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ARTICLE

Air Sampling and Analysis Method for Volatile Organic Compounds (VOCs) Related to Field-Scale Mortality Composting Operations

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In biosecure composting, animal mortalities are so completely isolated during the degradation process that visual inspection cannot be used to monitor progress or the process status. One novel approach is to monitor the volatile organic compounds (VOCs) released by decaying mortalities and to use them as biomarkers of the process status. A new method was developed to quantitatively analyze potential biomarkers—dimethyl disulfide, dimethyl trisulfide, pyrimidine, acetic acid, propanoic acid, 3-methylbutanoic acid, pentanoic acid, and hexanoic acid—from field-scale biosecure mortality composting units. This method was based on collection of air samples from the inside of biosecure composting units using portable pumps and solid phase microextraction (SPME). Among four SPME fiber coatings, 85 μm CAR/PDMS was shown to extract the greatest amount of target analytes during a 1 h sampling time. The calibration curves had high correlation coefficients, ranging from 96 to 99%. Differences between the theoretical concentrations and those estimated from the calibration curves ranged from 1.47 to 20.96%. Method detection limits of the biomarkers were between 11 pptv and 572 ppbv. The applicability of the prepared calibration curves was tested for air samples drawn from field-scale swine mortality composting test units. Results show that the prepared calibration curves were applicable to the concentration ranges of potential biomaker compounds in a biosecure animal mortality composting unit.

KEYWORDS: Air sampling; compost gas; GC-MS; dimethyl disulfide; dimethyl trisulfide; SPME; volatile fatty acids

INTRODUCTION

The development of new analytical techniques for volatile organic compounds (VOCs) emitted from animal production operations is an increasingly important public and regulatory issue. Composting is widely accepted as an on-farm treatment and disposal method for animal mortalities and is useful for daily management and in emergency animal disease outbreaks (*1*). In biosecure composting applications (*2*, *3*), mortalities are completely covered in an envelope containing large amounts of plant materials (e.g., straw, wood shavings/chips, old hay) and additional plastic barriers. The plastic barrier (e.g., tarp or wrap) and the thickness of the envelope plant material layers prevent the monitoring of the decomposition or decay of mortalities by visual inspection. Thus, an alternative assessment method for the completion of the animal tissue decay process is needed.

An understanding of the volatiles released during the animal mortality composting processes could provide useful insights in determining the status and completion of carcass degradation. Moreover, the composition of the compost exhaust air indicates the aeration status of the process and the quality of the final product (*4*, *5*). Previous research identified the probable biomarker gases released by swine mortalities inside biosecure compost systems (*6*−*8*) as dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS), and pyrimidine. Light molecular weight volatile fatty acids (VFAs) were also found in significant amounts and are known to be associated with anaerobic degradation during composting, along with products of carbohydrate fermentation (*9*), which are indicative of plant envelope material degradation.

Sampling and analyzing air from composting operations are challenging due to the reactive and polar properties of target (potential biomarker) VOCs. Conventional air sampling methods use sorbent tubes, impingers, and vacuum canisters and often focus on specific functional groups of chemical compounds separately. These methods require costly equipment, lengthy sample collection and preparation periods, and complicated extraction procedures. Solid phase microextraction (SPME) offers many advantages for air sampling, such as high precision

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Table 1. Physical Properties of the Quantified Compounds (Lide, 2004)

compound	CAS Registry No.	MW[a]	formula	density[b] (g/mL)	solubility in ethanol	vapor pressure[c] (kPa)
dimethyl disulfide	624-92-0	94.20	$C_2H_6S_2$	1.062	soluble[d]	3.0
dimethyl trisulfide	3658-80-8	126.26	$C_2H_6S_3$	1.202	soluble	0.8
pyrimidine	289-95-2	80.08	$C_4H_4N_2$	1.016	soluble	2.0
acetic acid	64-19-7	60.05	$C_2H_4O_2$	1.049	miscible	1.5
propanoic acid	79-09-4	74.07	$C_3H_6O_2$	0.980	miscible	0.3
3-methylbutanoic acid	503-74-2	102.13	$C_5H_{10}O_2$	0.931	miscible	0.2
pentanoic acid	109-52-4	102.13	$C_5H_{10}O_2$	0.933	soluble	0.02
hexanoic acid	142-62-1	116.15	$C_6H_{12}O_2$	0.920	soluble	0.02

[a] MW, molecular weight. [b] Density at 20 °C. [c] Vapor pressure at 20 °C. [d] Solubility in ethanol at 20 °C is not reported.

