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Abstract

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*Implications: Caution is advised when using polymeric materials for storage of livestock-relevant odorous volatile organic compounds. The odorants loss with storage time confirmed that long-term storage in whole-air form is ill advised. A focused short-term odor sample containment should be biased toward the most inert material available relative to the highest impact target odorant. Metallized FEP was identified as such a material to *p*-cresol as the highest impact odorant from confined animal feeding operations. Metallized FEP bags have much cleaner background than commercial Tedlar bags do. Significantly higher recoveries of methyl mercaptan and *p*-cresol were also observed with metallized FEP bags.*

Disciplines

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Testing odorants recovery from a novel metalized fluorinated ethylene propylene gas sampling bag

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Abbreviations

CAFO, confined animal feeding operation; VOC, volatile organic compound; GHG, greenhouse gas; FEP, fluorinated ethylene propylene; SPME, solid phase microextraction; GC-MS, gas chromatography-mass spectrometry; DMAC, N,N-dimethylacetamide; VSC, volatile sulfur compound; CAR/PDMS, Carboxen-polydimethylsiloxane; RSD, relative standard deviation

Abstract

Industry-standard Tedlar bags for odor sample collection from confined animal feeding operations (CAFOs) have been challenged by the evidence of volatile organic compound (VOC) losses and background interferences. Novel impermeable aluminum foil with a thin layer of fluorinated ethylene propylene (FEP) film on the surface that is in contact with a gas sample was developed to address this challenge. In this research, Tedlar and metalized FEP bags were compared for (a) recoveries of four characteristic CAFO odorous VOCs (ethyl mercaptan,

butyric acid, isovaleric acid and *p*-cresol) after 30 min and 24 hr sample storage time and for (b) chemical background interferences. All air sampling and analyses were performed with SPME followed by GC-MS. Mean target gas sample recoveries from metalized FEP bags were 25.9% and 28.0% higher than those in Tedlar bags, for 30 min and 24 h, respectively. Metalized FEP bags demonstrated the highest *p*-cresol recoveries after 30 min and 24 hr storage, $96.1 \pm 44.5\%$ and $44.8 \pm 10.2\%$ respectively, among different types of sampling bags reported in previous studies. However, a higher variability was observed for *p*-cresol recovery with metalized FEP bags. A 0% recovery of ethyl mercaptan was observed with Tedlar bags after 24 hr storage whereas an $85.7 \pm 7.4\%$ recovery was achieved with metalized FEP bags. Recoveries of butyric and isovaleric acids were similar for both bag types. Two major impurities in Tedlar bags' background were identified as N,N-dimethylacetamide and phenol, while that of metalized FEP bags were significantly cleaner. Reusability of metalized FEP bags was tested.

Keywords: whole air sampling, odor, VOCs, sample recovery, metalized FEP bags, Tedlar bags.

Implications

Caution is advised when using polymeric materials for storage of livestock-relevant odorous volatile organic compounds. The odorants loss with storage time confirmed that long-term storage in whole-air form is ill-advised. A focused short-term odor sample containment should be biased toward the most inert material available relative to the highest impact target odorant. Metalized FEP was identified as such a material to *p*-cresol as the highest impact odorant from confined animal feeding operations. Metalized FEP bags have much cleaner background than commercial Tedlar bags do. Significantly higher recoveries of methyl mercaptan and *p*-cresol were also observed with metalized FEP bags.

Introduction

In recent decades, intensive large-scale livestock production has grown rapidly in the U.S. and other parts of the world. The large number of animals raised in concentrated animal feeding operations (CAFOs) can affect air quality by emissions of odor, volatile organic compounds (VOCs), NH₃, H₂S, greenhouse gases (GHGs), and particulate matter (PM) (NRC, 2003; Heber et al., 2006a, 2006b; Jacobson et al., 2008; Hoff et al., 2009;). Air pollution and odor nuisance are a major challenge for livestock production (NRC, 2003; Kim et al., 2007; Parker et al., 2012; Cai et al., 2015; Zhang et al., 2016). Many researchers develop and test odor mitigation technologies (Akdeniz and Janni, 2012; Chen et al., 2009; Cai et al., 2007).

Measurements of odor concentrations are used for air quality assessment and for the development of odor mitigation technologies. Odor is caused by mixture of volatile organic compounds (VOCs), H₂S, NH₃ and other gases. Recently, nearly 300 VOCs have been identified in headspace of swine manure (Lo et al., 2008). Increasing number of studies show that only a relatively small subset of VOCs such as *p*-cresol and selected phenolics/indolics, volatile fatty acids, and sulfur VOCs is responsible for the characteristic livestock odor (Wright et al., 2005; Bulliner et al., 2006; Koziel et al., 2006; Laor et al., 2008). However, most of these odor-causing VOCs are polar, reactive, and highly sorptive onto surfaces of sampling media which increases the challenge for their measurement. The use of industry-standard Tedlar bags for odor sample collection from CAFOs has been challenged by the evidence of odorous VOC losses and background interferences (Keener et al., 2002a; Koziel et al., 2005; Trabue et al., 2006). It is also known that CAFO odor measurements are often associated with high uncertainties. Thus, there is a need to improve sample recoveries as means to improve the quality of odor assessment.

