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Evaluation of Sample Recovery of Malodorous Gases from Air Sampling Bags, SPME, and Sampling Canisters

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Abstract. *Odorous gases associated with livestock operations are complex mixtures of hundreds if not thousands of compounds. Research is needed to know how best to sample and analyze these compounds. The main objective of this research was to compare recoveries of a standard gas mixture of 11 odorous compounds from the Carboxen/PDMS 75 μ m SPME fibers, PVF (Tedlar), FEP (Teflon), foil, and PET (Melinex) air sampling bags, and standard 6 L Stabilizer™ sampling canisters after sample storage at room temperature. A standard mixture consisted of 7 VFAs from acetic to hexanoic, and 4 semi-VOCs including p-cresol, indole, 4-ethylphenol, and 2'-aminoacetophene with concentrations ranging from 5.1 ppb for indole to 1,270 ppb for acetic acid. On average, SPME had the highest mean recovery for all 11 gases of 106.2%, and 98.3% for 0.5 and 24 hrs sample storage time, respectively. This was followed by the PET bags (71.7% and 47.2%), FEP bags (75.4% and 39.4%), in-house-made Tedlar bags (47.3% and 37.4%), commercial Tedlar bags (67.6% and 22.7%), foil bags (16.4% and 4.3%), and canisters (4.2% and 0.5%), for 0.5 and 24 hrs, respectively. VFAs had higher recoveries than semi-VOCs for all bags and canisters. New FEP bags and new foil bags had the lowest and the highest amounts of chemical impurities, respectively. New commercial Tedlar bags had measurable concentrations of DMAC and phenol. Foil bags had measurable concentrations of acetic, propionic, butyric, valeric and hexanoic acids. Further research is warranted to determine how recoveries from bags affect odor concentrations as measured by olfactometry.*

Keywords. Air sampling, sample storage, SPME, sampling canister, SUMMA, Tedlar, Melinex, Nalophan, VFAs, p-cresol.

Introduction

Odorous gases associated with livestock operations are very complex mixtures of hundreds if not thousands of compounds. The chemical characterization of individual compounds in these mixtures is extremely challenging. Odor-defining gases are often semivolatile organic compounds (semi-VOCs) characterized by relatively high-molecular weight, high boiling points and high polarity (Wright et al. 2004). These compounds are particularly susceptible to being adsorbed onto contact surfaces and difficult to recover from sample containers such as air sampling bags. In addition, very low concentrations often preclude compound detection and identification with conventional GC-MS. These characteristics present a unique analytical challenge because special considerations are needed for air sample collection, preparation and analysis.

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Scientists have recognized for some time that Tedlar is not the perfect material for gas sampling bags. Though it is relatively inert, there is evidence of adsorption and desorption of some chemical species to the Tedlar (McGarvey and Shorten, 2000; van Harreveld, 2003). Keener et al. (2002) quantified recoveries of 19 odorous gases from Tedlar bags using sorbent tubes, and concluded that Tedlar bags emit acetic acid and phenol and greatly adsorb indole, skatole, p-cresol, 4-ethylphenole, nonanoic and octanoic acids.

Wright et al. (2004) identified more than 60 odorous compounds in exhaust air from a swine barn, many of which were also present in air at and downwind from a beef cattle feedlot. Wright et al. (2004) used SPME for air sample collection and a simultaneous chemical identification and olfactory analysis on a MDGC-MS-O system. The most preeminent compound for both the source and the distant locations was p-cresol. Other compounds including: 4 ethylphenole, 2'-aminoacetophenone, indole, and a suite of volatile fatty acids were also present in nearly every air sample collected with SPME. The highly polar and semivolatile compounds that appear to be odor-defining for livestock operations (Wright et al., 2004) are potentially the most offensive odorants for swine and cattle feedlots. However, no data exists on sample recoveries of these compounds from SPME.

The primary objective of this study was to determine sample recoveries from a standard gas mixture of odorous gases from SPME, 5 types of air sampling bags, and stainless steel (SS) sampling canisters under typical sample storage conditions, i.e., room temperature and 24 hrs. A secondary objective was to identify impurities in new air sampling bags and sampling canisters that can potentially affect air samples.

Materials and Methods

Standard Gases

A reliable and stable gas standard is needed when challenging different approaches for air sampling. Permeation sources have proven to be an effective and economical alternative to cylinders of compressed gas standards. Stable concentrations of 11 VOCs and semi-VOCs listed in Table 1 were maintained using permeation sources (Spinhirne and Koziel, 2003). The 7 volatile fatty acids (VFAs) were generated with a model 491M standard gas generator (Kintek, LaMarque, TX) with a permeation oven temperature of 80 °C. The 4 semi-VOCs were generated in an in-house-made gas generator utilizing a permeation oven temperature of 50° C. The homemade generator consisted of a 1 L glass container, a heating mantle (Glas-Col, Terre Haute, IN), a temperature controller ($\pm 0.2^\circ\text{C}$) (Cole Parmer, Vineland, NJ), and a 0-5 LPM mass flow controller (Aalborg, Orangeburg, NY). The components of the homemade generator were connected using pre-cleaned stainless steel tubing and Swagelok compression fittings.

Table 1. Target compounds and their respective concentrations used for sample recovery experiments.

Name	Mean Concentration (ppb)	Standard Deviation (ppb)	Variance (%)	Maximum Concentration (ppb)	Minimum Concentration (ppb)
Acetic acid	1,270	184	14.6	1,630	1,090
Propionic acid	601	141	23.4	867	481
Isobutyric acid	343	118	34.3	559	254
Butyric acid	378	73.8	19.5	520	310

Isovaleric acid	263	56.6	21.5	364	199
Valeric acid	235	58.3	24.8	343	179
Hexanoic acid	195	54.2	27.8	293	142
P-cresol	29.6	5.10	17.1	37.2	24.5
2'-Aminoacetophenone	13.2	12.8	96.8	34.2	1.30
Indole	5.10	5.10	98.7	11.1	0.70
4-Ethylphenol	13.6	16.1	119	41.3	3.50

The permeation tubes were weighed once every 2 weeks to measure emission rates and to estimate standard gas concentrations based on the weight loss, elapsed time, and the total air flow rate (Table 1). Standard gas concentrations were generally consistent with those measured at or downwind from livestock operations (Kozziel et al. 2004, McGinn et al., 2003, Zahn et al. 1997). Concentrations of VFAs were generally inversely proportional to MW. Also, concentrations of VFAs were higher than semi-VOCs. McGinn et al. (2003) measured concentrations of many target gases in downwind adjacent locations to beef cattle feedlots in Alberta and reported maximums ranging from 9 ppt for p-cresol to 46.5 ppb for acetic acid. Zahn et al. (1997) reported much higher concentrations in ambient air at a swine slurry basin in Iowa of nearly 200 ppb for both 4 ethylphenol and 2'-aminoacetophenone and VFA concentrations ranging from 155 ppb for hexanoic to 710 ppb for propionic acid.