and sensitivity, applicability to high-moisture samples, reusability, and compatibility with conventional analytical equipment (*10*−*15*). SPME has been used successfully in field air sampling of various types of agricultural operations (*16*, *17*). A method is available using two different SPME fiber coatings for the analysis of propanoic acid, butyric acid, and sulfur compounds from waste treatment systems (*18*). Volatile organic compound emissions (e.g., propanoic acid, butanoic acid, hexanoic acid, and DMDS) from landfills were characterized using SPME and gas chromatography−mass spectrometry (GC-MS) (*19*, *20*). SPME was also used to characterize headspace VOCs (e.g., propanoic acid, butanoic acid, and DMDS) from the commercial composts of 14 producers (*21*).

In this research, we used a continuous gas generation and flow-through system, which has advantages over batch-type container systems, such as minimizing the effects of adsorption to surfaces in the sampling system and continuous range dilution (*22*). We used syringe pump injection as a convenient quantification method, as it does not require preparing a large number of standard analyte solutions. Gas concentrations are controlled by injection and air flow rates.

The main objectives of the study were (a) to develop an air sampling and analysis method for the quantification of potential biomarker VOCs released by swine mortalities inside biosecure compost systems and (b) to test the applicability of the quantification method for a field-scale biosecure swine mortality composting operation.

MATERIALS AND METHODS

Standards and Reagents. HPLC-grade standards of DMDS, DMTS, pyrimidine, and VFAs were purchased from Sigma-Aldrich (Milwaukee, WI). Physicochemical properties for all target compounds are summarized in **Table 1** (*23*). Air cylinder (99.995%) and ethanol (200 proof) were purchased from the chemistry store at Iowa State University. Standard solutions in ethanol were prepared daily. After preparation, the vial with the standard mixture was manually agitated. Before use, glass sampling bulbs and other glassware were carefully washed, rinsed, and heated overnight at 110 °C.

Air Flow and Air Relative Humidity. Air flow rates were controlled by using a mass flow controller and a mass flow meter (Aalborg, Orangeburg, NY). To test the effects of relative humidity conditions on the extraction efficiency of the SPME fiber, a 15 mL humidifier (Supelco, Bellefonte, PA) was used (**Figure 1**). Results are reported for both dry air (~0% relative humidity, RH) and the maximum humid air that could be reached with the system (~97% RH).

Sampling Bulbs for SPME. Glass sampling bulbs (250 mL, Supelco, Bellefonte, PA) were used for the collection and transfer of the air samples in both laboratory-scale quantification and field-scale composting experiments. SPME was used to extract, store, and transfer VOCs into the GC injection port. Field air samples and gas standards were extracted from glass bulbs with SPME at identical room temperature and static (no air flow) conditions. In laboratory-scale quantification experiments, three sampling bulbs were connected in series to provide enough volume to homogeneously mix

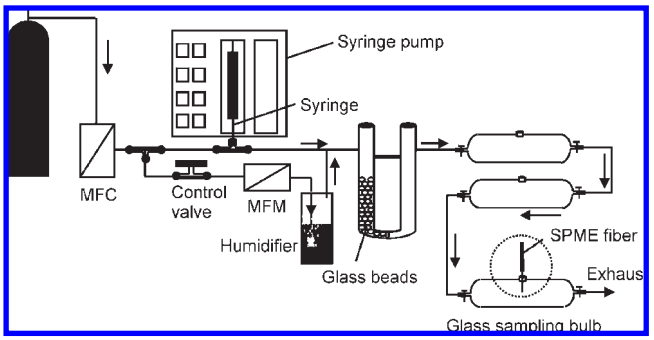

Figure 1. Schematic of the standard gas generation using syringe pump injection and SPME (MFC, mass flow controller; MFM, mass flow meter).

the analytes before SPME. After each concentration change, the system was allowed to reach steady state (the system was run at least for an hour). After steady state was attained, air samples were collected at static conditions (no air flow). For this purpose, polytetrafluoroethylene (PTFE) stopcocks of the last (third) glass bulb were closed and air samples were captured in this glass sampling bulb. VOCs were extracted from this bulb using a SPME fiber (please see the schematic of the system, **Figure 1**). Air samples from the field were also extracted with SPME at static conditions. Air temperature and relative humidity were measured at the time of sampling.