Forced-choice dilution olfactometry has become a standard method for assessing odors at CAFOs (Chen et al., 1997; Clanton et al., 1999; Dravnieks et al., 1978; CEN 1999). Odor samples are usually collected in 'plastic' bags constructed of Teflon, Tedlar, or polyethylene. Tedlar is currently the most widely used sample bag material in U.S. because of its relatively low cost and relative non-reactive qualities. However, previous research that established the use of olfactory scaling models for measurement of swine odor showed significant losses of odorous

CAFO-related compounds on glass, Tedlar, and other plastic surfaces during gas sampling (Zahn et al., 2001). Keener and Zhang had observed over 90% loss for *p*-cresol, indole and skatole after 4 hr storage in Tedlar bag at 22 °C, and significant loss of volatile fatty acids (VFAs) after a 24 hr storage (Keener et al., 2002b). Koziel et al reported 32.4% and 77.3% average losses for key odorants of 7 VFAs and 4 semi-VOCs after 0.5 hr and 24 hr storage (Koziel et al., 2004). Similar results were reported by Trabue and Anhalt (2006), and Parker et al (2010). Storage of other important air pollutants in CAFOs (H₂S, NH₃ and greenhouse gases) in gas sampling bags have been studied by Akdeniz et al. (2011).

Chemical background interferences and background odor are additional concern associated with odor sampling bags. Background compounds including phenol, N,N-dimethylacetamide (DMAC), acetic acid, propionic acid, and butyric acid, and other compounds were identified in Tedlar and polypropylene bags (Koziel et al., 2005; Trabue et al., 2006; Parker et al., 2003). Significant sample loss and background emission from Tedlar bags were also reported in studies on human breath constituents (Mochalski et al., 2009, 2013; Beauchamp et al., 2008). Background impurities likely result from solvents and process chemicals used during manufacturing. Other influencing factors on sample recovery include sample humidity, bag's filling degree and reusability (Mochalski et al., 2013).

Special cleaning strategies including purging and/or heating were used with limited success. Regardless, bias was still unavoidable for samples with relatively low concentration (Parker et al., 2003; Qu et al., 2006). Polyester aluminum bags were tested as a possible substitution of Tedlar bags by Kim et al. (2011) for aromatic compounds, ketones, alcohol and esters, and demonstrated improved performance in odorous VOC recoveries. Mochalski et al. (2009) used bags made from five different polymer materials to store volatile sulfur compounds (VSCs). The highest recovery of 90% for VSCs was achieved with Flexfoil bags (SKC, Inc., Eighty Four, PA) after 24 hr storage, while Tedlar bags had the highest recovery with 6 to 8 hr storage times.

Novel metalized fluorinated ethylene propylene (FEP) air sampling bags ('metalized' FEP bags) were developed by Microanalytics (Round Rock, TX) to offer another sampling choice for CAFO odor studies. The films upon which these bags were based are an outgrowth of the aerospace

industry; novel materials helping meet NASA's challenge of insulating astronauts from extremes of temperature swings (e.g. lunar daytime temperatures approaching ~130 °C while falling to -170 °C at night). It was determined that spacecraft could be effectively isolated from such environmental extremes through the use of multilayer insulation blankets consisting of many layers of these low emittance materials. The specific film chosen for the CAFO odor sample collection application were produced by the vapor deposition of an ~1000 Angstrom layer of aluminum onto a heat weldable fluorinated ethylene propylene (FEP) film substrate. Although a range of polymer film thicknesses were available, a 1 mil thickness was found to offer the optimum in robustness and flexibility. The impermeability of odorous gas molecules through the mirrored aluminum outer cladding coupled with the chemical inertness of the FEP internal surface held promise for enhanced recovery of difficult polar odorants from CAFO environments.

The objectives of this study were:

1. Compare the background impurities from commercial Tedlar bag with those from the metalized FEP bag.
2. Compare sample recoveries of four common CAFO odorants including ethyl mercaptan, butyric acid, isovaleric acid and *p*-cresol gas from Tedlar with those from metalized FEP bags for 30 min and 24 hr storage time.

Materials and Methods

Chemicals and materials

Metalized fluorinated ethylene propylene (FEP) air sampling bags (1 L) (Figure S1), with 1 L capacity were supplied by Microanalytics. A commercial heat welding seamer was used to construct gas sampling bags in a range of volumes, including the 1 L size which was chosen for this study. A commercially available PTFE septum interface (i.e. Alltech PN 4105A) was chosen for this evaluation effort insuring that all sample contact surfaces were inert Teflon based. Tedlar bags (1 L) (Figure S2) were obtained from SKC (Houston, TX).

Background impurities test

One L of air (99.995%, breathing air) was loaded to bags using a 1 L gas-tight syringe (SGE, Austin, TX). The 1 L gas-syringe was prefilled with air from a 99.995% breathing air cylinder via a filter filled with activated carbon. Both bags were purged once using the prefilled air in the 1 L gas-syringe before filling to remove headspace residue and to prepare for test on background emissions into bag headspace after 30 min and 24 hr storage. Figures 1, S3 and S4 (Supplemental Material) illustrate the connections for filling of bags with air. The filling procedure was as follows: outlet needle was sealed when air was introduced into syringe. Then, the syringe and carbon filter were disconnected, connection was sealed, and needle was inserted into bag through polytetrafluoroethylene (PTFE) septum (for metalized FEP bags) or through Teflon faced septa (for Tedlar bags) to load air into a bag. New bags (never used before) were used for each single data point. All tests were performed in triplicate. Air was stored in each bag for either 30 min or 24 hr storage time at room temperature and then analyzed.

Sample recovery test

Stock solutions of *p*-cresol, ethyl mercaptan, butyric acid and isovaleric acid were prepared in methanol and kept in refrigerator before use. The concentration of stock solution for each compound was as follows: *p*-cresol at 38.12 µg/mL in methanol, ethyl mercaptan at 21.03 µg/mL in methanol, a mixture of butyric acid at 72.60 µg/mL and isovaleric acid at 73.08 µg/mL in methanol, respectively. Analytical gas standards were prepared using volumetric injection. A known amount (1 µL) of each standard was injected into each bag through a septum using a gas-tight syringe (Hamilton, Reno, Nevada). Before this injection, each bag was purged once with breathing-grade air. Flushing air was vented by screwing off the valve cap (Figure 2). Then the bag was filled again with 1 L of air via 1 L gas-tight syringe. After injection, each bag was shaken vigorously 100 times to allow the injected solution to evaporate and equilibrate. The final theoretical gas concentration for each compound in 1 L bag prefilled with breathing air was 8.62 ppbv for *p*-cresol, 8.27 ppbv for ethyl mercaptan, 20.15 ppbv for butyric acid and 17.5 ppbv for isovaleric acid, respectively. Each bag was randomly assigned to each treatment.