Triplicate QA/QC samplings with a single Carboxen/PDMS 75 μ m SPME fiber were used to confirm the stability of the standard gas daily. Generated concentrations were stable for all VFAs and p-cresol. However, concentrations of 2'-aminoacetophenone, indole, and 4-ethylphenol varied widely. Thus, all results were normalized to changing standard gas concentrations.

SPME fibers were purchased from Supelco (Sigma Aldrich, Bellefonte, PA). All SPME fibers were conditioned according to manufacturer guidelines. The Carboxen/PDMS 75 μ m fiber coating was used because it adsorbed adequate amounts of VFAs with a relatively short sampling time (Kozziel and Spinhirne, 2002). Three SPME fibers were used for this experiment. The standard gas mixture was always sampled with SPME for 5 min. SPME was inserted to a continuously generated gas stream through a sampling port fitted with septum (Spinhirne and Kozziel, 2003). This was followed by immediate insertion of SPME into GC injector for time = 0 hrs. Alternatively, SPME assemblies with holders were wrapped with clean aluminum foil and left at room temperature (\sim 22 $^{\circ}$ C) for 0.5 or 24 hrs before analysis on GC-MS. MS detector response to 0 hrs sample storage time was used as a reference to which all samples preserved for 0.5 and 24 hrs were compared. It can be reasonably assumed that the loss (or gain if ambient air has target compounds) of gas samples within the few seconds between the end of sampling and the injection to GC injector is negligible. All SPME fibers were reused and cleaned by complete thermal desorption in the GC injector before each sampling. SPME fiber blanks were always tested between sample analyses to minimize the possibility of sample carry-over and other interferences.

Sample Recovery from Air Sampling Bags

Commercial Bags

All bags were 10 L capacity fitted with a single polypropylene septum fitting. The choice of bags was as follows: (a) Tedlar (polyvinyl fluoride, PVF), (b) in-house-made Tedlar, (c) FEP (Teflon),

(d) foil, and (e) PET. Bags (a) (cat. #232-08), (c) (custom-made to 10 L capacity), and (d) (cat. #245-28) were purchased from SKC (Houston, TX). FEP bags were chosen because of their inertness. PVF is currently the industry standard for sampling of odor in the U.S. FEP bags are advertised as the most chemically inert of any bags. Foil grab bags are a relatively new product specifically recommended for low molecular weight compounds which are unstable when collected with standard Tedlar bags. Foil bags are made with four layers consisting of the aluminum, low density polyethylene (LDPE), polypropylene, and LDPE (wet surface). Total wall thickness for all bags was measured with a micrometer and was equal to 0.050, 0.052, 0.050, 0.125, and 0.015 mm for bags (a) through (e), respectively.

In-house-made Bags

The in-house-made Tedlar bags (b) were made at the Olfactometry Laboratory at West Texas A&M University (Parker et al., 2003). The PVF film TST20SG4 was ordered directly from DuPont™ in 33 cm wide rolls of length 762 m. This type of Tedlar® film was recommended by DuPont™ for the construction of gas sampling bags (Dupont, 2003c). The film was cut into lengths of 92 cm for an approximate capacity of 10 L. The film was folded lengthwise, then heat sealed on the three edges using a Vertrad Model 14OB open back heat sealer with 0.63 cm seal width and 51 cm maximum seal length (Therm-O-Seal, Mansfield, TX). A polypropylene valve was installed in one end of the bag prior to making the last seal. All in-house made bags were subjected to conditioning consisting of a ~1 L fill with bottled ultra pure odor free air (MG Industries, Malvern, PA), followed by 24 hr heating at 100 °C in the standard drying oven (VWR Model 1325), purging with vacuum, second fill to ~8 L with ultra pure air, and the final purging with vacuum. Post-manufacturing conditioning was found to remove any residual odor (Parker et al., 2003).

The PET (a.k.a. Melinex) bags were made from a 5000 m x 1.14 m wide roll of polyethylene terephthalate film and polypropylene fittings by Geordie Galvin and Neale Hudson from The Queensland Department of Primary Industries in Toowoomba, Australia. PET bags meet the Australian (Australia Standards, 2001) and the European olfactometry standards where they are listed as “Nalophan” (CEN, 1999) and are popular choice of air sampling bags for collection of livestock odor samples (Galvin et al, 2002). All PET bags were the same size and used the same type of valves as the Tedlar, FEP, and foil bags.

Standard Gas Sampling

All bags were filled with the standard gas using a special dispensing port located immediately downstream from the SPME sampling bulb (Spinhirne and Koziel, 2003). Triplicate samples for 0.5 and 24 hrs holding/preservation time were collected in air sampling bags sequentially in 1-2 hrs intervals. The same volume of standard gas (5 L) was used to fill each bag. This was confirmed by checking gas flow rate and by measuring time needed to dispense 5 L of standard gas. The sequence was such that one bag was filled with 5 L, purged with vacuum, and then filled again for the sample at 0.5 hr storage time. Then another bag of the same material type was filled in the same manner and was held for 24 hrs before analysis. After 0.5 hr the first bag was sampled with SPME for 5 min and the resulting sample was immediately analyzed with GC/MS. Next, a SPME fiber blank was used to confirm that the SPME fiber and the GC column were free of target and non-target compounds. Then a QAQC 5 min SPME sample collected from the standard gas was analyzed to confirm that the concentration of the gases used to fill the bags were in fact stable. Then the process was repeated for the 2nd and 3rd replicates of both the 0.5 and 24 hr hold times. All bags were held on clean laboratory bench-top at room temperature. Sampling with SPME was facilitated by insertion of SPME through valve septum. SPME holders were secured with a ring stand and clamps during sampling.