Syringe Pump Injection. The standard gases of the potential biomarker VOCs were generated using a syringe pump injection into a controlled air stream. A KD Scientific syringe pump (model 200, Holliston, MA) and a 100 μL gastight syringe (Hamilton, Reno, NV) were used to deliver the solution of standard analytes through a Thermogreen LB-2 septum into a Swagelok mixing T (**Figure 1**). The injection rate was 0.1 μL/min. The temperature of the system was kept constant (20 °C) using the building temperature controller and continuously measured with a thermocouple (Omega Engineering, Stamford, CT) to check any possible change. The air flow rate of the system was set at 300, 600, or 900 mL/min to generate the desired concentration of the marker VOCs (eq 1). The theoretical analyte concentration for each analyte (in ppmv) was calculated using eq 1 (*22*)

$$C_{\text{analyte}} = \frac{Q_{\text{analyte}}}{Q_{\text{air}}} \times \frac{m_{\text{analyte}}}{m_{\text{total}}} \times 8.3144\left[\frac{\text{L} \times \text{kPa}}{\text{mol} \times \text{K}}\right] \times \frac{293\text{K}}{101.32\ \text{kPa}} \times \frac{1}{\text{MW}_{\text{analyte}}} \quad (1)$$

where Q_{analyte} is the analyte delivery rate (μg/min), Q_{air} is the air flow rate (L/min), m_{analyte} is the mass of the analyte of interest (μg), and m_{total} is the total mass of the mixture injected (μg). $\text{MW}_{\text{analyte}}$ is the molecular weight of the analyte of interest.

Before the experiments were begun, the standard gas generation system was tested for (1) the possibility of condensation, (2) accuracy of the syringe pump, (3) homogeneous mixing, (4) adsorption to walls, and (5) reactions between analytes. The highest concentrations used to prepare calibration curves (**Table 2**) were used for these tests to challenge SPME for possible competitive adsorption and limits of sorptive capacity. The possibility of condensation, adsorption to walls, and reactions between

Table 2. Calibration Curves with Correlation Coefficients, Concentration Ranges of the Calibration Curves (Seven Data Points), and Relative Standard Deviations (RSDs) of the Concentrations Used for Calibrations

	calibration curves			
compound	dry conditions	humid conditions	concn range (ppmv)	RSD range (%)
dimethyl disulfide	$y = 1.78 \times 10^7 x - 6.17 \times 10^4$ $R^2 = 0.998$	$y = 1.74 \times 10^7 x - 8.75 \times 10^4$ $R^2 = 0.998$	0.01−6.85	1.20−4.15
dimethyl trisulfide	$y = 1.51 \times 10^7 x - 3.33 \times 10^6$ $R^2 = 0.990$	$y = 1.46 \times 10^7 x - 2.86 \times 10^6$ $R^2 = 0.990$	0.02−5.95	1.07−4.73
pyrimidine	$y = 2.08 \times 10^7 x + 4.47 \times 10^6$ $R^2 = 0.976$	$y = 2.03 \times 10^7 x + 3.49 \times 10^6$ $R^2 = 0.979$	0.03−6.25	0.24−7.16
acetic acid	$y = 5.17 \times 10^6 x - 1.54 \times 10^6$ $R^2 = 0.993$	$y = 4.78 \times 10^6 x - 2.46 \times 10^6$ $R^2 = 0.986$	0.20−15.6	0.96−11.4
propanoic acid	$y = 9.92 \times 10^6 x - 4.87 \times 10^6$ $R^2 = 0.967$	$y = 8.50 \times 10^6 x - 3.20 \times 10^6$ $R^2 = 0.972$	0.16−13.2	0.72−14.8
3-methylbutanoic acid	$y = 2.24 \times 10^7 x - 9.09 \times 10^5$ $R^2 = 0.985$	$y = 2.07 \times 10^7 x - 3.56 \times 10^6$ $R^2 = 0.984$	0.11−6.12	0.57−11.2
pentanoic acid	$y = 2.51 \times 10^7 x - 2.81 \times 10^5$ $R^2 = 0.995$	$y = 2.30 \times 10^7 x - 8.03 \times 10^5$ $R^2 = 0.990$	0.11−7.24	0.40−7.26
hexanoic acid	$y = 2.32 \times 10^7 x - 1.94 \times 10^6$ $R^2 = 0.991$	$y = 2.28 \times 10^7 x - 2.55 \times 10^6$ $R^2 = 0.991$	0.09−5.54	0.47−12.4

