

Impact of sampling media on soil gas measurements

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ABSTRACT

To evaluate the vapor intrusion pathway for a building and to assess the associated human health risks, soil gas samples near the building site and under the building foundation may be collected. In order to meet risk assessment goals, the analytical laboratory is often required to report compounds of concern for these soil gas samples down to the part per billion ranges or lower. To insure data quality objectives are achieved, the appropriate sample tubing, collection media, and leak check compounds should be selected. Several types of tubing and collection media commonly used in the soil gas and sub-slab sample collection trains are evaluated for background contribution and adsorption of volatile organic compounds (VOCs). Additionally, quality considerations when applying a leak check compound are described.

INTRODUCTION

Soil gas measurements have become one of the primary tools in assessing vapor intrusion pathways. The analytical results from soil gas samples at a site often are used to determine whether a potential indoor inhalation risk is present. Site-specific inputs to models such as the Johnson-Ettinger Model can be used to predict indoor air concentrations. Alternatively, generic attenuation factors may be applied to estimate indoor air concentrations from soil vapor concentrations. Risk-based screening levels for soil gas contaminants have been published by the EPA and by various state agencies to assess the potential inhalation risk from subsurface contamination. For several of the carcinogenic compounds of concern, screening levels may be less than 1 ppbv and even in the pptv range. For example, in the EPA's *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway*, Trichloroethene has a generic screening level of 0.041 ppbv for shallow soil gas at the 10^{-6} risk level¹. The low reporting limits often dictated by the overseeing agency and the level of defensibility needed to support health risk assessments require a careful evaluation of the collection and analytical procedures used for soil gas measurements.

Oftentimes, achieving a risk-based screening level for a contaminant in soil gas is considered to be a laboratory concern with the challenge primarily residing in the analytical sensitivity of the instrumentation. However, the results generated by the laboratory are also a function of sample collection and storage. As the required reporting limits are pushed lower and lower by the regulatory agencies, the sampling procedures play a larger role in generating defensible results. The materials used for the sampling train, the media used for intermediate or final sample storage, and the leak check compound selected all need to be evaluated against the data quality goals of the project.

APPROACH

Evaluation of tubing

Collection of a soil gas sample requires the use of tubing to connect the soil gas probe to the sample train. Samplers often use tubing from their own inventory with little concern as to the potential impact on sample integrity. Four types of commonly used tubing were tested for cleanliness and adsorption of trace level VOCs. Table 1 summarizes the tubing types evaluated. Nylaflow®, Teflon® and polyethylene tubing are commonly used in the field for vapor sample collection, while PEEK tubing is often used in laboratory applications as an alternative to stainless steel when inert, flexible tubing is required.

Table 1. Tubing Types Evaluated

Type	Material	Dimensions	Manufacturer
LM Nylaflow®	Nylon	0.25" OD	S&L Plastics
PEEK	Polyetheretherketone	1/8" OD, 0.06" ID	Valco Instrument Co.
Teflon®	Fluoroethylene-propylene (FEP)	0.25" OD, 0.187" ID	Saint-Gobain, Performance Plastics
Polyethylene	Low Density Polyethylene (LD PE)	0.25" OD, 0.17" ID	Supplied by Cole-Parmer

Testing Protocol - Background Contribution

To evaluate background VOC contribution of the tubing, a zero-air 6L Summa canister prepared at 70% relative humidity (RH) was connected to a two-foot section of tubing using compression fittings. The other end of the tubing was attached to the loading interface of a GC/TOF-MS. The TOF-MS (Time of Flight Mass Spectrometer) was utilized because of its ability to measure pptv concentrations in the full scan mode. The full scan mode allowed for the identification and quantification of non-target compounds as well as the target list of VOCs. After an initial flush of up to 400 ml, three 400 ml aliquots were analyzed sequentially for each section of tubing. The sequential data indicated whether the concentrations decreased over time or if the contaminants reflected a more constant "off-gassing". Gas flow rates onto the TOF interface were set at 80 ml/min, similar to typical soil gas sampling rates of 100-200 ml/min.