Interfering Chemicals in New Air Sampling Bags

In addition, chemical backgrounds of all types of bags were studied using SPME extractions from new bags that came from the same batch as the bags used for sampling of standard gas. The importance of bag background is critical to accurately determine chemicals already present in new bags (Keener et al. 2003). Bag blanks were filled just like the standard gas samples (5 L fill, purge, 5 L fill) except that the pure air supply was used to fill the bags rather than the standard gas output. Pure air was generated by zero air generator (model 737, AADCO, Village of Cleves, OH). Air samples from bags were collected using 5 min extractions with SPME. Triplicates of bag blanks were used for in-house-made Tedlar for 0.5 and 24 hrs. For other bags, only 2 replications were used per 0.5 and 24 hrs holding/preservation times.

Sample Recovery from Sampling Canisters

Sampling canisters, often referred to as SUMMA canisters, are used in EPA methods TO-14 and TO-15 for sampling of VOCs in ambient air. They are a rugged, proven, and convenient way of collecting air samples in the field. No experimental data related to sample recovery for target compounds used in this study is available. However, Kelly and Holdren (1995) inferred that cresols and acetophenone are not likely to be stable in canisters. In our experiment we used Stabilizer™ canisters (model X56L-4MGC, 6 L, from Meriter, San Jose, CA) that were obtained on loan from the University of Texas at Austin. Stabilizer canisters are made from a low carbon 316L stainless steel and are subjected to electro-polishing that removes impurities from the inside surface while creating a passive layer enriched in chromium oxide. Canisters were cleaned using standard procedures and evacuated at the UT-Austin prior to the experiment in Amarillo. Canisters that served for background blanks were filled from the same port as their bag counterparts. All the canisters regardless of sample type were filled to atmospheric pressure using the gauge on the individual can. A small amount of stainless steel tubing was used to introduce standard gas in the recovery canisters due to their bulky dimensions. Just prior to sampling, a septa and modified Swagelok plug were inserted in place of the sample valve of the canister to seal off the void left by removing the valve. This allowed access with SPME without allowing mixing of ambient air and subsequent dilution or loss of sample. Sampling with SPME was identical to the one used for all bags.

Analyses on GC/MS

The samples collected on Carboxen/PDMS fibers were analyzed with a Varian 3800/Saturn 2000 GC/MS system. SPME fibers were introduced to GC injector and held at 250 °C in the splitless mode with a flow of 1 mL/min He for 33 min to completely desorb the sample. It is reasonable that a shorter desorption time would have adequately cleansed the fibers. However, it was more practical to leave the fiber in for the whole GC run time of 33 min and then immediately reuse it for another sampling rather than allowing it to be contaminated by ambient air within the laboratory between samplings.

The GC oven temperature program started at 60 °C then ramped up to 110 °C at a rate of 60 °C/min. The analytes of interest eluted in the next ramp of 10 °C/min that elevated the oven temperature from 110 °C to 220 °C. A final ramp of 60 °C/min increased the oven temperature to its maximum of 260 °C with a hold time of 20 min to clean the column and prevent carryover from one GC run to the next.

The ion trap MS measured a wide mass range between 30 and 460 m/z to aid in identification of background compounds. Only the strongest ion (quan ion) for the target compounds was used to calculate area as a MS detector response. This quan ion, usually different for each chemical,

was integrated for area counts. Area counts were then used to calculate percent recoveries for each of the 11 target compounds (Table 1). MS responses to triplicate SPME samples of gas standard with 0 hr holding/preservation time were used as a reference, i.e., 100% recovery for all samples with holding time of 0.5 and 24 hrs.

Results

Interfering Chemicals in New Air Sampling Bags

A comparison of typical chromatograms of chemicals present in new air sampling bags and sampling canisters is presented in Figures 1 and 2. Part A represents zero air while Parts B, C, D, E, F, and G represent Teflon bag (B), in-house-made Tedlar bag (C), commercial Tedlar bag (D), foil bag (E), PET bag (F), and SUMMA canisters (G), respectively. The scale for part E of Figure 1 is 10 times higher than the others because of the high levels of contaminants in the foil bag samples. Numbered peaks are listed in Table 2. All chemicals were identified based on the match with the NIST (Varian Instruments, 1998) spectral library. The target compounds, N,N-dimethyl acetamide (DMAC), and phenol were identified with a user spectral library. All chromatograms have a number of silanes and siloxanes represented by compounds #7, #9, #13, #15, #21, #23, #24 and #26 through #30 in Figure 1. These are typical interferences that possibly originated from bag septum or GC injector septum. Backgrounds of Tedlar and foil bags (Parts D and E) did not show many interfering silanes and siloxanes likely due to much greater amounts of other impurities with lower molecular weight (MW). This process of competitive adsorption to solid SPME coatings, preferential extraction of light MW compounds ahead of heavier MW compounds is typical for relatively short sampling times (Jia et al. 2000; Koziel et al., 2000).

