8	82.9	1.4%
1,1-Dichloroethene	50	86.8	81.3	6.6%	80.1	78.3	2.2%	80.4	88.9	10.0%	75.9	74.9	1.3%
Carbon disulfide	50	77.4	75.3	2.8%	66.0	66.6	0.9%	58.4	64.3	9.6%	49.6	50.3	1.5%
Acetone	50	928.6	87.4	165.6%	435.1	381.1	13.2%	82.8	87.1	5.1%	136.5	79.6	52.7%
2-Propanol	50	380.9	98.0	118.2%	209.6	194.8	7.3%	97.3	93.8	3.7%	100.9	90.1	11.3%
3-Chloropropene	50	79.3	69.2	13.6%	73.0	70.9	3.0%	70.0	68.1	2.8%	61.0	60.7	0.5%
Methylene Chloride	50	88.9	82.7	7.2%	82.1	80.7	1.8%	83.0	91.3	9.5%	76.2	81.3	6.4%
MTBE	50	79.8	68.6	15.0%	74.0	75.1	1.5%	70.9	50.8	33.1%	62.7	61.7	1.5%
trans-1,2-Dichloroethane	50	83.1	79.6	4.4%	74.1	73.0	1.6%	69.0	74.2	7.3%	62.2	66.1	6.0%
Hexane	50	3544.0	82.9	190.9%	1490.6	1322.4	12.0%	77.6	82.6	6.2%	140.0	74.7	60.8%
1,1-Dichloroethane	50	86.0	81.7	5.1%	79.3	76.9	3.0%	79.9	79.5	0.5%	72.9	72.8	0.2%
cis-1,2-Dichloroethene	50	85.6	79.4	7.5%	73.4	73.4	0.1%	69.8	74.8	7.0%	62.7	62.2	0.8%
2-Butanone	50	92.1	74.2	21.5%	77.9	79.6	2.1%	76.5	80.1	4.7%	69.6	68.4	1.8%
Tetrahydrofuran	50	85.0	75.9	11.3%	73.0	70.8	3.1%	72.5	74.5	2.6%	66.0	64.2	2.7%
Chloroform	50	85.2	80.0	6.3%	74.6	75.5	1.2%	75.4	77.9	3.3%	68.8	68.6	0.2%
Cyclohexane	50	87.4	78.8	10.3%	78.9	80.3	1.8%	78.9	83.2	5.3%	73.5	71.3	3.1%
1,1,1-Trichloroethane	50	90.0	81.6	9.9%	81.0	80.0	1.2%	79.3	81.4	2.6%	74.3	75.1	1.1%
Vinyl Acetate	50	104.6	72.9	35.7%	80.8	74.3	8.4%	74.0	69.6	6.0%	61.1	66.5	8.5%
Carbon tetrachloride	50	87.6	80.3	8.7%	78.2	77.1	1.4%	77.9	84.6	8.3%	74.3	72.5	2.4%
2,2,4-Trimethylpentane	50	86.4	77.9	10.3%	79.2	78.2	1.3%	79.7	81.9	2.7%	74.6	73.3	1.7%
Benzene	50	79.2	78.2	1.3%	68.9	69.5	1.0%	67.1	65.7	2.0%	59.8	57.8	3.5%
1,2-Dichloroethane	50	78.4	78.6	0.3%	68.9	71.1	3.2%	66.9	67.0	0.2%	60.4	59.5	1.4%
Heptane	50	3158.0	79.1	190.2%	1384.1	1230.3	11.8%	66.8	67.4	0.8%	125.7	58.2	73.4%
Trichloroethene	50	74.7	72.4	3.1%	61.6	65.2	5.7%	56.4	57.0	1.1%	47.5	47.3	0.4%
1,2-Dichloropropane	50	81.3	80.8	0.6%	71.7	72.5	1.2%	70.1	70.7	0.8%	64.5	63.8	1.1%
1,4-Dioxane	50	107.8	109.6	1.7%	98.5	101.1	2.6%	99.5	95.2	4.4%	84.5	83.5	1.1%
Bromodichloromethane	50	81.3	79.4	2.4%	68.6	69.9	1.9%	68.1	66.0	3.1%	56.6	56.6	0.0%
cis-1,3-Dichloropropane	50	74.1	71.1	4.0%	60.8	60.5	0.5%	53.2	52.9	0.5%	44.7	42.2	5.9%
4-Methyl-2-pentanone	50	68.9	68.0	1.4%	58.8	73.5	22.1%	62.2	64.3	3.4%	57.6	51.1	11.9%