Filled bags with standard gases were placed at room temperature for either 30 min or 24 hr sample storage time. After this prescribed storage time, solid phase microextraction (SPME) fiber was introduced into the bag headspace via septum for 30 min to collect air samples. Samples were prepared at different intervals and stored for concurrent analysis (not prepared at one time and analyzed through time) to avoid influence of sample extraction on the storage process. Carboxen-polydimethylsiloxane (CAR/PDMS) (85 μm film thickness) fibers were used for extractions (Koziel et al., 2005). Target VOCs were extracted by SPME fiber. Target compounds were simultaneously pre-concentrated using SPME which cannot be achieved with a common syringe extraction method. After each extraction, SPME fiber was removed from the bag and was directly inserted into the GC inject port for analysis. One specific chemical (mixture) in one kind of bag for different storage times (0 min, 30 min and 24 h) are considered to be one batch of samples, which was extracted by one same fiber to avoid variance caused by different extraction efficiency of different SPME fibers.

The control samples were prepared using the identical methodology, except for the sample storage time which was = 0 min. In this case, a CAR/PDMS SPME fiber was immediately inserted into the bag after shaking (i.e. control $t = 0$ min storage time) and analyzed using the same method. The SPME fiber was removed after 30 min of exposure in the bag headspace. The $t=0$ storage time was considered as reference (100% recovery) and was used for estimation of sample recoveries after 30 min and 24 hr storage time (Koziel et al., 2005). Three to five replicates were prepared and analyzed for each test. Recoveries from metalized FEP bags and Tedlar bags were compared by F-test using SAS statistical analysis software (version 9.4). Tested factors that would potentially influence recoveries were: 1. bag type (bag); 2. storage time (time); and 3. interaction between bag type and storage time (bag*time). Threshold value α was set as 0.05.

Reusability test for metalized FEP bags

The feasibility of reusing the metalized FEP bags was evaluated by comparing the sample recovery of *p*-cresol from the new metalized FEP bags and used (once) metalized bags. This part of research was completed because of concerns about the high cost of metalized FEP bag

manufacturing. The metalized FEP bags were purged 3 times with breathing-grade air between the first use and the subsequent reusability test. Then the same procedure used as in sample recovery testing was applied to measure *p*-cresol recovery. Statistical analysis (F-test) was used to determine differences between recovery performances of the new and used metalized FEP bags. Recoveries from new and used metalized FEP bags were compared by random test using R function program (version 2.1).

Standard gas sampling with SPME

The SPME holder for manual sampling and the CAR/PDMS (85 μm film thickness) fibers were from Supelco (Bellefonte, PA). The SPME fibers were conditioned in the injector port of the gas chromatograph according to instructions provided by the manufacturer. The integrity of SPME fiber was periodically checked by challenging it with sampling and analysis of a standard gas. Testing of sample recoveries was completed using the same sampling and sample preparation conditions. The SPME fiber was introduced into the sealed Tedlar bag or metalized FEP bag by piercing septa immediately after prescribed storage time (i.e., 0 min, 30 min, or 24 h) for 30 min extraction at room temperature (24 °C). The SPME fiber was positioned at the center of the bag to avoid variance caused by positioning of the SPME fiber. The fiber was then withdrawn into the SPME needle after the 30 min extraction and removed from the bag. Following air sampling, the SPME fiber was immediately transferred into the GC injector for desorption and sample introduction at 240 °C for $t = 15$ min. The same SPME fiber was used for all the background tests to avoid variance caused by different extraction efficiency of different fibers. For the same reason, one same fiber was used for all recovery tests. One specific target gas (or mixture in the case of organic acids) introduced to one kind of bag for different storage times (0 min, 30 min and 24 h) is considered to be one batch of samples, which was run in the same day to avoid variance of the instrument performance in different days. Figures 2 and S5 show schematics of SPME extraction of standard gases from 1 L bag.

Gas analysis with GC-MS

All chemical analyses were completed on a GC-MS system (Agilent 6890 GC / 5890A MS system with AromaTrax™ MDGC-MS-O modification by MOCON Inc. , Round-Rock, TX) equipped with a 60 m × 0.32 mm × 0.25 μm BP5 capillary column (SGE, Austin, TX). GC oven temperature programs were optimized for analyses of sample recovery and chemical background impurities in new bags. Temperature program for chemical background: initial temperature of 100 °C, followed by ramping at 10 °C /min to 220 °C where it was held for 3 min. Temperature program for *p*-cresol: initial temperature 100 °C, followed by ramping to 220 °C at 10 °C /min where it was held for 4 min. Temperature program for ethyl mercaptan: initial temperature 40 °C, followed by ramping of 12 °C /min to 220 °C, where it was held constant for 4 min. Temperature program for butyric acid and isovaleric acid mixture: initial temperature 100 °C, then raised to 220 °C at 10 °C /min, where it was held for 4 min. Inlet was at 240 °C and set to a splitless mode. Helium was the carrier gas, at the flow rate of 1.7 mL/min. For samples of ethyl mercaptan and *p*-cresol from storage in metalized bag, carrier gas flow rate of GC was changed to 2.7 mL/min because the instrument was updated and equipped with branch column onto GC-column.