The test was repeated a total of three times, utilizing a new section of tubing for each test. As a result, nine data points were generated for each tubing type. In the case of polyethylene tubing, only two sections (6 data points) were reported due to a leak in one of the three tubing connections. Both target analytes (more than 60 VOCs) and non-target analytes were evaluated. Only the VOCs detected and the frequencies of detection are summarized in Table 2. Prior to the test runs, the zero-air 6L canister was analyzed to measure blank levels of VOCs. Compounds that were detected in the tubing background at less than 2x blank levels were not considered significant, and were not included in the table.

Table 2. Summary of VOC Detections in Tubing

Compound	Nylaflow®		PEEK		Teflon®		Polyethylene	
	Average Conc. (ppbv)	Frequency of detection						
Propene	<DL	0%	0.070	44%	<DL	0%	<DL	0%
Ethanol	0.58	89%	<DL	0%	<DL	0%	<DL	0%
1,4-Dioxane	0.068	11%	<DL	0%	<DL	0%	<DL	0%
Carbon Disulfide	<DL	0%	<DL	0%	<DL	0%	0.15	100%
2-Propanol	<DL	0%	<DL	0%	<DL	0%	0.060	100%
Cyclohexane	<DL	0%	<DL	0%	<DL	0%	0.032	100%
2,2,4-Trimethylpentane	<DL	0%	<DL	0%	<DL	0%	0.016	100%
Isopentane	<DL	0%	<DL	0%	<DL	0%	0.10	83%
Benzene	0.13	78%	<DL	0%	<DL	0%	<DL	0%
Heptane	<DL	0%	<DL	0%	<DL	0%	0.052	83%
Trichloroethene	<DL	0%	<DL	0%	<DL	0%	0.016	100%
Tetrachloroethene	<DL	0%	<DL	0%	<DL	0%	0.20	100%
Chlorobenzene	<DL	0%	<DL	0%	<DL	0%	0.036	100%
Toluene	0.20	100%	<DL	0%	<DL	0%	3.8	100%
2-Hexanone	0.065	33%	<DL	0%	<DL	0%	<DL	0%
Ethyl benzene	<DL	0%	<DL	0%	<DL	0%	0.57	100%
m,p-Xylene	<DL	0%	0.058	11%	<DL	0%	1.1	100%
o-Xylene	<DL	0%	<DL	0%	<DL	0%	0.43	100%
Styrene	<DL	0%	<DL	0%	<DL	0%	0.88	100%
Cumene	<DL	0%	<DL	0%	<DL	0%	0.030	100%
Propylbenzene	0.066	89%	<DL	0%	<DL	0%	<DL	0%
1,2,4-Trimethylbenzene	<DL	0%	<DL	0%	<DL	0%	0.58	100%
1,3-Dichlorobenzene	<DL	0%	<DL	0%	<DL	0%	0.050	100%
1,4-Dichlorobenzene	<DL	0%	<DL	0%	<DL	0%	0.24	100%
1,2-Dichlorobenzene	<DL	0%	<DL	0%	<DL	0%	0.014	100%
Naphthalene	<DL	0%	<DL	0%	<DL	0%	0.20	100%
1,1-Difluoroethane	<DL	0%	<DL	0%	5.0	67%	<DL	0%
2-Ethyl-1-hexanol	<DL	0%	<DL	0%	0.24	67%	<DL	0%
Dimethyl Disulfide	<DL	0%	0.21	22%	<DL	0%	<DL	0%
2-Ethyl Benzenamine	0.85	67%	<DL	0%	<DL	0%	<DL	0%
Hydrocarbon 1	0.40	11%	0.71	56%	<DL	0%	<DL	0%
Hydrocarbon 2	0.37	11%	1.2	22%	<DL	0%	<DL	0%
Total C8 – C12 Alkenes	<DL	0%	<DL	0%	<DL	0%	500	100%
Total C8 – C12 Hydrocarbons	<DL	0%	<DL	0%	<DL	0%	28	100%