Toluene	50	79.6	72.4	9.5%	62.0	63.5	2.3%	52.7	52.3	0.7%	43.4	42.2	2.9%
trans-1,3-Dichloropropane	50	69.1	66.2	4.3%	52.3	52.6	0.5%	42.8	40.6	5.3%	34.8	33.3	4.5%
1,1,2-Trichloroethane	50	80.0	75.6	5.7%	62.3	63.8	2.3%	58.5	54.8	6.5%	48.1	49.3	2.4%
Tetrachloroethene	50	67.2	66.5	1.1%	49.3	50.4	2.2%	40.0	37.7	5.8%	30.7	29.5	4.2%
2-Hexanone	50	73.0	66.4	9.5%	56.7	60.1	5.7%	53.3	48.1	10.4%	42.9	41.5	3.3%
Dibromochloromethane	50	71.8	68.0	5.4%	54.5	56.1	2.8%	48.5	44.9	7.6%	38.0	37.5	1.5%
1,2-Dibromoethane	50	65.9	62.4	5.6%	44.9	45.8	2.0%	34.2	32.8	4.2%	25.4	24.4	3.8%
Chlorobenzene	50	64.1	62.0	3.3%	42.6	43.5	2.0%	31.4	31.7	0.9%	23.1	22.9	0.9%
Ethyl benzene	50	67.9	62.0	9.0%	45.1	48.1	6.5%	33.3	32.6	2.1%	25.0	24.7	1.4%
m,p-Xylene	50	64.7	58.5	10.0%	42.7	43.0	0.7%	27.0	29.3	8.0%	22.4	21.9	2.3%
o-Xylene	50	64.5	60.8	5.9%	41.3	44.6	7.7%	27.3	29.4	7.6%	21.5	22.3	3.5%
Styrene	50	56.8	53.0	6.8%	31.5	33.8	7.1%	19.7	20.1	1.9%	14.5	14.5	0.4%
Bromoform	50	61.4	60.9	0.8%	41.9	42.1	0.4%	28.9	29.6	2.2%	21.2	22.3	4.8%
Cumene	50	106.0	61.4	53.3%	61.2	60.0	1.9%	30.0	31.5	4.9%	25.0	22.7	9.3%
1,1,2,2-Tetrachloroethane	50	70.3	69.3	1.4%	53.2	54.3	1.9%	42.8	40.3	5.9%	33.1	32.7	1.3%
Propylbenzene	50	52.4	52.5	0.3%	30.1	32.5	7.7%	19.6	18.9	3.5%	12.9	13.4	4.0%
4-Ethyltoluene	50	49.0	48.2	1.7%	23.9	24.0	0.5%	15.5	15.2	2.0%	10.7	10.8	0.3%
1,3,5-Trimethylbenzene	50	46.5	44.4	4.6%	24.8	29.8	18.6%	15.6	14.5	7.3%	10.4	<10	NA
1,2,4-Trimethylbenzene	50	39.8	40.2	0.9%	19.9	22.2	10.9%	12.2	11.9	2.5%	<10	<10	NA
1,3-Dichlorobenzene	50	35.3	36.9	4.4%	15.7	15.8	0.6%	<10	<10	NA	<10	<10	NA
1,4-Dichlorobenzene	50	30.5	32.4	6.2%	13.0	13.0	0.2%	<10	<10	NA	<10	<10	NA
alpha-Chlorotoluene	50	34.4	35.7	3.7%	18.8	18.4	2.1%	<10	<10	NA	<10	<10	NA
1,2-Dichlorobenzene	50	35.9	37.4	4.1%	15.1	15.5	2.5%	<10	<10	NA	<10	<10	NA
1,2,4-Trichlorobenzene	50	<10	<10	NA	<10	<10	NA	<10	<10	NA	<10	<10	NA
Hexachlorobutadiene	50	31.6	32.4	2.5%	12.6	15.2	18.6%	<10	<10	NA	<10	<10	NA
Naphthalene	50	<40	<40	NA	<40	<40	NA	<40	<40	NA	<40	<40	NA
Surrogates													
1,2-Dichloroethane-d4	400	101.5	100.4	1.2%	101.9	101.09	0.8%	101.0	110.3	8.7%	101.6	103.3	1.7%
Toluene-d8	400	95.6	99.8	4.3%	98.23	96.21	2.1%	98.8	100.5	1.7%	98.4	97.4	1.0%
Bromofluorobenzene	400	101.1	101.8	0.6%	98.51	100.04	1.5%	98.6	98.5	0.1%	97.0	96.8	0.1%