Autotune of MS detector was performed every day before analyses. The scanning range of MS was between 33 and 280 *m/z*. The MS source temperature was 230 °C, and the MS Quadrupole temperature was 150 °C. The selected ions for selected-ion monitoring (SIM) mode were *m/z*=77, 107 and 108 for *p*-cresol; *m/z*=60, 73 and 87 for the mixture of butyric acid and isovaleric acid; and *m/z*=62 for ethyl mercaptan. The dwell time for each selected ion was 100 ms. Underlined ions were selected as quantification ions for each target gas, respectively.

Results and Discussion

Background impurities in new bags

Comparison of chromatograms of background impurities from Tedlar bag and metalized FEP bag is shown in Figure 3. Metalized FEP bags had a significantly cleaner background than that

of Tedlar bags which were contaminated with considerable amounts of DMAC and phenol as well as other interferences containing Si m/z signature ions originating from silicon septum material. Significant amounts of DMAC and phenol in Tedlar bags were previously reported by Koziel et al., (2005), Trabue et al. (2006) and Mochalski et al. (2013).

Mean (n=3) MS detector responses (in peak area counts) to DMAC and phenol recovered from new bags are summarized in Table 1. No DMAC or phenol was detected in metalized FEP bags. It is also important to report that after purging and refilling Tedlar bags with fresh pure air/standard chemical mixture, the apparent amount of DMAC and phenol increases with storage time. The amounts of these impurities nearly doubled from 30 min to 24 hr storage time. This also indicates that a significant amount of these impurities are inherent to Tedlar bags and each time after refilling the bags with fresh air/standard chemical mixture, impurities are continuously released to Tedlar bags headspace without reaching apparent equilibrium within 24 h. It is more likely that both phenol and DMAC are, in fact, distributed more or less, uniformly throughout the film cross-section (at any point in time). If this is the case, the emission from the film to the bag interior would be expected to be a long-term exponential decay process to the point where it drops below the detection limit of the analytical methodology. The apparent non-equilibrium desorption may lead to interferences with odor samples and may also contribute to variations in sample recovery. This is similar to the results reported by Trabue et al. (2006).

Acetic acid was not identified as one of the impurities in new bags. Some researchers have reported acetic acid presence (Keener et al., 2002a). However, it is also possible that this compound was actually DMAC but misidentified because their GC column retention times and MS spectra could be very similar. Polyvinyl fluoride (PVF) powder is used as the raw material for Tedlar manufacturing and it has to be dissolved in a latent solvent (usually DMAC). Thus, it is reasonable to expect DMAC in new Tedlar bags as a remainder of polymerization process (USCAR, 2003).

Phenol was also consistently present in the background of Tedlar bags. Phenol is a typical odorant identified in CAFO environments (Trabue et al., 2006; Schiffman et al., 2001; Wright et al., 2005). Compared with complex background of Tedlar bags, that of metalized FEP bags is

very clean. Koziel et al., 2005; Mochalski et al., 2009 also reported the relative cleaner background of Teflon bag than that of Tedlar bag.

Gas sample recovery tests

Gas samples were generated through evaporation of liquid solution in the headspace of bags. Experimental bias of concentration was observed between gases generated from liquid-phase standard and gas-phase standard (Kim et al., 2012; Kaatz et al., 1998). A bias is expected between actual concentrations of generated gas samples and theoretical concentrations in this study. Absolute concentrations of gas samples were not tested. Recoveries were determined semi-quantitatively. The $t=0$ storage time was considered as reference (100% recovery), and relative recoveries were tested on $t=30$ min and 24 hr storages. Bias of gas sample concentrations can be canceled out in relative recovery calculation. Sample recoveries and relative standard deviation (RSD) for target odorants are summarized in Table 2 (percent sample recovery \pm RSDs). Sample recoveries for 30 min and 24 hr storage time are also presented in Figure S6, respectively. Average recoveries of butyric acid, isovaleric acid, *p*-cresol and ethyl mercaptan of Tedlar bags were $74.4 \pm 5.3\%$ and $21.4 \pm 2.0\%$ for 30 min and 24 hr, respectively whereas the average recoveries of metalized FEP bag were $90.3 \pm 27.1\%$ and $49.4 \pm 8.4\%$, respectively.

Statistical analysis on recovery results was completed with SAS is shown in Table 2. All *p*-values testing time effect are lower than 0.05. Both of the bags suffered significant recovery decreases after longer storage time of 24 hr compared with 30 min storage on all of the tested chemicals. Significant recovery decrease over time was observed in previous studies (Koziel et al., 2004; Parker et al., 2010; Mochalski et al., 2009; Trabue et al., 2006; and Keener et al., 2002b).

Bag type effect is the major concern in this study and was tested with F-test using SAS. Recoveries of *p*-cresol using Tedlar bags are $53.9 \pm 7.0\%$ and $9.1 \pm 3.1\%$ after 30 min and 24 hr storage respectively. Recoveries of *p*-cresol, averaged among different metalized FEP bag groups, are $96.1 \pm 44.5\%$ and $44.8 \pm 10.2\%$ respectively after 30 min and 24 hr storage. Those for ethyl mercaptan were $83.2 \pm 6.6\%$ and 0% with Tedlar bags; and $98.2 \pm 4.4\%$ and $85.7 \pm$

7.4% with metalized FEP bags. According to the statistical test, metalized FEP bags yielded significantly higher recoveries of *p*-cresol and ethyl mercaptan.