DL = Detection Limit (Compound dependent, typically in the 0.05 ppbv range)

Testing Protocol - Reactivity

To evaluate the inertness of the tubing for trace level VOC soil gas applications, a multi-component standard was prepared at approximately 0.5 ppbv and 70% RH in a 6L Summa canister. The canister was analyzed by GC/TOF-MS to determine the actual concentration. A two-foot section of tubing was used to connect the canister to the loading interface of the GC/TOF-MS. The connections were made using Swagelock compression fittings. After flushing the tubing with approximately 400 ml of the VOC standard, three 400 ml aliquots were analyzed sequentially for each section of tubing. The initial 400 ml flush exceeds the typical field purging volume of three void volumes from the sampling system.

Each tubing type generated three data points for evaluation. Recovery was normalized to the measured concentration of the source standard. In addition, the reproducibility was measured by calculating the relative standard deviation (RSD). The results are summarized in Table 3. Recoveries outside of 70-130% and precision criterion outside 30%RSD are highlighted. The recovery test was repeated on a new section of tubing to confirm initial results. Non-compliant results that were not confirmed in the repeated test are not highlighted.

Table 3. Summary of VOC Recovery through Tubing

Compound	Nylaflow®		PEEK		Teflon®		Polyethylene	
	Average Recovery	%RSD	Average Recovery	%RSD	Average Recovery	%RSD	Average Recovery	%RSD
Freon 114	77	0%	83	7%	86	2%	98	1%
Chloromethane	90	2%	94	7%	92	1%	103	2%
Vinyl Chloride	74	2%	79	7%	87	1%	104	4%
1,3-Butadiene	74	6%	81	7%	79	12%	101	7%
Bromomethane	103	5%	118	13%	86	1%	102	4%
Chloroethane	118	4%	121	5%	95	1%	102	2%
Freon 11	106	2%	106	6%	89	1%	100	3%
Ethanol	140 ^a	4%	91	2%	83	4%	84	6%
1,1-Dichloroethene	92	2%	89	4%	92	1%	98	1%
Freon 113	70	1%	68 ^a	4%	83	2%	103	3%
Carbon Disulfide	106	3%	86	4%	92	1%	98	9%
Acetone	87	2%	58 ^a	1%	84	1%	100	13%
2-Propanol	86	6%	78	3%	92	11%	111	4%
3-Chloroprene	84	2%	84	7%	95	4%	102	5%
Methylene Chloride	101	4%	97	7%	106	19%	147	22%
trans-1,2-Dichloroethene	82	15%	123	37% ^a	91	2%	112	33% ^a
Methyl tertiary butyl ether	93	14%	106	31% ^a	81	4%	99	33% ^a
Hexane	136 ^a	4%	123	4%	89	5%	86	2%
1,1-Dichloroethane	113	1%	109	4%	94	3%	96	2%
cis-1,2-Dichloroethene	102	0%	97	5%	91	2%	91	2%
2-Butanone	91	1%	80	5%	92	1%	95	11%
Chloroform	97	1%	97	2%	97	2%	92	1%
Tetrahydrofuran	84	5%	80	8%	91	2%	97	8%
Cyclohexane	87	1%	85	4%	91	2%	93	3%
1,1,1-Trichloroethane	94	1%	95	5%	98	1%	96	1%
Carbon Tetrachloride	93	1%	92	5%	96	2%	92	2%
2,2,4-Trimethylpentane	83	1%	86	7%	92	1%	94	3%
Benzene	116	2%	91	3%	98	1%	86	5%
Heptane	103	2%	98	4%	104	1%	84	4%
1,2-Dichloroethane	101	4%	96	1%	106	1%	88	1%
Trichloroethene	93	2%	94	3%	102	0%	73	2%
1,2-Dichloropropane	98	2%	95	1%	102	1%	89	1%
1,4-Dioxane	100	2%	79	5%	77	5%	113	7%
Bromodichloromethane	101	2%	96	2%	103	1%	82	1%
Cis-1,3-Dichloropropene	92	3%	88	2%	100	1%	74	2%
4-Methyl-2-pentanone	99	2%	101	1%	100	3%	89	3%
Toluene	130	1%	92	1%	99	0%	332	42%
trans-1,3-Dichloropropene	94	5%	92	2%	100	3%	63 ^a	5%
1,1,2-Trichloroethane	109	2%	104	1%	106	1%	74	2%
Tetrachloroethene	104	1%	91	2%	100	1%	53	5%
2-Hexanone	101	5%	107	3%	94	2%	76	6%
Dibromochloromethane	93	2%	92	2%	99	1%	59	5%