60% ≤ Recovery < 70%
50% ≤ Recovery < 60%
10% ≤ Recovery < 50%
Recovery <10% or Not Detected

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Table 2b. Syringe VOC recovery performance - 1000 ppbv

Compound	Spiked Conc. (ppbv)	Time = 0 min % Recovery Run 1	Run 2	%RPD	Time = 5 min % Recovery Run 1	Run 2	%RPD	Time = 15 min % Recovery Run 1	Run 2	%RPD	Time = 30 min % Recovery Run 1	Run 2	%RPD
Propylene	1000	104.3	101.2	3.0%	100.6	97.7	2.9%	97.8	96.2	1.6%	99.6	98.1	1.5%
Dichlorodifluoromethane	1000	90.5	88.0	2.8%	89.0	88.6	0.5%	88.1	86.9	1.4%	89.3	87.0	2.6%
Freon 114	1000	94.5	92.6	2.0%	94.5	94.3	0.2%	95.9	94.1	1.8%	96.2	94.2	2.0%
Chloromethane	1000	92.0	91.0	1.0%	91.5	91.0	0.5%	90.0	88.4	1.8%	89.9	88.3	1.8%
Vinyl Chloride	1000	101.8	99.6	2.2%	99.5	99.5	0.0%	98.5	97.2	1.3%	98.5	97.0	1.6%
1,3-Butadiene	1000	110.8	108.6	2.0%	109.6	108.5	1.0%	108.8	108.1	0.7%	108.8	106.3	2.3%
Bromomethane	1000	83.4	82.2	1.5%	82.5	83.0	0.6%	80.8	80.4	0.4%	80.0	78.0	2.5%
Chloroethane	1000	69.3	69.5	0.2%	69.8	69.1	1.0%	69.3	67.9	2.0%	68.5	66.9	2.4%
Trichlorofluoromethane	1000	90.6	88.5	2.4%	88.8	88.5	0.4%	87.8	86.8	1.2%	88.3	86.6	2.0%
Ethanol	1000	66.1	68.1	3.1%	67.7	69.2	2.2%	68.2	68.0	0.4%	67.2	67.0	0.3%
Freon 113	1000	89.9	89.1	0.9%	89.9	90.0	0.1%	90.0	89.4	0.6%	91.4	89.7	1.8%
1,1-Dichloroethene	1000	93.1	91.1	2.1%	89.9	89.0	1.0%	87.1	85.9	1.4%	85.8	84.1	2.0%
Carbon disulfide	1000	84.4	82.4	2.4%	74.9	74.1	1.1%	65.9	65.0	1.4%	58.8	58.0	1.3%
Acetone	1000	84.7	87.9	3.7%	87.1	83.3	4.5%	82.7	84.7	2.4%	86.2	84.3	2.2%
2-Propanol	1000	68.9	69.1	0.3%	72.3	74.0	2.3%	73.6	73.8	0.3%	73.0	71.5	2.0%
3-Chloropropene	1000	72.8	73.4	0.8%	73.3	74.2	1.3%	73.7	72.4	1.7%	70.6	69.6	1.4%
Methylene Chloride	1000	88.4	86.0	2.8%	85.2	84.9	0.4%	81.2	81.1	0.2%	79.0	77.4	2.1%
MTBE	1000	29.3	30.3	3.3%	30.5	32.1	5.4%	32.4	32.7	0.9%	32.6	31.5	3.4%
trans-1,2-Dichloroethane	1000	87.5	85.0	2.8%	81.6	80.8	1.0%	76.0	75.0	1.2%	70.9	70.5	0.7%
Hexane	1000	89.3	87.7	1.8%	86.6	86.1	0.6%	82.8	82.3	0.6%	81.4	79.9	1.9%