However, the average recoveries of both types of bags for two acids were similar. After 30 min and 24 hr storage, Tedlar bags yielded $78.9 \pm 4.1\%$ and $32.2 \pm 2.8\%$ recoveries for butyric acid, compared with $74.8 \pm 3.6\%$ and $31.3 \pm 8.6\%$ for metalized FEP bags. For isovaleric acid, it was $81.8 \pm 3.5\%$ and $44.3 \pm 2.2\%$ with Tedlar bags, while $80.5 \pm 3.7\%$ and $40.6 \pm 6.5\%$ with metalized FEP bags. No significant difference between the two bags on butyric acid and isovaleric acid recoveries was observed.

Comparison of sample recoveries for target VOCs from bags made with different materials in different studies is shown in Table 3. All commercial Tedlar bags in this study and cited studies were purchased from SKC, Inc., Eighty Four, PA. The average recoveries of Tedlar bags for butyric acid and isovaleric acid for 30 min and 24 hr storage time were $80.4 \pm 3.8\%$ and $38.3 \pm 2.5\%$, respectively. These results are similar to those reported by Koziel et al. (2005), but the 24 hr storage recoveries are about 40% lower than those reported by Keener et al. (2002b), who used nitrogen to fill 10-L Tedlar bags. Trabue et al. (2006) also achieved higher recovery on butyric acid with 10-L Tedlar bags sampling emission from aqueous synthetic odor solution. The humidity in the study by Trabue et al. (2006) was estimated to be 62%. Moisture in air can affect sample stability. Mochalski et al. (2013) observed poorer stability of humid samples. Recoveries tended to decrease with increasing molecular weight in presence of moisture. Beghi and Guillot (2006) reported that water vapor can readily penetrate into Tedlar bags, while non-permeable (FlexFlo-type) bags retain moisture. Thus, further research on the role of moisture on sample stability is warranted. Lower fatty acid and *p*-cresol recoveries with Tedlar bags were reported by Parker et al. (2010). The larger volume of the bags (10 L) could result in a higher surface to volume ratio and generate lower recoveries (Figure S6). For the *p*-cresol recoveries of Tedlar bags, 2 to 5 times higher recoveries were observed in our study than those reported by Koziel et al., (2005), Keener et al., (2002b) and Trabue et al. (2006).

Compared with recovery performances of Teflon (FEP) bags with same polypropylene septum fitting evaluated by Koziel et al., (2005), novel metalized FEP bags revealed around 10% lower

recovery for the 30 min storage of the 2 VFAs, and about 20% lower recovery for the 24 hr storage of the 2 acids. However, recoveries of *p*-cresol from metalized FEP bags after 30 min and 24 hr storage were approximately 29.2% and 16.1% higher respectively, than those of FEP bags reported by Koziel et al., (2005). A test comparing *p*-cresol recovery with metalized FEP bags in this study and FEP bags tested by Koziel et al. showed that p-values for differences with 30 min and 24 hr storage were 0.0208 and 0.0007 respectively, and significant improvement in *p*-cresol storage (30 min and 24 h) was achieved with metalized FEP bag in our study compared with results reported in other cited studies (Table 3). Koziel et al. (2005) also tested a foil bag with polyethylene and polypropylene layers on livestock gases sampling, and the foil (low-density polyethylene) bags generated the lowest recovery among all other tested bags: i.e., polyethylene terephthalate, FEP, and Tedlar. A significant recovery increase was achieved in this study with metalized bag with FEP layer (Table 3). Kim et al. (2011) also reported higher recoveries with polyester aluminum bags on ambient aromatic VOCs, compared with Tedlar bags.

Another factor analyzed with F-test is the interaction between bag and time (bag*time). This interaction indicates whether recovery differences between the two bags increase or decrease against storage time. The interaction factor was demonstrated to have a significant impact on ethyl mercaptan storage. Ethyl mercaptan recovery with Tedlar bags dropped from 83.2±6.6% at 30 min storage to 0% at 24 h, while for metalized FEP bags, recovery was 98.2±4.4% at 30 min and 85.7±7.4% at 24 h. Interaction effect with time was also observed by Kim et al. (2011) comparing polyester aluminum bags with Tedlar bags. Mochalski et al. (2009) tested recovery of volatile sulfur compounds (VSCs) with different types of bags. Tedlar bag exhibited the best performance on ethyl mercaptan storage and overall VSCs storage in 6 to 8 h, while Flexfoil bag was preferable among Tedlar, black Tedlar, Teflon and Nalophan bags for storage up to 24 h.

A higher recovery of ethyl mercaptan than this study was achieved with all types of bags by Mochalski et al. (2009) (Table 3). Ethyl mercaptan is highly reactive with OH radicals as a photolysis product in ambient air, and has a half-life time of 0.23 days (Barnes et al., 1986). The major contributor to the loss of ethyl mercaptan is likely its photolysis-related degradation. The 100% loss of ethyl mercaptan in Tedlar bags in this study is reasonable given the high reactivity.

The higher recoveries obtained by Mochalski et al. (2009) is expected to be resulted from using N₂ as bag filling gas and preventing reaction of ethyl mercaptan with OH radicals. Compared with Tedlar bags, metalized FEP bags in this study are non-transparent which can prevent the photolysis related degradation of ethyl mercaptan. The non-transparency of metalized FEP bags in contrast with transparent Tedlar bags explains the significant bag*time effect in statistical analysis.

Metalized FEP bags had significantly higher recoveries of *p*-cresol and ethyl mercaptan for 30 min and 24 hr storage time. Recoveries of ethyl mercaptan from metalized FEP bags were evaluated using previously used metalized FEP bags. However, the result was as valid as that generated from new metalized FEP bags according to reusability test results (Table 5).

It is worth mentioning that after 24 hr storage in Tedlar bags, amounts of ethyl mercaptan were under the detection limit, while an 85.7±7.4% recovery was determined for metalized FEP bags. This is a significant improvement for sampling of sulfides from CAFO as sulfides are well known to be high-impact odorants from CAFO but they are very reactive. With the conventional sampling method, it is a significant challenge for sampling and storing such kind of compounds.