Table 3 continued. Summary of VOC Recovery through Tubing

Compound	Nylaflow®		PEEK		Teflon®		Polyethylene	
	Average Recovery	%RSD						
1,2-Dibromoethane	103	3%	103	2%	104	2%	38	11%
Chlorobenzene	106	2%	106	1%	102	1%	29	13%
Ethylbenzene	104	0%	103	1%	100	1%	77	22%
m,p-Xylene	105	1%	101	1%	103	1%	68	21%
o-Xylene	110	2%	103	1%	102	1%	55	16%
Styrene	117	3%	106	2%	104	3%	89	18%
Bromoform	92	4%	98	2%	94	1%	25	21%
Cumene	103	3%	102	1%	100	1%	24	12%
1,1,2,2-Tetrachloroethane	109	4%	110	1%	102	2%	438	17%
Propylbenzene	117	2%	99	2%	99	1%	94	7%
4-Ethyltoluene	107	4%	101	1%	100	1%	60	47%
1,3,5-Trimethylbenzene	115	5%	102	1%	104	1%	57	1%
1,2,4-Trimethylbenzene	135 ^a	5%	104	2%	104	1%	70	2%
1,3-Dichlorobenzene	114	11%	98	2%	98	2%	8	11%
1,4-Dichlorobenzene	113	12%	99	2%	98	2%	34	1%
alpha-Chlorotoluene	88	14%	104	2%	101	2%	<10	NA
1,2-Dichlorobenzene	110	14%	97	2%	98	2%	<10	29%
1,2,4-Trichlorobenzene	45	50%	94	4%	89	5%	<10	NA
Hexachlorobutadiene	126	11%	102	1%	102	2%	<10	23%
Naphthalene	31	59%	97	8%	87	7%	12	13%
Surrogates								
1,2-Dichloroethane-d4	91	1%	90	3%	96	1%	100	1%
Toluene-d8	88	2%	90	2%	99	1%	101	0%
Bromofluorobenzene	100	1%	92	2%	94	0%	106	3%

NA = Not Calculated because one or more points were below the detection limit.

a = Results from the repeat test were within the 70-130% recovery or the +/-30%RSD criteria.

Discussion of Results

The background levels in each of the tubing types were acceptable for most soil gas applications. The target VOCs that were detected generally have risk-based screening levels that are at least one order of magnitude higher than the background concentrations measured in the section of tubing. Recovery through the tubing was problematic in several types of tubing for VOCs with low vapor pressure.

Nylaflow® tubing exhibited several low concentrations of background VOCs, including an average Toluene concentration of 0.20 ppbv detected in all nine runs. Benzene, Propylbenzene, and Ethanol were detected in the majority of the runs and several non-target compounds were occasionally detected as well. Evaluating the concentration for each consecutive run, the trend indicated that the off-gassing did not decrease significantly during the sequence of test runs, suggesting a constant off-gassing of the VOCs from the tubing.