Table 3. Comparison of Theoretical and Measured Concentrations and Method Detection Limits (MDL[a]) for Dry and Humid Air Conditions

		measured $C_{analyte}$(SPME, ppbv)					
		at dry conditions			at humid conditions		
compound	$C_{analyte}$ (theory,[b]ppbv)	av[c]	% diff[d]	MDL ppbv	av[c]	% diff[d]	MDL ppbv
dimethyl disulfide	28	30 A[e]	7.14	1	27 A	3.57	1.1
dimethyl trisulfide	23	20 A	13.04	5.7	19 A	17.39	5.5
pyrimidine	2	2.1 A	0.50	0.01	2 A	0.00	0.011
acetic acid	430	789 A	9.30	520	765 B	12.09	551
propanoic acid	610	631 A	3.44	580	601 B	1.47	572
3-methylbutanoic acid	225	251 A	11.55	120	233 B	3.55	180
pentanoic acid	229	195 A	14.87	40	181 B	20.96	36
hexanoic acid	197	210 A	6.59	110	202 A	5.00	120

[a] Ten measurements were made for each MDL value presented. [b] Theoretical concentrations calculated based on standard gas generation rates. [c] Measured concentrations calculated from the calibration curves. [d] Percent difference between the theoretical and measured concentrations. [e] Means within a column that are not followed by the same letter are significantly different.

analytes was tested for both dry (0% RH) and humid (97% RH) conditions.

In the study, the injection T port was not heated, and because of this, the possibility of condensation inside the T was checked. For this purpose, the mixing T was replaced with a glass sampling bulb, and air with standard analytes was allowed to pass through for 2 h (average run time of the syringe pump). The glass bulb was then washed with ethanol. This washed ethanol was directly injected into the GC. None of the compounds were found in the ethanol wash. It is concluded that if there is no condensation after 2 h of testing time, then there will not be any significant condensation in the system. This finding was also supported with visual inspection of the glass sampling bulbs.

The accuracy of the syringe pump delivery rate was confirmed through two approaches. In the first, the preweighed syringe was used to deliver a mixture of VOCs for a period of time. The pump delivery rate was calculated on the basis of the weight difference ($n = 5$). In the second approach, the volume difference was recorded and the delivery rate was calculated on the basis of this difference ($n = 5$). The relative standard deviation of these 10 measurements was 0.19%. Only a 0.014% difference was found between the theoretical delivery rate and the delivery rates calculated from these two approaches.

The homogeneous mixing of air and standards before the sampling port (situated in the third glass sampling bulb) was also tested. The preliminary experiments showed that when only three glass sampling bulbs were used, homogeneous mixing was not achieved before the third glass bulb. Thus, 6 mm diameter Pyrex glass beads (113 g, Fisher Scientific, Pittsburgh, PA) were used to improve the mixing (**Figure 1**). A U-shape tube was filled with glass beads and connected to the first glass sampling bulb. After this modification, standards were extracted from the second and third glass sampling bulbs. No significant difference was found between the MS detector response of standards from the second and third sampling bulbs. It was concluded that using glass beads resulted in homogeneous mixing of the standards before the VOCs reach the sampling port.

The possibility of adsorption to the walls in the standard generation system was also tested. Before sampling, the system was run for 1 h to reach equilibrium and to minimize wall adsorption effects. To test equilibrium conditions, samples were collected from the second and third sampling bulbs after the system had been run for an hour. Results show that there is no significant difference between the MS detector response of standards from the second and third sampling bulbs and that 1 h is enough to reach equilibrium.

The possibility of reactions between analytes in a gas standard sample was tested by directly injecting the mix into the injection port of the GC. The concentrations reported in **Table 3** (theoretical concentrations) were used in this experiment. No formation of new compound was detected.

SPME Fiber Selection. Four commercially available SPME fibers were compared in a 1 h extraction time by evaluating peak area values, that is, the amount of the analytes extracted by the fibers (*25*). The tested fibers were 85 μm carboxen/polydimethylsiloxane (CAR/PDMS), 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), and 85 μm polyacrylate (PA) (Supelco, Bellefonte, PA). This selection was based on a literature review and previous experience with target analytes. New SPME fibers were first conditioned according to the manufacturer's directions. In addition, SPME fibers were inserted into the injection port of the GC for 5 min to thermally desorb impurities on the

fiber immediately before sampling. All of the GC-MS conditions were the same for all fibers tested.