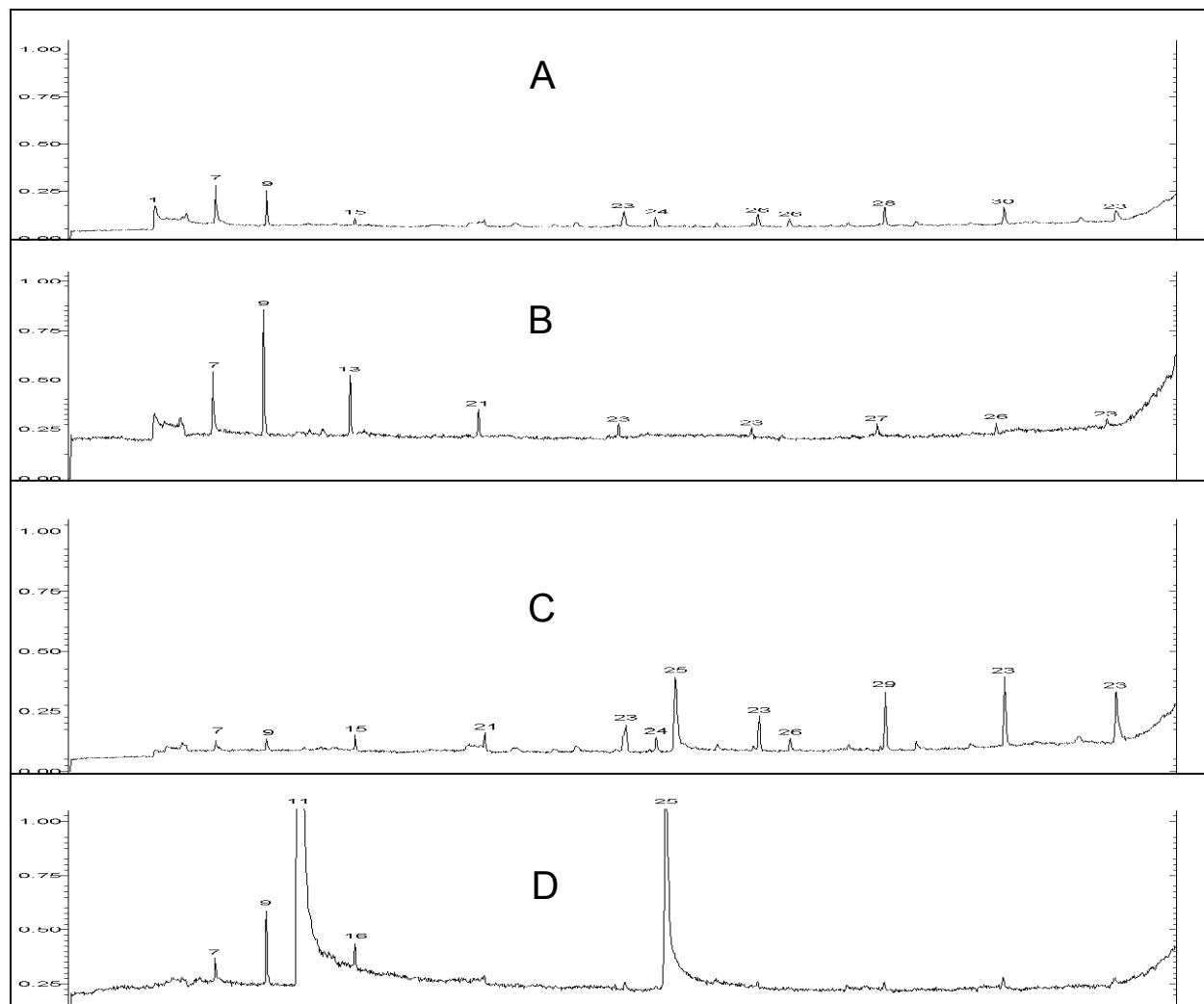


Figure 1. Chromatograms of 5 min extractions with SPME of zero air directly from pure air generator (A), from a Teflon bag (B), from an in-house Tedlar bag (C), from a commercial Tedlar bag (D), and from a commercial foil bag (E). The vertical scale for part E of Figure 1 is 10 times higher than the others. Numbered peaks are listed in Table 2.

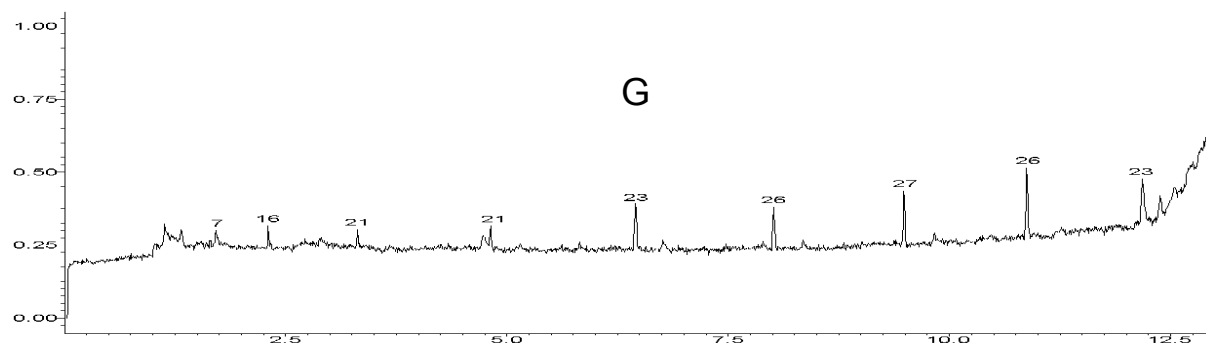
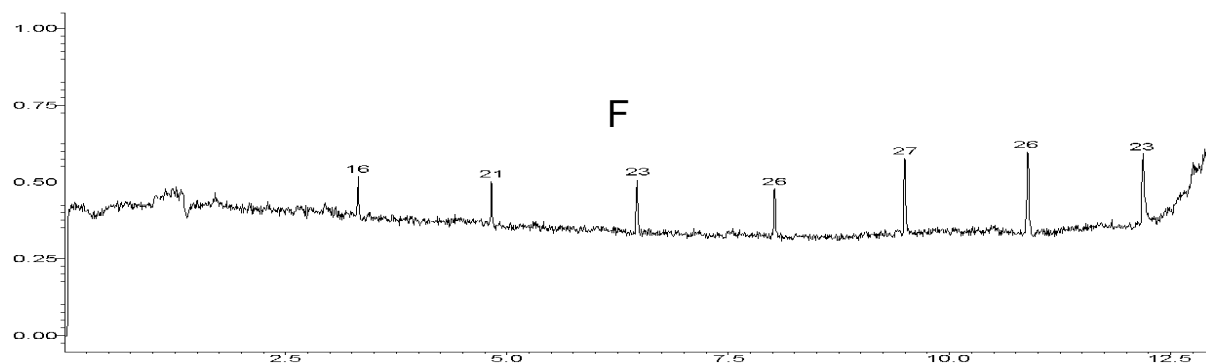


Figure 2. Chromatograms of 5 min extractions with SPME of zero air directly from (F) PET bag and (G) from SUMMA sampling canister. Numbered peaks are listed in Table 2.