As for *p*-cresol, new metalized FEP bags yielded about 46% higher recoveries after 30 min storage than Tedlar bags did. However, high variability (as RSD = 41.8%) was observed for *p*-cresol recovery from metalized FEP bags. Several possible reasons could be responsible for this variability. In this study, Tedlar bags used were equipped with stainless steel injection ports, sealed with Teflon fluorocarbon resin septum, which was found to be more air tight than Teflon valve attached to metalized FEP bags (Wang et al., 1996). The surface-to-volume ratios of the two kinds of bags were about the same. The fastest rate of VOC losses in Tedlar bags was observed at the initial storage time, and the rate decreased over time, which suggests sorption as a major contributor to VOC losses in Tedlar bags (Wang et al., 1996; Beghi et al., 2006). Surface-to-volume ratio is a factor which influences sorption effect. In this study, the inner surface areas of all metalized FEP bags and Tedlar bags are between 600 cm² to 650 cm². Relative standard deviation (RSD) values for recovery tests of metalized FEP bags can be as high as ~55%, while Tedlar bags are all of low RSD values no more than 7%. There are some

abnormal individual results generated from the odorant storage in metalized FEP bags, which were included in data record. They contribute to the high RSDs of recoveries from metalized FEP bags. These occasional individual errors might be resulted from variation during manufacture such as process of vapor deposition of the 1000 Angstrom aluminum cladding onto the weldable FEP film substrate.

Another reason could be variability due to the evaporation of liquid standard mix of target chemicals after its introduction to tested bag. Evaporation of semi-volatiles may not occur instantaneously and uniformly in mid-air but rather could be characterized by surface deposition of droplets. These variations are related to sample preparation procedure. In this case, the difference in apparent precision between Tedlar and metalized FEP could result from differences in surface interactions (i.e., beading versus filming; surface residual density after solvent evaporation) between these two film types and the standard solvent base (i.e., based upon differences in surface / solvent compatibilities). As for bag themselves, variation of surface-to-volume ratio of the bags is contributive to the deviation considering sorption effect as well as to the variability of standard gases generation/evaporation from injected liquid standard solution. There is possibility of permeation and reaction of sample gases with OH radicals from water and/or NO_x in real sample with the plastic valves and silicone septa (Koziel et al., 2005).

Reusability test of metalized FEP bags

To evaluate the reusability of metalized FEP bags, the metalized FEP bags used for recovery test previously were reused for *p*-cresol storage recovery test, and additional data was obtained. This also helps to confirm the validity of the data of *p*-cresol and ethyl mercaptan recoveries of metalized FEP bags generated from used metalized FEP bags.

To determine whether significant difference exists between the used metalized FEP bags and new ones, for groups of 1, 2, 3, and 4 in Table 4, random test and F-test on peak area counts were applied. Total of the 21 peak area counts from 6 groups of treatments were tested. In random test, to give statistical meaning to the whole set of data, storing chemicals of *p*-cresol or the mixture of the two acids and then testing recoveries of *p*-cresol are considered as one treatment.

Then treatment assignment is described as in Table 4. Numbers of permutation, M value, were selected as 5000 for comparison between two groups, while 50000 for comparison among four groups with more peak area data points (Table 5).

According to the treatments to the bags and peak area count results, random tests and F-tests were applied to data in Table 4. In Table 5, for groups of 3 and 4, $F_{0.05}(1,4) = 7.709$, higher than the reference F value of 1.80082. According to the F-test, there is no significant difference among the groups of the lowest p-value, group 3 and group 4. Therefore, there is no significant difference among other groups with higher p-values.

According to p-value from the random tests, high enough p-values were generated indicating there was no significant difference between used and new metalized FEP bag for the recovery of *p*-cresol. No significant difference was observed comparing reused metalized FEP bags used for storage of *p*-cresol or butyric acid and isovaleric acid, against new metalized FEP bags.

Conclusions

Metalized FEP bags have much cleaner background emissions than Tedlar bags do. The phenol and DMAC identified from Tedlar bag background emissions can potentially cause interference to CAFO odorant assessment and olfactory data. The metalized FEP bags with relatively clean background should have no interference regarding CAFO odor evaluations. However, the average recoveries of *p*-cresol and ethyl mercaptan in metalized FEP bags were significantly higher than those in Tedlar bag. Metalized FEP bags demonstrated the highest *p*-cresol recoveries after 30 min and 24 hr storage, $96.1 \pm 44.5\%$ and $44.8 \pm 10.2\%$ respectively, among all previously reported results with different types of sampling bags. Ethyl mercaptan recovery after 24 hr was increased from 0% with Tedlar bag, to $85.7 \pm 7.4\%$ with metalized FEP bag. The reason for the increase of recovery might be the nontransparent feature of metalized bag preventing photocatalysis degradation of ethyl mercaptan. No significant differences were observed with average recoveries of butyric acid and isovaleric acid in Tedlar bags and those in metalized FEP bags. The reproducibility of recovery tests for four selected odorants for Tedlar bags were better than those for metalized FEP bags. According to statistical analysis, after

purging the used metalized FEP bags with pure breathing air 3 times, the used metalized FEP bags had statistically the same *p*-cresol recovery as new metalized FEP bags.

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Table 1. Chemical impurities in new bags. Comparison of MS detector response to air samples collected from new unused Tedlar and metalized FEP bags using 30 min SPME 85 μ m CAR/PDMS fiber.