Sampling Time Selection. The practical sampling time was optimized for the 85 μm CAR/PDMS fiber coating. Sampling times of 1, 3, 10, 60, 360, and 720 min were tested. Because CAR/PDMS is an adsorptive-type fiber coating, analytes were extracted under nonequilibrium conditions. The sampling time was chosen as the longest practical time for linear extraction (mass extracted vs sampling time) that does not result in competitive extraction under the worst-case scenario (i.e., highest observed concentrations of target analytes in field samples).

Demonstration of the Quantitative Analysis. An example of the quantitative analysis of target VOCs was demonstrated for air samples collected from field-scale swine mortality composting units. Details of the composting units were described in previous publications (*25*, *26*). On the 10th day of the process, air samples were drawn from the center location of the composting units using SKC pumps (model 224-PCXR4, Bellefonte, PA). It is generally known that VOC production is most intense in the first 10 days of a composting process (*8*, *27*). This intense VOC production period was selected to collect VOC samples to show the applicability of the developed calibration curves for the possible highest concentrations of VOCs. The applicability of the calibration curves for the lowest concentrations is shown by method detection limits. Air samples were captured inside a single 250 mL glass sampling bulb. The air flow rate during sampling was 1.0 L/min, and the sampling start time was 5 min (20 hydraulic residence times) to allow the system to reach steady state conditions. VOCs were sampled using the selected SPME fiber and sampling time.

Sample Analysis. All gas analyses were performed using an integrated multidimensional 6890N GC and 5973 MS system assembled by Microanalytics (Round Rock, TX) based on the Agilent Inc. (Wilmington, DE) platform. Ultrahigh-purity (99.995%) helium was used as the carrier gas at constant pressure mode. The injector and SPME fiber desorption temperatures were 260 °C. The initial temperature of the GC oven was 40 °C with a 3 min holding time, followed by a ramp of 10 °C/min to 220 °C, at which it was held for 10 min. Two capillary columns connected in series were used to separate compounds. The precolumn was a 12 m × 0.53 mm BP5 with an inside diameter (i.d.) of 0.25 μm, and the analytical column was a 25 m × 0.53 mm i.d. × 0.25 μm BP20 (both from SGE, Austin, TX). The heart-cut valve between the precolumn and analytical column was opened between 0.05 to 28 min, and the backflush of the precolumn was activated between 28 and 31 min to prepare the system for the following run. The MS mass/charge (m/z) ratio was set between 33 and 150 for the first 8 min. After that, the MS m/z ratio was between 34 and 280. The transfer line, quadrupole, and MS source temperatures were 240, 150, and 230 °C, respectively. The standard gas method detection limit (MDL) was calculated at the 99% confidence level for a signal-to-noise ratio of 5 and a standard deviation of 10 replicate measurements (*24*).

Data Analysis. Chromatography data acquisition software consisting of MSD ChemStation (Agilent, Wilmington, DE) and BenchTop/PBM V. 3.2.4 (Palisade Corp., Ithaca, NY) was used to analyze data. Separated compounds were identified using mass spectral matches with ChemStation's NIST MS and PBM Benchtop MS libraries. Spectral matches and column retention times were compared with those of standard analytes.

Statistical Analysis. Experiments were run in triplicate (n = 3). All data were analyzed using the statistical package JMP v. 6.0.2 (SAS Institute, Inc., Cary, NC). Data were subjected to a one-way analysis of variance (ANOVA). Treatment means were compared using Tukey's honestly significant difference (HSD) test at the 95% confidence level. Correlation coefficients of the calibration curves were calculated using Excel tools.

RESULTS

Fiber Selection. The optimized SPME fiber coating was selected on the basis of a comparison of the amount of analyte SPME fibers extracted in a 1 h sampling time (**Figure 2**). The concentrations ranged from 2.81 ppmv for hexanoic acid to 7.9 ppmv for acetic acid. These concentrations were in the middle range of the calibration curves. The relative standard deviations (RSDs) ranged from 1 to 9%. The 85 μm CAR/PDMS fiber

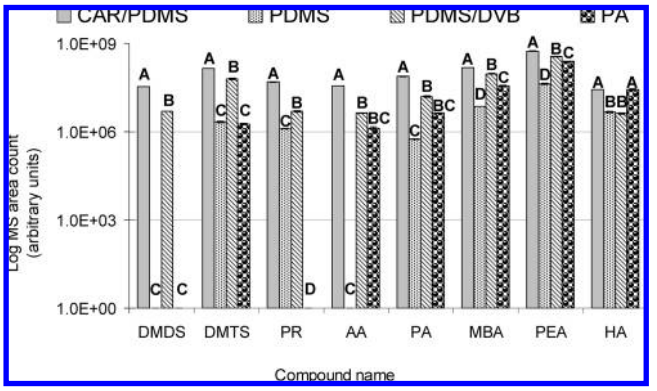

Figure 2. Extraction efficiencies of different SPME fiber coatings (SPME at room temperature and in a 1 h extraction time). Means (within a compound) that are not associated with the same letter are significantly different; n = 3; $p \leq 0.05$.