Teflon bags (Figure 1, Part B) had the lowest number and amount of interfering compounds. No compounds other than silanes and siloxanes were identified. The in-house made Tedlar bags (Part C) had the second lowest background. The only interfering chemical from the in-house Tedlar bags was phenol (peak #25). However, the amount of phenol was approximately 10 times lower than in commercial Tedlar bags (part D). Large quantities of phenol in Tedlar bags were also reported by Keener et al., 2003.

Commercial Tedlar bags also had a significant amount of DMAC (peak #11), one of the most common latent solvents used in manufacturing Tedlar (USCAR, 2003). DMAC has a similar structure and MS spectrum to acetic acid. The apparent difference between the amount of impurities in commercial (Part D) and in-house-made (Part C) Tedlar bags is likely due to the additional steps used in post-manufacturing conditioning, i.e., fill, heat, purge, fill, and purge. The foil bags had the greatest amounts of impurities of all bags tested. The largest impurities occurred in the low MW compound region of the chromatogram, where these types of bags are designed to preserve gases better than others. Foil bags also had significant impurities of acetic, propionic, butyric, valeric, and hexanoic acids, i.e., target gases in this study. The concentrations of VFAs in foil bags were on the order of those typical in livestock operations. Thus, foil bags could potentially produce false positives for ambient air sampling at livestock facilities. Background impurities in PET bags and SUMMA canisters was very low.

Table 2. Chemicals identified in chromatograms of air samples from new air sampling bags and sampling canisters (Figures 1 and 2). Silanes and siloxanes are likely interferences from silicone septa. RT = residence time (min) in GC capillary column.

Peak#	RT	Peak Name
1	1.02	3-Amino-2-ethyl-butyric acid
2	1.06	Hexane, 1-(hexyloxy)-4-methyl-
3	1.10	Cyclopentane, 1-hydroxymethyl-1,3-dimethyl-
4	1.21	Isopinocampnone
5	1.30	?
6	1.60	Ethane, isothiocyanate-
7	1.73	Cyclopentasiloxane, decamethyl-
8	1.87	Silane, tetraethyl-
9	2.23	Cyclohexasiloxane, dodecamethyl-
10	2.68	Acetic acid
11	2.69	N,N-dimethyl acetamide
12	3.16	Propionic acid
13	3.31	1,1,1,3,5,7,9,11,11,11-Decamethyl-5-(trimethylsiloxy)hexasiloxane
14	3.32	Pinacolyl alcohol
15	3.37	Cycloheptasiloxane, tetradecamethyl-
16	3.37	Cyclotetrasiloxane, octamethyl-

17	3.71	Propionic acid, 2-methyl-, anhydride
18	4.00	Butanoic acid, 2-methyl-
19	4.53	Valeric acid
20	4.70	meso-2,5-Dimethyl-3,4-hexanediol
21	4.82	Silane, [[4-[1,2-bis[(trimethylsilyloxy)ethyl]-1,2-phenylene]bis(trimethyl-
22	5.45	Hexanoic acid
23	6.46	Cyclononasiloxane, octadecamethyl-
24	8.12	1,1,1,5,7,7,7-Heptamethyl-3,3-bis(trimethylsilyloxy)tetrasiloxane
25	7.01	Phenol
26	8.09	Tetracosamethyl-cyclododecasiloxane
27	9.49	Benzeneacetic acid, .alpha., 3,4-tris[(trimethylsilyloxy)-, trimethyl ester
28	9.58	Silane, [[4-[1,2-bis[(trimethylsilyloxy)ethyl]-1,2-phenylene]bis(oxy)]bis(trimethyl-
29	9.59	Thiosalicylic acid, O,S-di-trimethylsilyl-
30	10.98	Estra-1,3,5(10)-trien-17-one, 3,4-bis[(trimethylsilyloxy)-

Sample Recovery from SPME

Comparison of recoveries of 11 gases in standard mixture for room temperature sample storage and storage time of 0.5 and 24 hrs, respectively, is presented in Table 3. SPME fibers showed an excellent sample recovery. Average sample recovery for all 11 compounds sampled with 3 SPME fibers was 106% ($\pm 20.2\%$) for 0.5 hr storage time and 98% ($\pm 18.6\%$) for 24 hr storage time. This suggests that it could be expected to retain nearly all if not all target compounds in field samples if the sample is stored at room temperature and the storage time does not exceed 24 hrs. Longer than 24 hrs storage time may also be reasonable as there is no apparent decreasing trend for the majority of target compounds. However, further experiments are necessary to test this hypothesis. The sample recovery for p-cresol was 116.9% ($\pm 8.7\%$) and 92.5% ($\pm 10.3\%$) for 0.5 and 24 hrs sample storage times. The smallest variability between the 3 SPME fibers was observed for propionic acid ($\pm 2.3\%$) and the largest variability was observed for acetic acid and indole ($\pm 38.9\%$). The source of acetic acid variability was likely caused by acetic acid used in an adjacent laboratory.

Table 3. Comparison of recoveries of 11 gases in a standard mixture for room temperature sample storage and storage time of 0.5 and 24 hrs, respectively.