Additionally, Nylaflow® demonstrated good inertness for sub-ppbv VOC concentrations with recoveries generally meeting the 70-130% recovery criteria. Three compounds exceeded the upper limit of 130%. The background concentrations of Ethanol measured in the Nylaflow® tubing contributed to its high recovery. Both 1,2,4-Trichlorobenzene, and Naphthalene exhibited low recovery. The data for 1,2,4-Trichlorobenzene and Naphthalene reflects an improvement in recovery for each sequential test standard. The first test run through the tubing yielded a recovery of 22% and 12% for 1,2,4-Trichlorobenzene and Naphthalene respectively. The second run yielded 46% and 33% respectively, with the final run yielding recoveries of 67% and 48%. This indicates that active sites may be present on the inner surface of the Nylaflow® tubing and exposure to the humidified VOC standard may deactivate the surface. These results suggest that 6L canister samples, for example, would have less bias than 400 cc canister samples, if equal lengths of tubing were used in the sample collection, because the volume of any affected vapor would be a smaller portion of the larger sample.

The PEEK tubing exhibited less background than the Nylaflow® tubing both in terms of the number of VOCs detected and the frequency. PEEK tubing performance for VOC recovery was also generally acceptable. Several compounds were outside the recovery and precision requirements, but the non-compliance was not confirmed in the repeated test.

Teflon® tubing demonstrated the best performance with very low VOC background contribution and excellent inertness. The only detection of significance for the Teflon® tubing was the non-target compound 1,1-Difluoroethane with an average concentration of 5.0 ppbv in 67% of the test runs. Because Teflon® is a polymer of fluorinated ethylene, the 1,1-Difluoroethane is most likely originating from the Teflon® material. Teflon® also demonstrated the best performance as measured by reactivity. All VOCs recovered within 70-130%, and the relative standard deviation was well below 30% across the board.

Of the four types of tubing, polyethylene exhibited the highest frequency and concentration of artifacts and the poorest performance for VOC recoveries. Both low concentrations of target VOCs and unexpectedly high concentrations of heavier hydrocarbons were present in the background tests. Of note, Trichloroethene and Tetrachloroethene were detected in all six runs as well as were Carbon Disulfide, Toluene, Ethyl Benzene, Xylenes, Styrene, 1,2,4-Trimethylbenzene, 1,4-Dichlorobenzene and Naphthalene. Concentrations were relatively consistent over the consecutive runs with only marginal decreases in background concentrations observed. This trend indicates that the off-gassing of VOCs from the tubing may be relatively constant over a sampling period. The hydrocarbons detected were generally alkenes in the C8 to C12 range. Unlike the target VOCs, these hydrocarbons exhibited a more marked decrease in concentration with each consecutive run.

Polyethylene performed poorly in the reactivity test as well. In general, the VOC recovery through polyethylene tubing decreased as a function of vapor pressure. The VOCs with the lowest vapor pressure exhibited extremely poor recovery with several

compounds recovering less than 10% of the expected concentration. Additionally, several VOCs demonstrated a large positive bias through the polyethylene tubing. 1,1,2,2-Tetrachloroethane recovery was high due to an interference with a co-eluting hydrocarbon peak, and Toluene recovery was elevated due to contribution from the tubing material. The presence of background VOCs coupled with VOC losses through the tubing suggest competitive adsorption is occurring on the polyethylene surface. These surface interactions would appear to have the most detrimental impact when polyethylene tubing is used to collect VOCs in the sub-ppbv concentration range.

The polyethylene tubing used for the testing was obtained directly from the distributor in a sealed plastic bag and was tested after only minimal exposure to the ambient air. Storing tubing in an open environment or purging the tubing may minimize VOC concentrations from the polyethylene material. As a follow-up test, a section of polyethylene tubing used in the field was evaluated to compare background concentrations. Similar VOCs were detected, albeit at lower concentrations. Specifically, the hydrocarbons were reduced by several orders of magnitude in this limited test. The variability in the tubing background detections for polyethylene tubing suggests that the collection of field blanks through the sample tubing may be an important quality control measure to identify background VOCs and aid in the interpretation of soil gas measurements at the sub-ppbv levels.