provided the highest extraction efficiency and was found to be statistically significantly different in comparison with the other SPME fibers tested. On the basis of the amount of analytes extracted, efficiencies of the fibers were ranked from highest to lowest as CAR/PDMS > PDMS/DVB > PDMS ≈ PA (**Figure 2**). These results can be explained by the characteristics of the fiber coatings as mixed phase coatings (CAR/PDMS and PDMS/DVB) having complementary properties compared to homogeneous phase coatings (PDMS and PA). Because the majority of interaction is determined by the adsorption process on a porous surface, CAR/PDMS and PDMS/DVB are suitable for more VOCs compared to PDMS and PA fiber coatings (*28*). Thus, DMDS, DMTS, pyrimidine, and VFAs were extracted at higher amounts by CAR/PDMS and PDMS/DVB compared to PDMS and PA (**Figure 2**). The DVB phase is mainly mesoporous and ideal for trapping C_6−C_{15} analytes. Unlike DVB, CAR is microporous and traps C_2−C_6 analytes (*29*). This explains the better extraction efficiency of CAR/PDMS compared to PDMS/DVB for the compounds ranging from C_2 from C_6 (**Figure 2** and **Table 1**).

Extraction Time Selection. Carboxen/PDMS is an adsorptive SPME fiber coating and is susceptible to competitive adsorption if overloaded. Six extraction times were tested for this SPME fiber coating. The amounts of analytes extracted are shown in **Figure 3**. The RSDs of means ranged from 1 to 14%. For the 6 and 12 h extraction times, an increase in extraction time did not lead to a significant increase in the amount of analyte extracted (**Figure 3**). This was likely caused by the limited sorptive capacity of SPME. The 1, 3, 10, and 60 min sampling times were graphed separately (**Figure 4**), and the linearity of the response was evaluated. Correlation coefficients of the curves ranged from 96 to 99%. In a 1 h sampling time, there was no apparent displacement of the compounds, and 1 h was chosen as the proper sampling time for the CAR/PDMS fiber coating to quantify DMDS, DMTS, pyrimidine, and low molecular weight VFAs.

Calibration Curves and Method Detection Limits. The quantification of target VOCs was based on the calibration curves for the optimized 1 h sampling time. Calibration curves were prepared for both dry (~0% RH) and humid (~97% RH) air conditions (**Table 2**). The concentration ranges of the compounds and RSDs are shown in **Table 2**. The concentrations ranged from 0.01 to 6.85 ppmv for dimethyl disulfide and from 0.2 to 15.6 ppmv for acetic acid. The replicates had RSDs ranging from 0.32 to 5.01%. No significant difference in extraction efficiency was detected between dry and humid air conditions for DMDS, DMTS, pyrimidine, and hexanoic acid. However, significant

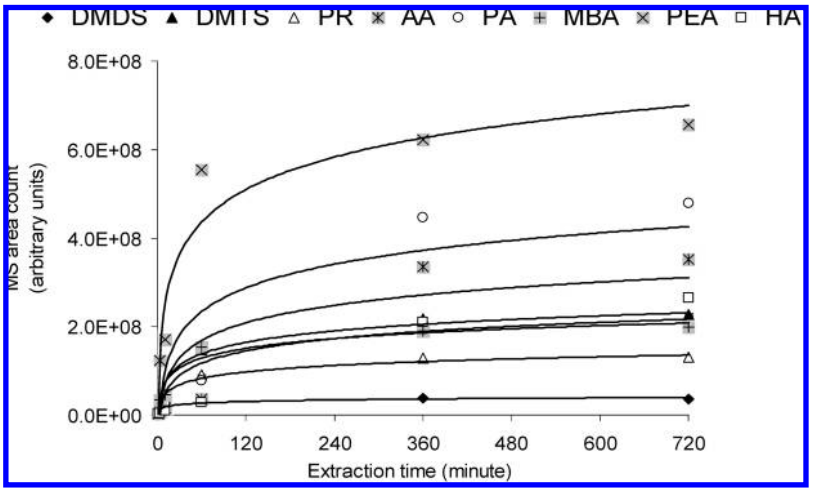

Figure 3. Extraction efficiencies in 1, 3, 10, 60, 360, and 720 min sampling times (85 μm CAR/PDMS SPME fiber, room temperature).