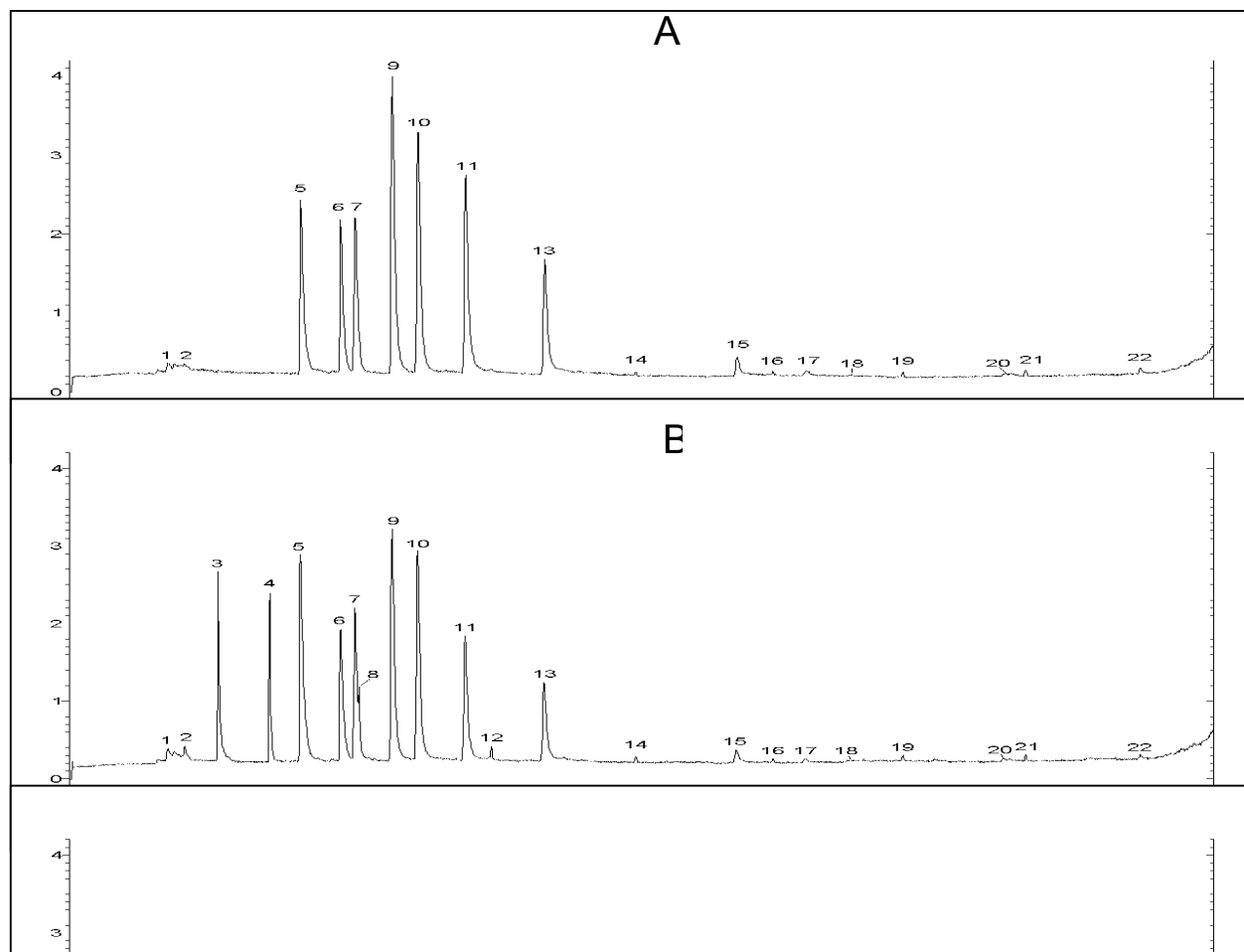
	Time (hr)	Sample Recovery (%)										
		AC	PR	IB	BU	IV	VA	HE	CR	EP	AM	IN
SPME (Cxn/PDMS)	0.5	119 (38.9)	105 (2.3)	108 (14.2)	99.9 (5.0)	127 (34.8)	109 (12.4)	105 (3.0)	117 (8.7)	86.3 (30.9)	89.7 (33.2)	102 (38.9)
	24	116 (34.2)	111 (2.0)	109 (10.6)	109 (3.6)	81.6 (40.4)	110 (9.7)	101 (5.6)	92.5 (10.3)	74.9 (28.0)	79.2 (32.4)	96.3 (27.8)
PET (Melinex)	0.5	84.8 (15.6)	88.0 (15.9)	105.1 (29.5)	81.9 (17.2)	88.6 (24.0)	67.6 (27.5)	63.0 (23.3)	36.0 (23.1)	36.4 (11.0)	27.4 (31.9)	0.0 (0.0)
	24	27.6 (10.6)	61.4 (15.1)	108.6 (41.7)	73.9 (32.6)	102 (30.2)	51.1 (33.2)	38.2 (21.2)	5.6 (4.2)	0.9 (1.6)	0.5 (11.7)	0.0 (0.0)

FEP (Teflon)	0.5	101 (8.2)	100 (7.9)	96.5 (9.2)	88.2 (6.6)	85.5 (4.0)	73.8 (1.6)	59.0 (4.9)	66.9 (6.3)	66.1 (8.6)	48.2 (32.9)	38.2 (38.7)
	24	45.4 (2.9)	65.8 (14.9)	67.8 (9.4)	53.8 (2.3)	61.8 (6.4)	24.9 (1.6)	12.5 (0.4)	28.6 (3.4)	24.3 (4.5)	20.4 (26.7)	24.7 (31.5)
In-house PVF (Tedlar)	0.5	68.6 (22.2)	85.8 (9.9)	84.6 (17.4)	70.1 (14.2)	74.3 (17.7)	62.7 (31.1)	51.1 (27.9)	13.3 (7.4)	0.0 (0.0)	0.5 (1.6)	8.5 (14.8)
	24	23.0 (13.2)	53.5 (16.1)	79.8 (20.3)	44.5 (13.5)	61.6 (11.6)	24.8 (10.3)	14.2 (7.4)	22.7 (34.3)	4.1 (5.0)	46.3 (76.9)	23.2 (9.9)
Commercial PVF (Tedlar)	0.5	72.9 (5.1)	83.1 (23.2)	86.2 (3.6)	84.7 (5.2)	86.2 (1.2)	72.3 (2.8)	64.3 (2.4)	16.0 (5.0)	28.9 (11.9)	33.4 (20.0)	67.4 (10.4)
	24	20.4 (4.0)	43.2 (9.9)	57.1 (12.4)	37.4 (15.7)	52.6 (15.8)	20.6 (11.2)	13.7 (8.4)	3.1 (0.9)	1.3 (2.2)	0.0 (0.0)	0.0 (0.0)
Foil (LDPE)	0.5	29.7 (57.5)	0.0 (3.9)	47.9 (17.3)	0.0 (4.4)	35.0 (4.6)	12.8 (1.5)	12.6 (6.5)	2.7 (4.2)	5.3 (4.2)	15.5 (24.7)	19.6 (39.4)
	24	0.0 (17.8)	0.0 (61.1)	23.0 (20.0)	6.2 (58.1)	12.9 (11.3)	0.0 (63.1)	0.5 (15.5)	3.7 (3.4)	0.8 (1.3)	0.0 (0.0)	0.0 (0.0)
Sampling canisters	0.5	10.2 (17.6)	12.5 (21.4)	2.2 (3.9)	3.1 (5.3)	1.6 (2.8)	1.0 (1.7)	0.8 (1.3)	2.9 (5.0)	0.4 (0.8)	7.5 (13)	0.0 (0.0)
	24	2.7 (3.2)	1.4 (2.5)	0.0 (0.0)	0.4 (0.7)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)

AC = acetic acid, PR = propionic acid, IB = isobutyric acid, BU = butyric acid, IV = isovaleric acid, VA = valeric acid, HE = hexanoic acid, CR = p-cresol, EP = 4-ethylphenol, AM = 2'-aminoacetophenone, IN = indole. Numbers in parentheses signify one standard deviation around the mean.