Evaluation of media

When soil gas samples are submitted to a fixed laboratory for analysis, Summa canisters are typically the collection media of choice for trace level analysis due to their inertness. Samples can be stored up to 30 days for most VOCs^{2,3} and canisters may be certified as clean down to sub-ppbv levels by the laboratory. However, Tedlar® bags are sometimes used as a collection device, either as an intermediate or final container. As an intermediate container, the Tedlar® bag allows the sampler to conveniently perform "real-time" tests for the leak check compound, evaluate purge volumes, and obtain data on biogenic gases using hand-held devices. After the measurements have been performed, the Tedlar® bags can be transferred to Summa canisters for shipment to the laboratory for VOC analysis and confirmation of biogenic gases. As a final container, the Tedlar® bag may be analyzed on-site for VOCs immediately following sample collection. The short residence times for samples stored in Tedlar® bags are expected to minimize potential VOC losses.

While the lack of chemical inertness is typically cited as a limitation of Tedlar® bags, very little information is available regarding the background contribution from Tedlar® bags. Neither the background contribution nor the reactivity of Tedlar® bags has been evaluated for trace level VOC analysis under conditions of short hold times typically employed in the field.

Testing Protocol - Background Contribution

To evaluate background VOC contribution of the Tedlar® bag, a zero-air 6L Summa prepared at 70% RH was used to flush and fill six 1L Tedlar® bags. Each bag was flushed with approximately 800 ml of the humidified zero air a total of three times. A final aliquot of 800 ml was metered into the bag for analysis. To simulate the short sample residence times in the Tedlar® bags, an aliquot from each Tedlar® bag was analyzed by GC/TOF-MS after twenty minutes had elapsed. More than 60 target VOCs were evaluated as well as unknown VOCs. Only the detected compounds are presented in Table 4. VOC concentrations detected at less than 2x background levels were not considered significant.

Table 4. Summary of VOC Detections in Tedlar® Bags

Compound	Average Conc. (ppbv)	Frequency of detection
Propene	0.053	17%
Chloromethane	0.056	67%
Ethanol	2.2	100%
Carbon Disulfide	0.84	100%
Acetone	1.6	100%
2-Propanol	2.6	100%
Methylene Chloride	0.25	100%
Hexane	0.092	33%
2-Butanone	0.16	100%
Toluene	0.16	100%
m,p-Xylene	0.073	100%
Styrene	0.080	100%
Naphthalene	0.33	100%
Phenol	39	100%
Hydrocarbon C6	1.4	17%
Hydrocarbon C7	0.43	17%
Hydrocarbon C8	1.2	33%
Hydrocarbon C9	1.6	100%
Hydrocarbon C9	1.7	50%
Hydrocarbon C9	1.9	17%
Hydrocarbon C9	0.57	17%
Hydrocarbon C10	1.0	17%
Hydrocarbon C11	0.34	17%
Hydrocarbon C14	2.4	100%
Hydrocarbon C14	1.2	100%
Hydrocarbon C14	2.5	100%
Hydrocarbon C14	1.4	100%
Hydrocarbon C14	1.1	83%
Hydrocarbon C14	0.97	67%
Hydrocarbon C14	1.1	50%
Hydrocarbon C14	1.1	33%
Hydrocarbon C14	1.2	33%

Testing Protocol - Reactivity

To evaluate the inertness of Tedlar® bags for trace level VOC soil gas applications, a calibration standard prepared at approximately 0.5 ppbv and 70% RH was used as the vapor source. The standard was analyzed directly to determine the actual concentrations. Each 1L Tedlar® bag was flushed three times with the calibration standard prior to use. Approximately 800 ml of the standard was added to each Tedlar® bag. After a duration of 20 minutes, each bag was analyzed by GC/TOF-MS. The results are summarized in Table 5. The asterisked compounds were detected as background VOCs in the evaluation of Tedlar® bag background contribution. Recoveries outside of 70-130% and precision outside 30%RSD are highlighted.

