Evaluation of Sample Recovery of Odorous VOCs and Semi-VOCs From Odor Bags, Sampling Canisters, Tenax TA Sorbent Tubes, and SPME

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Abstract
Odor samples collected in field research 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 μm SPME fibers, PVF (Tedlar), FEP (Teflon), foil, and PET (Melinex) air sampling bags, sorbent Tenax TA tubes and standard 6 L Stabilizer™ sampling canisters after sample storage for 0.5, 24, and 120 (for sorbent tubes only) hrs at room temperature. The standard gas mixture consisted of 7 volatile fatty acids (VFAs) from acetic to hexanoic, and 4 semi-VOCs including p-cresol, indole, 4-ethylphenol, and 2’-aminoacetophenone 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 Tenax TA sorbent tubes (94.8% and 88.3%) for 24 and 120 hrs, respectively; PET bags (71.7% and 47.2%), FEP bags (75.4% and 39.4%), commercial Tedlar bags (67.6% and 22.7%), in-house-made Tedlar bags (47.3% and 37.4%), 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 N, N-dimethyl acetamide and phenol. Foil bags had measurable concentrations of acetic, propionic, butyric, valeric and hexanoic acids.

Keywords
cchromatography, sensors, chemical analysis

Disciplines
Agriculture | Bioresource and Agricultural Engineering

Comments
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Evaluation of Sample Recovery of Odorous VOCs and Semi-VOCs From Odor Bags, Sampling Canisters, Tenax TA Sorbent Tubes, and SPME

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Abstract. Odor samples collected in field research 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 µm SPME fibers, PVF (Tedlar), FEP (Teflon), foil, and PET (Melinex) air sampling bags, sorbent Tenax TA tubes and standard 6 L Stabilizer™ sampling canisters after sample storage for 0.5, 24, and 120 (for sorbent tubes only) hrs at room temperature. The standard gas mixture consisted of 7 volatile fatty acids (VFAs) from acetic to hexanoic, and 4 semi-VOCs including p-cresol, indole, 4-ethylphenol, and 2'-aminoacetophenone 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 Tenax TA sorbent tubes (94.8% and 88.3%) for 24 and 120 hrs, respectively; PET bags (71.7% and 47.2%), FEP bags (75.4% and 39.4%), commercial Tedlar bags (67.6% and 22.7%), in-house-made Tedlar bags (47.3% and 37.4%), 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 N,N-dimethyl acetamide and phenol. Foil bags had measurable concentrations of acetic, proionic, butyric, valeric and hexanoic acids.

Keywords: Odor, VOCs, sampling, sample recovery.

PACS: 01.30.Cc.

INTRODUCTION

Odorous gases encountered in field research such as 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. Many of these compounds are particularly susceptible to being adsorbed onto contact surfaces, with less than 100% recovery 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.

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 water permeation, adsorption, and desorption of some chemical species to the Tedlar. Keener et al. 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-ethylphenol, nonanoic and octanoic acids. Nagata (2003) used polyester odor bags and reported recovery rates from these bags for 35%, 40%, 39%, and 6.5% for isobutyric, butyric, isovaleric acids and indole, respectively. Wright et al. 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

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beef cattle feedlot. Wright et al. used SPME for air sample collection and for 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-ethylphenol, 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 are potentially the most offensive odorants for swine and cattle feedlots. However, no data exists on sample recoveries of these compounds from SPME and other sampling devices.

The primary objective of this study was to determine sample recoveries from a standard gas mixture of odorous gases from several popular air sampling devices including SPME, 5 types of air sampling bags, Tenax TA sorbent tubes, 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.

EXPERIMENTAL AND METHODS

Standard Gases

Stable concentrations of 11 VOCs and semi-VOCs including acetic, propionic, isobutyric, butyric, valeric, isovaleric and hexanoic acids, p-cresol, 2'-aminoacetophenone and 4-ethyl phenol were maintained using permeation sources. The 7 volatile fatty acids (VFAs) were generated with a standard gas generator based on permeation devices. The 4 semi-VOCs were generated in an in-house-made gas generator utilizing a permeation devices. In this research, we used SPME as an air sampler and also as a sampling and sample introduction technology used to evaluate sample recoveries from other devices except the sorbent tubes. Sampling with SPME was relatively short (5 min) and identical for all evaluations. Triplicate QA/QC samplings with a single Carboxen/PDMS 75 μm SPME fiber were used to confirm the stability of the standard gas daily.

The standard gas mixture was always sampled with SPME fiber for 5 min. This was followed by immediate insertion of the SPME fiber into GC injector for time = 0 hrs.

Sample Recovery from Air Sampling Bags

Commercial bags. All bags were 10 L capacity fitted with a single polypropylene septum valve 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).

In-house-made bags. The in-house-made Tedlar bags (b) were made at West Texas A&M University. The PVF film was ordered directly from DuPont. All in-house made bags were subjected to conditioning. Post-manufacturing conditioning was found to remove any residual odor.

The PET (a.k.a. Melinex) bags were made from a 5000 m × 1.14 m wide roll of polyethylene terephthalate film and polypropylene fittings. PET bags meet the Australian and the European olfactometry standards where they are listed as “Nalophan” and are popular choice of air sampling bags for collection of livestock odor samples.

Standard gas sampling. All bags were filled with the standard gas using a special dispensing port located immediately downstream from the SPME sampling bulb. Triplicate samples for 0.5 and 24 hrs holding/preservation time were collected in air sampling bags sequentially in 1 to 2 hrs intervals.

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.

Sample Recovery from Sampling Canisters

Sampling canisters are used in EPA methods TO-14 and TO-15 for sampling of VOCs in ambient air. 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.