Sample Recovery from Air Sampling Bags

A typical chromatogram of standard gas sample sampled for 5 min with SPME (storage time = 0 hr) (Part A), from a commercial Teflon bag after 0.5 hr storage time (Part B), and from a commercial Teflon bag after 24 hrs storage time (Part C) is presented in Figure 3.



C

Figure 3. Chromatograms of standard gas sampled for 5 min with SPME directly from a standard gas and 0 hr storage time (Part A), from a Teflon bag after 0.5 hr storage time (Part B), and from a commercial Teflon bag after 24 hrs storage time (Part C). Peak #: 5 = acetic acid, 6 = propionic acid, 7 = isobutyric acid, 9 = butyric acid, 10 = isovaleric acid, 11 = valeric acid, 13 = hexanoic acid, 15 = p-cresol, 17 = 4-ethylphenol, 18 = 2'-aminoacetophenone, 20 = indole.

All chromatograms have identical scale to visualize the differences in sample recoveries. Teflon bags were chosen for this comparison because they had the most consistent standard gas sample recoveries of all 4 kinds of bags tested. Teflon bags had the lowest variability of between the 3 bags tested. Figure 3 shows the losses of standard gas introduced to Teflon bags. This loss is greater with time and is likely due to adsorption to bag wall, bag septum, and permeation to the ambient air outside the bag. Permeation sources commonly used for standard gas generation use Teflon for permeation (controlled diffusion) membranes. Other identified compounds were silanes and siloxanes similar to those listed in Table 1. No apparent products of chemical reactions were identified inside bags. This is consistent with the fact that the standard gas had no moisture or NO_x, i.e., substrates that could trigger chemical reactions. Chemical reactions involving target gases inside bags could occur in field air samples where moisture and possibly other substrate gases are abundant.

The sample recoveries for bags were generally less than those associated with SPME (Table 3). There was also a greater variability in recoveries between target compounds. Sample recoveries after 0.5 hrs were generally greater than recoveries after 24 hrs. PET bags had the best mean recoveries for target compounds among all bags tested. The average sample recovery was 71.7% and 47.2% for 0.5 and 24 hrs sample storage time, respectively.

Teflon bags had the second best recoveries equal to 75.4% ($\pm 11.7\%$) and 39.4% ($\pm 9.5\%$) for 0.5 and 24 hrs sample storage time, respectively. Light MW VFAs (from acetic to isovaleric) had a better mean recovery equal to 94.2% ($\pm 7.2\%$) and 58.9% ($\pm 7.2\%$) for 0.5 and 24 hrs sample storage times compared to recoveries for semi-VOCs equal to 59.8% ($\pm 15.5\%$) and 23.2% ($\pm 11.5\%$) for 0.5 and 24 hrs sample storage times, respectively. Teflon bags had a low variability of less than 15% for the 3 bags tested and all target compounds except 2'-aminoacetophenone (up to 32.9%) and indole (up to 38.6%). This variability was lower, on average, than the variability associated with SPME fibers. The sample loss was dependent on storage time. This was consistent with the information presented in Figure 3. The sample recovery for p-cresol was 67.5% ($\pm 6.3\%$) and 29.0% ($\pm 3.0\%$) for 0.5 and 24 hrs sample storage times. The 24 hr sample recovery for acetic acid was 45.4%. DuPont (2004a) lists the permeability of 13 compounds through FEP foil of which only the acetic acid was part of the standard gas mixture use in this study. The permeability of acetic acid is comparable to water

and lower than acetophenone with a similar chemical structure to the 2'-aminoacetophenone (DuPont, 2004a).

Tedlar bags made in-house had an average recovery of 11 target compounds equal to 47.3% ($\pm 14.9\%$) and 36.2% ($\pm 20.8\%$) for 0.5 and 24 hrs sample storage time, respectively. Sample recoveries had a greater variability compared to those of Teflon. Also, the recoveries of semi-VOCs were greater for 24 hrs storage compared to 0.5 hr storage. The recovery of p-cresol was 13.3% ($\pm 7.4\%$) and 22.7% ($\pm 34.3\%$) for 0.5 and 24 hrs sample storage time, respectively. One bag had a 580% recovery for indole compared to the average of the remaining 2 bags equal to 23.2%. This single recovery for indole was excluded from the mean recovery estimate. The reason for the variability associated with semi-VOCs is unknown. One possible explanation could be an experimental error.

Commercial Tedlar bags had an average recovery of 11 target compounds equal to 67.6% ($\pm 7.6\%$) and 22.7% ($\pm 7.4\%$) for 0.5 and 24 hrs sample storage time, respectively. The initial losses at 0.5 hr storage time were smaller compared to the Tedlar bags made in-house. However, less standard gas was recovered from commercial Tedlar bags after 24 hrs. Sample recoveries were similar to Teflon bags and had a smaller variability compared to Tedlar bags made in-house. The recoveries for p-cresol, 4-ethylphenole, and indole were 23.6% ($\pm 4.8\%$) and 3.1% ($\pm 0.9\%$), 31.2% ($\pm 11.6\%$) and 1.3% ($\pm 2.2\%$), 0% ($\pm 0\%$) and 0% ($\pm 0\%$) for 0.5 and 24 hrs sample storage time, respectively. These results are generally lower by 10 to 30% for VFAs and very similar for semi-VOCs to those reported by Keener et al (2002). Keener et al. (2002) found 5%, 7% and 0% recoveries for 24 hr storage time in Tedlar bags at room temperature for p-cresol, 4-ethylphenol, and indole, respectively. The 24 hr sample recovery for acetic acid was 20.4%, i.e., much smaller than those reported by Keener (2002). One possibility, is a large amount of co-eluting and interfering DMAC found in Tedlar bags (Figure 1, Part D). The permeability of acetic acid listed by DuPont (2004b) is higher than permeability of water.