Table 5. Summary of VOC Recovery from a Tedlar® Bag

Compound	Average Recovery	%RSD
Freon 114	94%	9%
Chloromethane	104%	2%
Vinyl Chloride	101%	8%
1,3-Butadiene	89%	17%
Bromomethane	101%	9%
Chloroethane	95%	8%
Freon 11	98%	4%
Ethanol*	128%	38%
1,1-Dichloroethene	99%	7%
Freon 113	99%	7%
Carbon Disulfide*	259%	43%
Acetone*	252%	45%
2-Propanol*	355%	80%
3-Chloroprene	102%	7%
Methylene Chloride*	185%	64%
trans-1,2-Dichloroethene	149%	15%
Methyl tertiary butyl ether	149%	13%
Hexane	98%	6%
1,1-Dichloroethane	97%	7%
cis-1,2-Dichloroethene	97%	7%
2-Butanone*	102%	3%
Chloroform	98%	7%
Tetrahydrofuran	100%	6%
Cyclohexane	101%	5%
1,1,1-Trichloroethane	97%	7%
Carbon Tetrachloride	98%	6%
2,2,4-Trimethylpentane	97%	7%
Benzene	96%	6%
Heptane	97%	7%
1,2-Dichloroethane	95%	9%
Trichloroethene	96%	7%
1,2-Dichloropropane	94%	8%
1,4-Dioxane	103%	5%

Compound	Average Recovery	%RSD
Bromodichloromethane	95%	8%
cis-1,3-Dichloropropene	93%	8%
4-Methyl-2-pentanone	99%	8%
Toluene*	120%	6%
trans-1,3-Dichloropropene	92%	8%
1,1,2-Trichloroethane	93%	8%
Tetrachloroethene	95%	6%
2-Hexanone	94%	9%
Dibromochloromethane	92%	8%
1,2-Dibromoethane	93%	8%
Chlorobenzene	91%	7%
Ethylbenzene	98%	5%
m,p-Xylene*	98%	4%
o-Xylene	94%	5%
Styrene*	94%	5%
Bromoform	89%	8%
Cumene	93%	7%
1,1,2,2-Tetrachloroethane	88%	8%
Propylbenzene	95%	8%
4-Ethyltoluene	96%	7%
1,3,5-Trimethylbenzene	92%	9%
1,2,4-Trimethylbenzene	95%	8%
1,3-Dichlorobenzene	84%	9%
1,4-Dichlorobenzene	83%	9%
alpha-Chlorotoluene	79%	11%
1,2-Dichlorobenzene	87%	9%
1,2,4-Trichlorobenzene	68%	11%
Hexachlorobutadiene	91%	8%
Naphthalene*	126%	19%
Surrogates		
1,2-Dichloroethane-d4	101%	2%
Toluene-d8	102%	1%
Bromofluorobenzene	104%	2%

Discussion of Results

Despite the short residence time of the zero air in the Tedlar® bag and pre-flushing of the bag prior to filling, a significant number of VOCs were detected at ppbv levels. Thirteen compounds were detected in all six bags and nine compounds had concentrations above 1 ppbv. Several low volatility compounds were detected including Phenol at an average concentration of 39 ppbv as well as several heavy C14 hydrocarbons. As with the tubing, the target VOCs that were detected generally have risk-based screening levels that are several orders of magnitude higher than the background concentrations measured in the Tedlar® bags.