1,1-Dichloroethane	1000	88.3	86.1	2.5%	86.1	85.6	0.6%	84.1	83.2	1.1%	82.8	81.2	1.9%
cis-1,2-Dichloroethene	1000	86.4	83.9	2.9%	80.8	80.6	0.2%	75.8	74.5	1.7%	71.4	70.6	1.2%
2-Butanone	1000	87.0	85.6	1.7%	82.4	81.5	1.0%	80.8	80.7	0.1%	76.0	76.7	1.0%
Tetrahydrofuran	1000	86.4	84.3	2.5%	82.0	81.3	0.9%	77.5	76.9	0.7%	74.7	73.4	1.8%
Chloroform	1000	88.7	85.8	3.3%	83.0	82.6	0.6%	79.1	78.0	1.5%	76.5	74.7	2.3%
Cyclohexane	1000	90.1	87.9	2.5%	87.6	87.1	0.5%	84.5	83.7	0.9%	83.1	81.8	1.6%
1,1,1-Trichloroethane	1000	86.1	84.6	1.8%	84.1	83.8	0.4%	81.6	81.5	0.2%	80.6	79.3	1.6%
Vinyl Acetate	1000	84.2	84.0	0.2%	83.4	84.6	1.5%	78.6	78.2	0.5%	77.7	76.2	1.9%
Carbon tetrachloride	1000	88.7	86.8	2.1%	85.4	84.5	1.0%	82.0	81.1	1.1%	80.2	78.8	1.8%
2,2,4-Trimethylpentane	1000	88.1	86.2	2.2%	86.6	86.2	0.5%	84.2	83.4	0.9%	83.8	82.4	1.7%
Benzene	1000	86.8	86.8	0.0%	81.2	81.0	0.3%	74.1	73.4	0.9%	69.8	69.7	0.1%
1,2-Dichloroethane	1000	85.9	84.7	1.4%	78.5	78.3	0.3%	72.2	71.1	1.5%	66.7	66.7	0.0%
Heptane	1000	83.9	84.2	0.4%	77.6	78.0	0.5%	71.0	69.3	2.4%	66.5	66.0	0.8%
Trichloroethene	1000	83.4	82.6	1.0%	72.9	72.1	1.0%	62.9	62.2	1.1%	55.8	56.2	0.8%
1,2-Dichloropropane	1000	87.7	87.5	0.2%	83.4	83.4	0.0%	77.4	76.5	1.2%	74.6	73.9	1.0%
1,4-Dioxane	1000	85.1	87.0	2.2%	82.9	83.4	0.6%	76.0	76.6	0.9%	74.2	74.2	0.0%
Bromodichloromethane	1000	86.1	84.9	1.5%	78.3	78.1	0.3%	70.5	69.6	1.2%	65.2	65.0	0.3%
cis-1,3-Dichloropropane	1000	81.3	80.8	0.6%	70.7	70.3	0.5%	59.4	58.8	1.0%	52.7	52.3	0.8%
4-Methyl-2-pentanone	1000	86.2	84.6	1.8%	82.7	82.6	0.1%	76.9	76.6	0.4%	74.0	73.5	0.7%
Toluene	1000	78.4	78.2	0.3%	65.2	64.9	0.6%	53.1	52.4	1.3%	45.5	45.8	0.6%
trans-1,3-Dichloropropane	1000	80.8	81.1	0.3%	66.1	66.3	0.3%	52.5	52.4	0.2%	43.8	43.8	0.0%
1,1,2-Trichloroethane	1000	87.0	86.6	0.4%	77.3	77.9	0.7%	67.5	66.6	1.3%	60.2	60.0	0.3%
Tetrachloroethene	1000	77.8	77.6	0.3%	61.3	61.5	0.2%	47.5	46.3	2.6%	37.6	37.7	0.2%
2-Hexanone	1000	80.6	82.0	1.8%	73.3	73.9	0.7%	62.9	62.7	0.4%	56.0	55.4	1.1%