Foil bags had an average recovery of 11 target compounds equal to 57.1% ($\pm 5.2\%$) and 25.5% ($\pm 22.2\%$) for 0.5 and 24 hrs sample storage time, respectively. However, new foil bags have significant amounts of acetic, propionic, butyric, valeric, and hexanoic acids. When these impurities are subtracted, the recoveries are lowered to 16.4% ($\pm 15.3\%$) and 4.3% ($\pm 22.9\%$). The recovery of p-cresol was low and equal to 2.7% ($\pm 4.2\%$) and 3.7% ($\pm 3.4\%$).

Sample Recovery from Sampling Canisters

Sample recoveries from SS sampling canisters are presented in Table 3. The recoveries were equal to 4.2% ($\pm 7.3\%$) and 0.5% ($\pm 0.6\%$) for 0.5 and 24 hrs sample storage time, respectively. There was no recovery for all target compounds after 24 hrs with the exception of acetic and propionic acids (2.7%) and ($\pm 1.4\%$). This poor recovery could be caused by adsorption to the walls of canisters and/or reactions in the presence of chromium oxides which coat the inside surface of canisters. The adsorption to stainless steel of VOCs and semi-VOCs has been known. However, the extent to which the sample loss occurred is somewhat surprising. Sampling with canisters cannot be repeated or enriched by priming, i.e., it is not possible to prime a canister, purge it, and then fill it with a sample again. Priming could be achieved with flow-through canisters (not SUMMA-type canisters that use vacuum to collect samples without a pump). In addition, we tried heating of several canisters to 50° C in the oven for 1 hr in an attempt to increase sample recovery. The second SPME sampling for 5 min was initiated immediately after the removal from oven. The resulting recoveries were not better than recoveries from canisters that were not subjected to elevated temperature.

Discussion

SPME Carboxen/PDMS 75 μm fibers appear to be excellent samplers for the target gases used in this study with the average sample recovery equal to 98% ($\pm 18.6\%$) for 24 hr storage time at room temperature. This information could be useful to the researchers using SPME for field sampling. The use of clean aluminum foil is recommended to prevent sample contamination. The effects of storage temperature, duration longer than 24 hrs, or sample recoveries of field samples were not tested, yet.

Sample recoveries for all other types of sampling media, i.e., bags and SS canisters were significantly lower. Some FEP and Tedlar films can permeate acetic acid (DuPont, 2004a and DuPont, 2004b). However, further studies are needed to determine the fate of target compounds for all types of air sampling bags used in this study. Sample recoveries for all types of media were associated with high variability except Teflon bags. The sources of variability can be associated with the (a) standard gas variability, (b) use of SPME fibers and their variable selectivity and affinity to target compounds, (c) use of plastic valves and silicone septa, (d) possibility of adsorption to walls and/or permeation. In real field air samples, water vapor and NO_x could also be present. Thus, gas reactions with OH radicals and NO_x could affect the concentrations and the make up of samples. However, more controlled experiments are needed to test these hypotheses. Priming, purging, and finally the collection of real air samples could affect sample recoveries. If adsorption to walls occurs, then priming may be aiding sample recoveries. This could be offset by permeation (depletion of samples from the inside of bags to the ambient air). The effects of priming and the possibility of permeation, adsorption, and cross-contamination for bags should be studied in greater extent.

Mean sample recoveries from all types of bags for 7 VFAs were always much higher than sample recoveries for 4 semi-VOCs. Mean recoveries for VFAs/semi-VOCs were 66.1%/2.4%, 47.4%/24.5%, 43.1%/24.1%, 31.0%/1.1%, 6.1%/1.1% for PET, Teflon, in-house Tedlar, Tedlar, and foil bags, respectively. This suggests that the bag material affects sample recoveries of chemical function groups. This information could be useful to select bag material that may better preserve target analytes. For example, PET bags retained more VFAs than the other types of bags. On the other hand, recoveries of semi-VOCs from PET bags were poor. Teflon and in-house Tedlar had the best recoveries for semi-VOCs.

It should be emphasized that the effects of sample storage time on odor detection threshold were not tested. Odor concentrations were not measured. In fact, standard gas mixture use in this study was not an "odor sample". All 11 compounds used in this study are odorous and commonly detected near livestock facilities. However, real odor samples are complex mixtures of hundreds of gases including significant amounts of NH₃, H₂S, and water vapor. More experiments are needed to (a) determine the effects of sample storage time on odor detection thresholds for gas standard used in this study, and (b) determine the effects of sample storage time on the recovery of target compounds and odor detection thresholds for real odor samples.

Conclusions

Several preliminary conclusions can be drawn from these experiments:

- (1) SPME Carboxen/PDMS 75 μm fibers had the highest average sample recovery equal to 98% ($\pm 18.6\%$) for 24 hr storage time at room temperature for the 11 target gases
- (2) Sample recoveries for target gases from air sampling bags and sampling canisters were lower than SPME Carboxen/PDMS 75 μm . Sample recoveries were generally greater for 0.5 hr sample storage time compared to 24 hrs storage time. Sample recoveries for VFAs were significantly greater than semi-VOCs. PET bags had the best recoveries for VFAs and in-house made Tedlar bags had the best sample recoveries for semi-VOCs.

On average, PET bags had the best sample recoveries, followed by Teflon, in-house made Tedlar, Tedlar, and foil bags.

- (3) Sample recoveries from sampling canisters were lower than all others.
- (4) New PET and Teflon bags, and sampling canisters had no residual interfering compounds. In-house made Tedlar bags had a small amount of phenol, however, the amount was 10 times less than phenol inside commercial Tedlar bags. These bags also had a measurable amount of DMAC. Purging and heating after manufacturing of in-house Tedlar bags appears to reduce impurities in Tedlar bags. Foil bags had measurable amounts of acetic, propionic, butyric, valeric, and hexanoic acids.
- (5) SPME fibers were useful in evaluating sample recoveries from air sampling bags and sampling canisters.
- (6) Further research is warranted to determine how recoveries from bags affect odor concentrations as measured by olfactometry.

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