When evaluating the VOC recovery in the Tedlar® bags, several compounds demonstrated high recovery and variability. Ethanol, Carbon Disulfide, Acetone, 2-

Propanol, and Methylene Chloride were all detected at ppbv levels in the background study resulting in high recovery at a spiking concentration of 0.5 ppbv. Additionally, the recoveries for this set of compounds were highly variable suggesting inconsistent background contributions from the each bag. While trans-1,2-Dichloroethene and Methyl tertiary butyl ether were not detected as background VOCs, they both exhibited high recovery but acceptable precision. Similar to the Nylaflow® tubing recovery study, 1,2,4-Trichlorobenzene exhibited low recovery. The acceptable recovery for Naphthalene was unexpected, since previous internal tests performed by the laboratory yielded recoveries of <50% from a Tedlar® bag. However, the background concentration (~0.33 ppbv) measured in the Tedlar® bag appears to have contributed to the final concentration in the recovery study.

Leak Test Considerations

In addition to the tubing and collection media used in the sampling train, selection of the leak check compound can also have implications in meeting the required data quality objectives. Leak tests are performed by exposing potential leak sites such as sample train fittings and the probe seals to a known compound during sample collection. The soil gas sample is then analyzed either in the field or by the fixed laboratory to determine if the sample was compromised by ambient air intrusion.

Various leak check compounds are suggested in regulatory guidance. Some of the leak check compounds currently being used in the field are "over the counter" products such as rubbing alcohol (2-Propanol), shaving cream (Isobutane), and Butane lighters. Other recommended leak check compounds include Helium and Sulfur Hexafluoride (SF₆).⁴ The "over the counter" leak check compounds are readily accessible and inexpensive, while Helium requires a pressurized cylinder and regulator and SF₆ is typically available by special order only.

Several factors should be considered when choosing the leak check compound for soil gas sampling at a vapor intrusion site. First, the leak check compound should not be present at the contaminated site. For example, using a hydrocarbon leak check compound such as butane or pentane is not appropriate for a fuel-contaminated site and may lead to an erroneous positive leak test. SF₆ is a safe choice since it is not found in nature; however, one drawback of SF₆ is its high cost.

Secondly, potential analytical interference from the leak check compound needs to be evaluated. Many of the recommended leak check compounds exhibit volatility similar to the compounds of concern. The presence of these leak check compounds in soil gas samples may compromise the laboratory reporting limits even at concentrations considered to pass the leak test criterion. As an example, the leak check criterion of <10 µg/L cited in the Cal EPA 2003 Advisory⁵ translates to a 2-Propanol concentration of approximately 4 **ppmv**. When the data quality objectives require **ppbv** reporting limits for risk assessment, concentrations of the leak check compound nearing the part per million ranges require the laboratory to severely dilute the sample so as not to overwhelm the instrumentation. Helium and SF₆ do not interfere with VOC analysis by TO-15 and

are recommended as leak check compounds when soil gas screening levels require low analytical reporting limits.

Finally, careful consideration should be given to the purity of the leak check compound. Some of the "over the counter" products contain VOC impurities that may be compounds of concern at a vapor intrusion site. For example, laboratory analysis of a commercially available Butane lighter indicated the presence of Benzene in the Butane. The presence of unexpected impurities from the leak check compound in soil gas samples may confound the vapor intrusion pathway assessment. With screening levels in the sub-ppbv range, purity may become an issue when using an "over the counter" product.

CONCLUSION

As soil gas measurements become more widely used to assess vapor intrusion pathways, sampling media and procedures must be carefully evaluated to insure that data integrity is maintained and project objectives are met. When sub-ppbv reporting limits are required for soil gas samples to meet risk-based screening levels, sample train components and sampling protocols have the potential to impact the soil gas measurement. The background evaluations and the recovery tests performed on Nylaflo[®], PEEK, Teflon[®], and polyethylene tubing as well as Tedlar[®] bags demonstrate the potential for artifacts and recovery bias due to the media selection. Additionally, the appropriate selection of the leak check compound for the leak test can provide quality control in the field without compromising the analytical data or the reporting limit. To successfully meet the challenge of lower screening levels for soil gas, the laboratory and the engineering firm overseeing the field activities must partner to insure quality objectives are met.

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