Dibromochloromethane	1000	82.4	81.5	1.1%	68.8	68.9	0.2%	56.4	55.2	2.3%	47.6	47.3	0.6%
1,2-Dibromoethane	1000	75.4	75.3	0.1%	55.2	54.7	0.9%	40.4	39.4	2.4%	31.4	31.2	0.7%
Chlorobenzene	1000	72.7	72.8	0.1%	52.0	51.8	0.3%	37.6	36.5	2.9%	28.9	28.9	0.0%
Ethyl benzene	1000	74.3	74.2	0.2%	55.9	55.1	1.4%	41.2	40.3	2.2%	31.7	32.0	0.9%
m,p-Xylene	1000	71.5	72.5	1.3%	51.0	50.2	1.5%	36.3	35.2	3.0%	27.3	27.6	1.1%
o-Xylene	1000	75.0	75.8	1.1%	55.3	54.4	1.7%	39.3	38.5	2.0%	30.0	30.2	0.7%
Styrene	1000	67.2	67.3	0.2%	43.6	42.0	3.8%	28.3	27.3	3.3%	21.0	20.6	1.7%
Bromoform	1000	73.6	73.8	0.4%	52.6	52.7	0.2%	37.6	36.6	2.8%	28.8	28.3	1.7%
Cumene	1000	75.4	76.7	1.7%	58.3	57.8	1.0%	42.7	41.4	3.0%	33.1	32.9	0.5%
1,1,2,2-Tetrachloroethane	1000	80.2	81.1	1.1%	65.5	65.7	0.4%	50.8	50.0	1.7%	41.7	41.2	1.2%
Propylbenzene	1000	67.4	68.4	1.4%	42.7	41.7	2.4%	26.8	25.8	3.7%	18.9	18.9	0.3%
4-Ethyltoluene	1000	59.9	62.0	3.4%	34.1	32.8	3.8%	22.0	19.2	13.6%	13.7	15.0	9.0%
1,3,5-Trimethylbenzene	1000	68.5	67.1	2.1%	40.4	39.7	1.8%	22.2	23.4	5.0%	17.4	15.5	11.9%
1,2,4-Trimethylbenzene	1000	57.4	58.8	2.5%	30.4	29.4	3.3%	17.1	16.2	5.2%	11.5	11.4	0.2%
1,3-Dichlorobenzene	1000	48.6	48.9	0.7%	21.9	20.1	8.7%	11.7	11.3	3.3%	8.0	8.1	0.9%
1,4-Dichlorobenzene	1000	43.2	45.1	4.1%	18.3	17.0	7.2%	9.6	9.5	1.2%	6.6	6.6	0.3%
alpha-Chlorotoluene	1000	52.1	53.5	2.7%	25.3	23.8	6.0%	13.7	13.3	2.6%	9.1	9.2	1.3%
1,2-Dichlorobenzene	1000	48.2	49.9	3.4%	21.8	21.0	3.8%	11.9	11.4	3.6%	8.2	8.2	0.9%
1,2,4-Trichlorobenzene	1000	15.5	16.4	5.4%	4.4	4.1	8.0%	1.9	1.9	1.1%	1.2	1.2	4.1%
Hexachlorobutadiene	1000	44.8	47.8	6.5%	20.6	19.8	3.7%	10.4	9.4	10.7%	6.9	6.9	0.1%
Naphthalene	200	15.0	15.5	3.4%	4.2	3.9	6.2%	<10	<10	NA	<10	<10	NA
Surrogates													
1,2-Dichloroethane-d4	400	99.4	94.7	4.8%	95.3	94.2	1.2%	94.9	94.9	0.0%	94.1	92.4	1.8%
Toluene-d8	400	95.9	94.4	1.5%	93.7	92.8	1.0%	92.4	93.0	0.6%	92.8	94.5	1.8%
Bromofluorobenzene	400	103.8	105.8	1.9%	104.2	103.6	0.6%	104.4	104.2	0.3%	104.4	104.7	0.3%