Peak # (Figure 3)	Compound	Tedlar bag		Metalized FEP bag	
		Sample storage time		Sample storage time	
		30 min	24 hr	30 min	24 hr
6	DMAC	2.00(\pm 0.41) $\times 10^7$ n=5	5.37(\pm 0.49) $\times 10^7$ n=5	Not detected	Not detected
8	phenol	3.24(\pm 0.51) $\times 10^7$ n=5	5.97 (\pm 0.77) $\times 10^7$ n=5	Not detected	Not detected

Table 2. Mean percent sample recovery (\pm RSDs)/% for target odorants and statistical analysis of recovery results.

VOC	Sample storage time						F-test results					
	0 min (reference)		30 min		24 hr		p time [†]	SD	p bag [‡]	SD	p bag*time [§]	SD
	Tedlar	metalized FEP	Tedlar	metalized FEP	Tedlar	metalize d FEP						
<i>p</i> -cresol	100 \pm 5.2 (n=5)	100 \pm 54.4 (n=4)	53.9 \pm 7.0 (n=3)	100.1 \pm 41.8 (n=4)	9.1 \pm 3.1 (n=5)	—	0.0320	Yes	0.0342	Yes		
		[¶] 100 \pm 56.3 (n=4)		[¶] 82.1 \pm 68.8 (n=4)		48.5 \pm 14.5 (n=4)	0.0191	Yes	0.0379		0.7044	No
		[#] 100 \pm 41.2 (n=4)		[#] 106 \pm 22.9 (n=4)		[#] 41.0 \pm 5.8 (n=4)	<.0001	Yes	<.0001		0.0741	No
butyric acid	100 \pm 3.1 (n=4)	100 \pm 5.6 (n=3)	78.9 \pm 4.1 (n=3)	74.8 \pm 3.6 (n=3)	32.2 \pm 2.8 (n=4)	31.3 \pm 8.6 (n=5)	<.0001	Yes	0.0659	No	0.2563	No
isovaleric acid	100 \pm 3.3 (n=4)	100 \pm 5.7 (n=3)	81.8 \pm 3.5 (n=3)	80.5 \pm 3.7 (n=3)	44.3 \pm 2.2 (n=4)	40.6 \pm 6.5 (n=5)	<.0001	Yes	0.0797	No	0.4047	No
ethyl mercaptan	100 \pm 4.9 (n=3)	^{††} 100 \pm 3.2 (n=3)	83.2 \pm 6.6 (n=3)	^{††} 98.2 \pm 4.4 (n=3)	ND (n=5)	^{††} 85.7 \pm 7.4 (n=5)	<.0001	Yes	<.0001	Yes	<.0001	Yes

Note: RSD: relative standard deviation, were calculated from 3 to 5 replicates of each treatment. ND: not detected; SD: significant difference. [†]Reported *p*-value was obtained from F-test on the effect of storage time on recovery difference. [‡]Reported *p*-value was obtained from F-test on the effect of bags on recovery difference. [§]Reported *p*-value was obtained from F-test on the effect of interaction between bags with storage time on recovery difference. The threshold value was set as 0.05, i.e. *p*-value lower than 0.05 indicates a significant difference resulted from the tested factor (bag, and bag*time). Data marked with [¶] were generated from metalized FEP bags used for blank background test; data marked with [#] were generated from metalized FEP bags used for storage of *p*-cresol; and data marked with ^{††} were generated from metalized FEP bags used for storage of acid mixture.

Table 3. Comparison of sample recoveries for target VOCs from bags made with different materials in different studies.

Study	Bag, capacity	Storage Time (hr)	Sample Recovery (%)											Filling Gas		
			Butyric acid	Isovaleric acid	<i>p</i> -Cresol	Ethyl mercaptan										
This study	Tedlar, 1 L	0.5	78.9	81.8	53.9	83.2								Air		
		24	32.2	44.3	9.1	0										
	Metalized FEP, 1 L	0.5	74.8	80.5	96.1	98.2										
		24	31.3	40.6	44.7	85.7										
Kozziel et al., 2005		Storage Time (hr)	Butyric acid	Isovaleric acid	<i>p</i> -Cresol	Acetic acid	Propanoic acid	Isobutyric acid	Valeric acid	Hexanoic acid	4-Ethyl phenol	Indole	2'-Aminoacetophenone	Air		
	polyethylene terephthalate (PET; Melinex), 10 L	0.5	81.9	88.6	36	84.8	88.0	105.1	67.6	63.0	36.4	0.0	27.4			
		24	102	73.9	5.6	27.6	61.4	108.6	51.1	38.2	0.9	0.0	0.5			
	fluorinated ethylene propylene copolymer (FEP; Teflon), 10 L	0.5	88.2	85.5	66.9	101	100	96.5	73.8	59.0	66.1	38.2	48.2			
		24	53.8	61.8	28.6	45.4	65.8	67.8	24.9	12.5	24.3	24.7	20.4			
	In-house made polyvinyl fluoride (PVF; Tedlar), 10 L	0.5	70.1	74.3	13.3	68.6	85.8	84.6	62.7	51.1	0.0	8.5	0.5			
		24	44.5	61.6	22.7	23.0	53.5	79.8	24.8	14.2	4.1	23.2	46.3			
	Commercial PVF (Tedlar), 10 L	0.5	84.7	86.2	16	72.9	83.1	86.2	72.3	64.3	28.9	67.4	33.4			
		24	37.4	52.6	3.1	20.4	43.2	57.1	20.6	13.7	1.3	0.0	0.0			
	Foil (LDPE), 10 L	0.5	0	35	2.7	29.7	0.0	47.9	12.8	12.6	5.3	19.6	15.5			
		24	6.2	12.9	3.7	0.0	0.0	23.0	0.0	0.5	0.8	0.0	0.0			
	Parker et al., 2010		Storage Time (hr)	Butyric acid	Isovaleric acid	<i>p</i> -Cresol	Acetic acid	Propanoic acid	Isobutyric acid	Valeric acid	Hexanoic acid					Air
		In-house made polyvinyl fluoride (PVF; Tedlar), 10 L	1	17.9	27	2.4	19.0	21.5	38.4	4.7	14.5					
			24	11.7	18	1.6	13.5	12.6	34.3	3.3	9.7					
Commercial polyvinyl fluoride (PVF; Tedlar), 10 L		1	18.6	27.7	4.5	14.2	19.4	40.1	4.9	3.7						
	24	12.4	20.2	3.9	9.4	13.7	35.6	2.3	2.4							