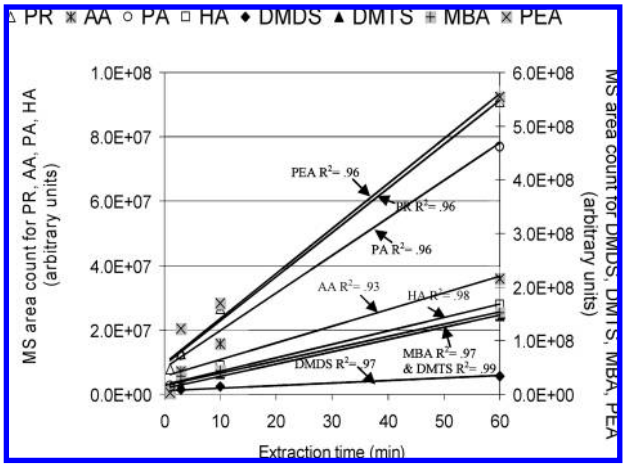

Figure 4. Extraction efficiencies in 1, 3, 10, and 60 min extraction times and correlation coefficients (85 μm CAR/PDMS SPME fiber, room temperature).

differences were detected for acetic, propanoic, 3-methylbutanoic, and pentanoic acids at 97% RH conditions compared to dry air (0% RH) conditions. Lower concentrations of these acids were detected at 97% RH humid conditions compared to 0% RH dry conditions. This is important because in a typical swine mortality composting operation, air samples collected in the early stage of the process are expected to have a very high RH (approximately 100%). However, in further stages, compost materials lose some of their moisture and air samples have a RH ranging from 0 to 100%. If the RH of the air samples is not known, concentrations of the DMDS, DMTS, pyrimidine, and hexanoic acid can be calculated using either of the calibration curves. However, if the RH is not known, calculating exact concentrations of acetic, propanoic, 3-methylbutanoic, and pentanoic acids will not be possible. In this situation, a range of concentrations can be reported by using both the calibration curves prepared for dry (~0% RH) and humid (~97% RH) conditions.

The concentrations calculated on the basis of standard gas generation rates (theoretical concentrations) were compared with the measured concentrations estimated from the calibration curves (**Table 3**). The theoretical concentrations were chosen arbitrarily but were in the low range of concentrations considering the challenges of sampling and analysis at low concentrations. The estimated concentrations from the field-scale composting units were all above MDLs (**Table 3**) and, thus, reliable. Measured concentrations were found to be different from the theoretical concentrations at levels ranging from 1.47 to 20.96%, which is within the range of differences reported between theoretical and measured *n*-alkane concentrations, 2−17% (*22*), and considered to be acceptable.

Application to Field Air Sampling. An example of a total ion chromatogram of the air samples drawn from field-scale swine mortality composting units is shown in **Figure 5**. VOC concentrations were calculated using both the calibration curves prepared for dry (~0% RH) and humid (~97% RH) conditions (**Table 4**). Gas concentrations of the compounds ranged from 0.06 to 7.39 ppmv. This is the typical range of concentrations measured from the biosecurity barriers of field-scale swine mortality composting units (*8*). These concentrations were lower than the high concentration range of the calibration curves, but higher than the MDLs. It is shown that the prepared calibration curves can be used for the concentration ranges detected from a field-scale composting unit. The developed method considers both the dry and humid conditions of the composting process and is applicable to quantitatively analyzing VOCs from field-scale swine mortality composting operations.

DISCUSSION

A new method was developed to quantitatively analyze DMDS, DMTS, pyrimidine, acetic acid, propanoic acid, 3-methylbutanoic acid, pentanoic acid, and hexanoic acid from field-scale mortality composting operations. The 85 μm CAR/PDMS SPME fiber is shown to extract the highest amount of analytes in a 1 h sampling time. It is observed that in this sampling time there is no risk of analyte displacement for typical concentrations of target analytes. The prepared calibration curves have high correlation coefficients, ranging from 96 to 99%.