Table 3. Quality control sample results

Compound	Day 1 50 ppbv % Recovery Cal Check	Day 1 50 ppbv % Recovery End Check	Day 2 1000 ppbv % Recovery Cal Check	Day 2 1000 ppbv % Recovery End Check	%RPD
Propylene	100.0	NA	100.2	93.7	6.7%
Dichlorodifluoromethane	106.5	NA	99.7	92.6	7.3%
Freon 114	100.7	NA	100.3	95.0	5.4%
Chloromethane	101.7	NA	99.2	94.5	4.9%
Vinyl Chloride	101.7	NA	99.9	95.7	4.2%
1,3-Butadiene	102.6	NA	99.3	95.2	4.2%
Bromomethane	99.9	NA	100.5	95.4	5.2%
Chloroethane	103.0	NA	99.0	95.5	3.5%
Trichlorofluoromethane	101.5	NA	99.2	92.7	6.7%
Ethanol	126.6	NA	98.4	93.8	4.8%
Freon 113	104.0	NA	99.8	94.4	5.6%
1,1-Dichloroethene	103.4	NA	99.3	93.8	5.7%
Carbon disulfide	103.4	NA	100.5	95.0	5.6%
Acetone	107.4	NA	99.5	93.7	6.0%
2-Propanol	125.4	NA	98.0	93.9	4.3%
3-Chloropropene	101.5	NA	100.6	95.4	5.2%
Methylene Chloride	104.7	NA	100.0	93.3	7.0%
MTBE	98.3	NA	103.2	91.7	11.8%
trans-1,2-Dichloroethane	105.0	NA	100.8	94.5	6.4%
Hexane	104.2	NA	99.8	94.2	5.8%
1,1-Dichloroethane	100.0	NA	99.7	93.9	6.0%
cis-1,2-Dichloroethene	103.5	NA	98.8	93.6	5.4%
2-Butanone	106.0	NA	98.1	94.5	3.7%
Tetrahydrofuran	103.5	NA	99.4	92.8	6.9%
Chloroform	102.2	NA	99.8	93.1	6.9%
Cyclohexane	103.6	NA	100.0	95.2	4.9%
1,1,1-Trichloroethane	103.7	NA	98.8	92.5	6.6%
Vinyl Acetate	114.7	NA	101.6	96.8	4.8%
Carbon tetrachloride	102.7	NA	99.3	92.7	6.9%
2,2,4-Trimethylpentane	103.2	NA	99.3	94.0	5.5%
Benzene	102.3	NA	102.1	95.2	7.1%
1,2-Dichloroethane	102.3	NA	100.7	91.9	9.1%
Heptane	100.8	NA	101.0	93.4	7.9%
Trichloroethene	99.9	NA	102.2	94.4	7.9%
1,2-Dichloropropane	103.1	NA	102.1	94.9	7.3%
1,4-Dioxane	130.5	NA	99.2	96.7	2.5%
Bromodichloromethane	103.7	NA	101.9	93.7	8.4%
cis-1,3-Dichloropropane	102.9	NA	101.4	93.8	7.8%
4-Methyl-2-pentanone	92.9	NA	103.8	94.6	9.3%
Toluene	103.0	NA	101.4	93.8	7.8%
trans-1,3-Dichloropropane	103.1	NA	104.3	96.4	7.8%
1,1,2-Trichloroethane	104.1	NA	103.8	96.5	7.2%
Tetrachloroethene	102.8	NA	103.3	95.7	7.6%
2-Hexanone	100.4	NA	101.5	94.3	7.4%
Dibromochloromethane	103.8	NA	102.5	95.2	7.4%
1,2-Dibromoethane	106.4	NA	103.5	95.9	7.6%
Chlorobenzene	101.3	NA	103.3	96.8	6.5%
Ethyl benzene	102.7	NA	104.2	95.7	8.5%
m,p-Xylene	102.2	NA	101.8	95.7	6.2%
o-Xylene	99.7	NA	102.6	96.4	6.2%
Styrene	103.1	NA	102.5	96.1	6.4%
Bromoform	103.0	NA	101.1	94.5	6.8%
Cumene	103.3	NA	103.3	95.5	7.9%
1,1,2,2-Tetrachloroethane	105.6	NA	102.0	94.9	7.2%
Propylbenzene	103.1	NA	102.2	95.7	6.6%
4-Ethyltoluene	104.3	NA	99.0	94.9	4.2%
1,3,5-Trimethylbenzene	100.6	NA	106.0	94.2	11.7%
1,2,4-Trimethylbenzene	102.7	NA	102.1	96.0	6.2%
1,3-Dichlorobenzene	104.4	NA	103.6	95.7	8.0%
1,4-Dichlorobenzene	101.9	NA	99.3	94.0	5.5%
alpha-Chlorotoluene	101.8	NA	102.5	94.4	8.2%
1,2-Dichlorobenzene	104.2	NA	101.6	94.5	7.2%
1,2,4-Trichlorobenzene	108.6	NA	101.9	95.3	6.6%
Hexachlorobutadiene	108.4	NA	101.4	93.4	8.2%
Naphthalene	115.8	NA	101.4	95.2	6.3%
Surrogates					
1,2-Dichloroethane-d4	100.6	NA	98.1	88.3	10.5%
Toluene-d8	101.3	NA	98.2	97.6	0.6%
Bromofluorobenzene	99.9	NA	100.0	100.5	0.4%