Trabue et al., 2006	Tedlar, 10 L	Storage Time (hr)	Butyric acid	Isovaleric acid	<i>p</i> -Cresol	Acetic acid	Propanoic acid	2-Methylpropanoic acid	Pentanoic acid	4-Methylpentanoic acid	Hexanoic acid	Heptanoic acid	Phenol	Headspace of air purging aqueous solution	
		0.5	98.4		27.6	147.1	104.9	98.0	93.6	90.6	86.0	55.7	2050.0		
		24	68.5		5.3	273.0	72.0	84.8	50.3	59.4	48.0	0	2792.7		
		Storage Time (hr)	4-Ethylphenol	Indole	3-Methylindole										
		0.5	30.4	0	0										
		24	13.0	0	0										
Keener et al., 2002	Tedlar, 10 L	Storage Time (hr)	Butyric acid	Isovaleric acid	<i>p</i> -Cresol	Acetic acid	Propionic acid	Isobutyric acid	Valeric acid	Hexanoic acid	Isocaproic acid	Heptanoic acid	Octanoic acid	N ₂	
		4	87	96	10	96	89	96	96	69	82	40	24		
		24	68	83	5	107	50	83	83	46	62	18	12		
		Storage Time (hr)	Nonanoic acid	Phenol	4-Ethylphenol	Indole	Skatole	Pyrazine	2-Methylpyrazine	2,3,5,6-Tetramethyl					
		4	2	609	17	8	9	67	81	89					
		24	0	819	7	0	8	58	64	68					
Mochalski et al., 2009 [†]	Transparent Tedlar, 1 L	Storage Time (hr)	Ethyl mercapta	H ₂ S	Dimethyl sulfide	CS ₂	Methyl mercapta _n	Carbonyl sulphide						N ₂	
		1	98	92	98	96	100	98							
	30	92	64	90	80	88	90								
	Flexfoil, 1 L	1	100	98	96	100	104	98							
		26	88	58	68	88	88	87							
	Teflon, 3 L	1	105	108	98	96	106	95							
		24	56	58	55	52	56	67							
	Black Tedlar, 1 L	1	98	104	96	98	100	94							
		24	90	76	92	94	90	95							
	Homemade Nalophan, 1 L	1	99	108	100	104	96	102							
		24	42	30	66	66	38	82							

Table 4. Treatment assignment description for random test on reusability of metalized FEP bags.

Group	Treatment	GC Peak area
1	test 0 min storage response of <i>p</i> -cresol with used bag for 0 min storage of <i>p</i> -cresol	210,285
		66,784
		183,029
		219,833
2	test 0 min storage response of <i>p</i> -cresol with new bag	200,396
		30,434
		144,990
		165,527
3	test 30 min storage recovery of <i>p</i> -cresol with used bag for 30 min storage of <i>p</i> -cresol	222,514
		173,256
		145,569
4	test 30 min storage recovery of <i>p</i> -cresol with used bag for 30 min storage of mixture of butyric acid and isovaleric acid	147,466
		139,769
		160,349
5	test 30 min storage recovery of <i>p</i> -cresol with used bag for 24 hr storage of mixture of butyric acid and isovaleric acid	161,823
		149,494
		138,814
6	test 30 min storage recovery of <i>p</i> -cresol with new bag	186,596
		55,617
		160,169
		139,277

Table 5. Results from random test and F-test on reusability of metalized FEP bags.

Comparison among groups (Table 4)	M-value	p-value	F
1,2	5000	0.4862	0.46209
3,4,5,6	50000	0.6131	0.81936
3,4	5000	0.2890	1.80082
3,5	5000	0.3022	1.67907
3,6	5000	0.3398	1.40236
4,5	5000	0.7980	0.00898
4,6	5000	0.7682	0.16900
5,6	5000	0.8002	0.18953

Note: R function program was used to perform random test to generate p-value. M-value: a parameter in R programming to perform random test, indicates the number of permutation.

Figure Captions

Figure 1. Schematic of experimental set up for filling pure air into bags for background analyses. (1) Cylinder with 99.995% pure breathing grade compressed air equipped with valve, (2) Activated carbon filter, (3) Gastight syringe, (4) Outlet connected to a needle.

Figure 2. Schematic of air sampling collection from metalized FEP fluorinated ethylene propylene (or Tedlar) bag with solid phase microextraction (SPME). (1) metalized/Tedlar bag, (2) valve with septa, (3) SPME holder, (4) SPME needle cap, (5) silica fiber, (6) 85 μm Carboxen-polydimethylsiloxane coating. After piercing the septa inside the valve with SPME needle cap, SPME fiber inside the SPME needle cap was exposed for extraction. The fiber stayed at the same position in the center of the bag during extraction.

Figure 3. Total ion chromatogram overlay of blank background of Tedlar bag and metalized FEP bag. Blue plot is the blank background chromatogram of breathing air sample stored in metalized fluorinated ethylene propylene bag for 24 h, and red plot is the blank background chromatogram of breathing air sample stored in Tedlar bag for 24 h. (1) CO_2 , (6) N,N-dimethylacetamide, (8) phenol. Peaks (2) to (5) and (7) were associated with significant abundance of $m/z=73$, 133, and 147 ions characteristic of Si and likely originating from silicone grease or septum.