Sample Recovery from Tenax TA Sorbent Tubes

Stainless steel desorption tubes (Supelco, Bellefonte, PA) filled with Tenax-TA adsorbent were used to collect standard gas mixture. Triplicate sorbent tubes were used to store samples for 24 hr and 120 hrs.
Analyses on GC/MS

The samples collected on Carboxen/PDMS fibers were analyzed with a Varian 3800/Saturn 2000 GC/MS system equipped with a 25 m × 0.25 mm × 0.2 μm film CP-WAX 58/FFAP capillary column (from Chrompack/Varian). The ion trap MS measured a wide mass range between 30 and 460 m/z to aid in identification of background compounds. MS responses to triplicate SPME samples of gas standard with 0 hr holding/preservation time were used as a reference for all samples with holding time of 0.5 and 24 hrs.

All desorption tubes were analyzed on a Turbomatrix automated thermal desorption (ATD) unit (Perkin-Elmer, Boston, MA) connected to the GC/MS system.

RESULTS

Interfering Chemicals in New Air Sampling Bags

Teflon bags had the lowest number and amount of interfering compounds. No compounds other than silanes and siloxanes were identified. The in-house made Tedlar bags had the second lowest background. The only interfering chemical from the in-house Tedlar bags was phenol. However, the amount of phenol was approximately 10 times lower than in commercial Tedlar bags. Large quantities of phenol in Tedlar bags were also reported by Keener et al.3

Commercial Tedlar bags also had a significant amount of DMAC. 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. Background impurities in PET bags and canisters were very low.

Sample Recovery from SPME

SPME fibers showed an excellent sample recovery. Average sample recovery for all 11 compounds sampled with 3 SPME fibers was 106% (±20.2%) for 0.5 hr storage time and 98% (±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. The sample recovery for p-cresol was 116.9% (±8.7%) and 92.5% (±10.3%) for 0.5 and 24 hrs sample storage times.

Sample Recovery from Air Sampling Bags

The sample recoveries for bags were generally less than those associated with SPME. 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% (±11.7%) and 39.4% (±9.5%) for 0.5 and 24 hrs sample storage time, respectively. Light MW VFAs had a better mean recovery equal to 94.2% (±7.2%) and 58.9% (±7.2%) for 0.5 and 24 hrs sample storage times compared to recoveries for semi-VOCs equal to 59.8% (±15.5%) and 23.2% (±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%). The sample loss was dependent on storage time. The sample recovery for p-cresol was 67.5% (±6.3%) and 29.0% (±3.0%) for 0.5 and 24 hrs sample storage times. The 24 hr sample recovery for acetic acid was 45.4%.

Tedlar bags made in-house had an average recovery of 11 target compounds equal to 74.5% (±11.7%) and 39.4% (±9.5%) for 0.5 and 24 hrs sample storage time, respectively. Light MW VFAs had a better mean recovery equal to 94.2% (±7.2%) and 58.9% (±7.2%) for 0.5 and 24 hrs sample storage times compared to recoveries for semi-VOCs equal to 59.8% (±15.5%) and 23.2% (±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%). The sample loss was dependent on storage time. The sample recovery for p-cresol was 67.5% (±6.3%) and 29.0% (±3.0%) for 0.5 and 24 hrs sample storage times. The 24 hr sample recovery for acetic acid was 20.4%, i.e., much smaller than those reported by Keener et al.3 One possibility is a large amount of co-eluting and interfering DMAC found in Tedlar bags.

Foil bags had an average recovery of 11 target compounds equal to 67.6% (±7.6%) and 22.7% (±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 24 hr sample recovery for acetic acid was 20.4%, i.e., much smaller than those reported by Keener et al.3 One possibility is a large amount of co-eluting and interfering DMAC found in Tedlar bags.

Sample bags had an average recovery of 11 target compounds equal to 57.1% (±5.2%) and 25.5% (±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% (±15.3%) and 4.3% (±22.9%). The recovery of p-cresol was low and equal to 2.7% (±4.2%) and 3.7% (±3.4%).

Sample Recovery from Sampling Canisters

Average recoveries for canisters were equal to 4.2% (±7.3%) and 0.5% (±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 (±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.

Sample Recovery from Sorbent Tenax TA Tubes

Average recoveries from Tenax TA sorbent tubes were equal to 94.5% (±26.1%) and 88.3% (21.0%) for 24 and 120 hrs sample storage time, respectively. Recoveries of SVOCs (95.5% and 105.1%) were slightly better than recoveries for VFAs (93.9% and 76.4%). Recoveries for all compounds were excellent with the exception of acetic and propionic acids and 2'-aminoacetophenone.

DISCUSSIONS

Both the SPME Carboxen/PDMS 75 µm fibers and Tenax TA appear to be excellent samplers for the target gases used in this study with the average sample recovery equal to 98% (±18.6%) for SPME and the average sample recovery equal to 94.5% (±26.1%) for Tenax TA for 24 hrs storage time at room temperature. This information could be useful to researchers using SPME for field air sampling.

Sample recoveries for all other types of sampling media, i.e., bags and stainless steel (SS) canisters were significantly lower. 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 of semi-VOCs from PET bags were poor. Teflon and in-house Tedlar had the best recoveries for semi-VOCs.

CONCLUSIONS

Several conclusions can be made:

1. Tenax TA sorbent tubes and SPME Carboxen/PDMS 75 µm fibers had the highest average sample recovery equal to 94.5% (±26.1%) and 98% (±18.6%), respectively, 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. 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, commercial Tedlar, in-house made Tedlar, and foil bags.

3. Sample recoveries from sampling canisters were lower than all others.

4. New PET, 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. Foil bags had measurable amounts of acetic, propionic, butyric, valeric, and hexanoic acids.

5. Further research is warranted to determine how recoveries from bags affect odor concentrations.

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