The recovery data showed several clear trends. In Figures 1a and 1b, the recoveries of a subset of VOCs were plotted for each hold-time period. The VOCs were ordered in terms of their vapor pressure from highest on the left to the lowest on the right.

Figure 1a. VOC recovery for 50 ppbv test mix

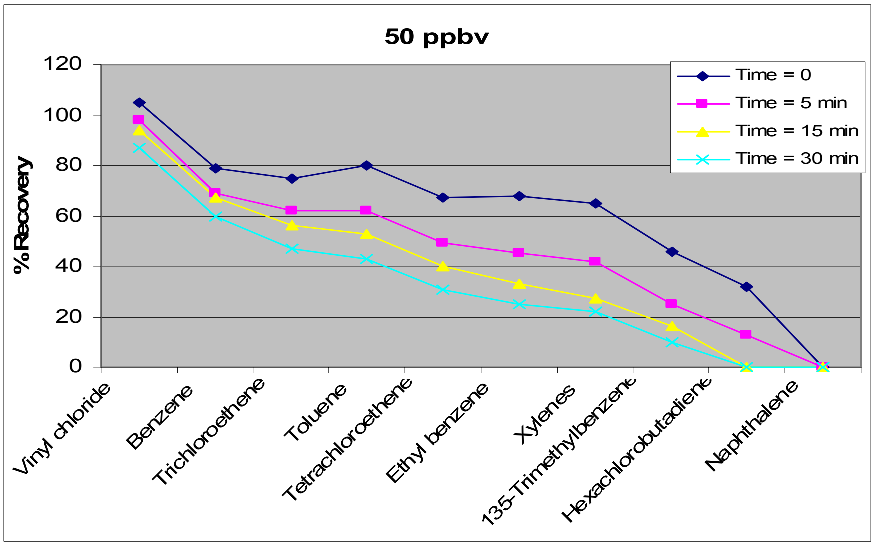
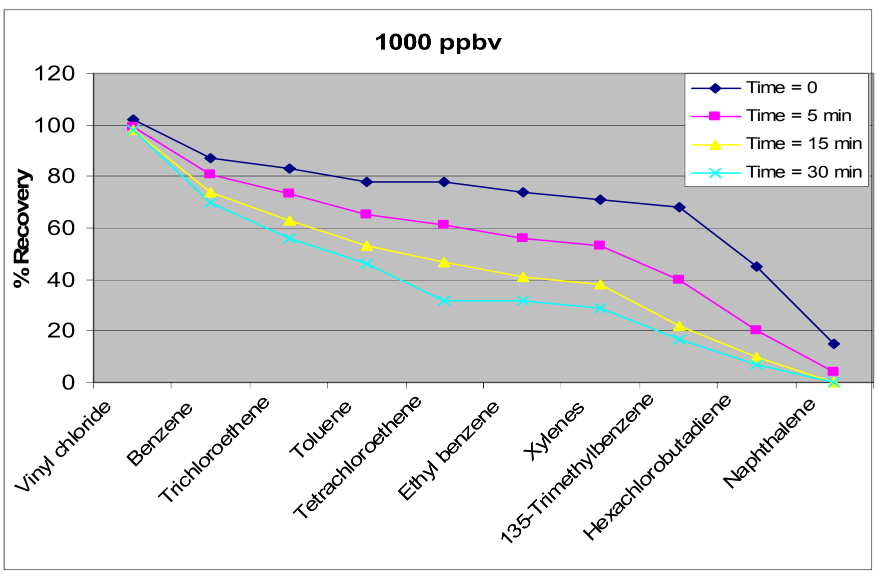


Figure 1b. VOC recovery for 1000 ppbv test mix



At both VOC concentrations tested, the recoveries decreased with decreasing vapor pressure. In addition, the VOC recovery decreased as the hold-time period increased. Recovery dropped more dramatically in the 50 ppbv test as compared to the 1000 ppbv test for each hold-time. Even when the sample was analyzed immediately after collection (time = 0), ten VOCs with the lowest vapor pressures recovered at less than 50%. Naphthalene was not detected in the 50 ppbv test for any of the holding times. While the 1000 ppbv test mix showed slight improvement in recoveries relative to the 50 ppbv test mix, recovery of six of the heaviest VOCs were still less than 50% when analyzed immediately after sample collection. Naphthalene (spiked at 200 ppbv) and 1,2,4-trichlorobenzene recovered at less than 20%. After only a 5 minute hold-time for the 50 ppbv concentration and a 15 minute hold-time for the 1000 ppbv concentration, tetrachloroethene recovery dropped to approximately 50%. After 30 minutes in the syringe, many of the VOCs in the 50 ppbv test including trichloroethene fell below 50% recovery. At the higher concentration of 1000 ppbv toluene and heavier compounds dropped below 50% after 30 minutes of storage in the syringe.

Although photodegradation of light-sensitive VOCs has been cited as a concern when using non-opaque containers[4], the trends noted in this study cannot be explained through this mechanism. The UV exposure from fluorescent lights in the laboratory is minimal as compared to UV exposure from natural daylight[5], and the halogenated VOC recoveries indicate that photodegradation does not play a significant role in explaining the observed trends.

The responsible mechanism appears to be adsorption of the VOCs onto the interior surface of the syringe barrel and/or plunger. Adsorption of a compound onto a surface tends to increase with time, and compounds with lower vapor pressures tend to adsorb to surfaces to a greater degree. Additionally, adsorption effects are less pronounced when a surface is in contact with a higher VOC concentration.

Conclusions

The potential for low VOC recoveries when using polyethylene/polypropylene disposable syringes should be considered when selecting sample collection media for soil gas investigations. Because vapor phase standards and disposable syringes are not generally used to validate the accuracy and precision of the on-site 8260B analytical equipment, low VOC recoveries observed in this study will not be reflected in any of the 8260B quality control samples. This means that initial and daily calibration standards generated using 8260B methanol standards can meet method acceptance criteria yet the soil gas sample data may reflect a low bias. As demonstrated in this study, the low bias can be significant for VOCs with low vapor pressure even under conditions of short hold-times. Consequently, soil gas measurements collected using disposable syringes do not provide the level of quality and defensibility required for vapor intrusion investigations and health risk assessments.

References

1. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-15, Second Edition*, U.S. Environmental Protection Agency: Research Triangle Park, NC, January 1999; EPA 600/625/R-96/010b.

2. Hayes, H.C., Benton, D.J., and Khan, N., Impact of sampling media on soil gas measurements, A&WMA Symposium Vapor Intrusion: The Next Great Environmental Challenge – An Update, Los Angeles, CA, September 13-15, 2006.

3. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods: Method 8260B, Revision 2,* U.S. Environmental Protection Agency, Washington, D.C. 1996; SW-846.

4. *Advisory – Active Soil Gas Investigations*, Department of Toxic Substances Control: Glendale, CA and California Regional Water Quality Board Los Angeles Region: Los Angeles, CA, January 2003.

5. NEMA White paper LSD 7-1999, Ultraviolet Radiation from Fluorescent Lamps, Rosslyn, VA, May 4, 1999.