Measured concentrations were found to be different from the theoretical concentrations at a level ranging from 1.47 to 20.96%. These differences are within the range of differences reported between theoretical and measured *n*-alkane concentrations of 2−17% (*22*) and considered to be acceptable. No significant difference is found for DMDS, DMTS, pyrimidine, and hexanoic acid concentrations extracted under dry (0% RH) and humid (97% RH) conditions. However, lower concentrations of acetic acid, propanoic acid, 3-methylbutanoic acid, and pentanoic acid were detected at 97% RH conditions compared to dry conditions (0% RH). A range of these VOC concentrations can be calculated

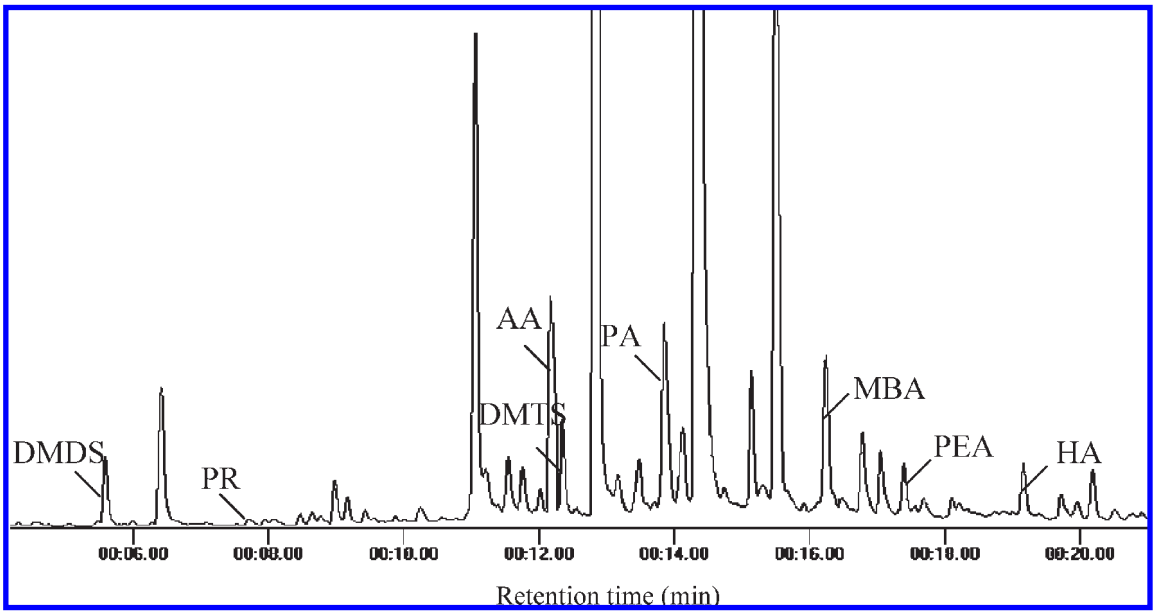

Figure 5. Total ion chromatogram of air sample collected from a field-scale swine mortality composting operation (85 μm CAR/PDMS SPME fiber, 1 h sampling time, room temperature).

Table 4. Measured VOC Concentrations in Air Samples Collected from a Field-Scale Swine Mortality Composting Operation 10 Days after Construction

			concn (ppmv)	
retention time[a] (min)	compound	MS area counts (arbitrary units)	dry conditions	humid conditions
5.55	dimethyl disulfide	1.1×10^7	0.59	0.60
7.86	dimethyl trisulfide	4.7×10^6	0.07	0.06
12.10	pyrimidine	3.3×10^7	6.84	7.39
12.27	acetic acid	9.9×10^6	0.43	0.48
13.78	propanoic acid	2.3×10^7	2.76	3.02
16.17	3-methylbutanoic acid	1.9×10^7	0.88	1.08
17.34	pentanoic acid	8.5×10^6	0.35	0.41
19.10	hexanoic acid	1.2×10^7	0.64	0.66

[a] GC column retention times and MS spectra of the compounds were matched with the standard analytes.

using the calibration curves prepared for dry (~0% RH) and humid (~97% RH) air conditions.

The applicability of the prepared calibration curves was tested for air samples drawn from a field-scale swine mortality composting unit. Results show that the calibration curves were valid for the highest possible concentrations (in the headspace) that can be measured from a field-scale composting operation. MDLs were found to range from 11 pptv (pyrimidine) to 572 ppbv (propanoic acid). SPME and standard gas generation using syringe pump injection are found to provide good estimates of the concentrations of DMDS, DMTS, pyrimidine, and VFAs. These techniques can be used for relatively rapid and sensitive quantitative analysis of VOCs from composting operations. The findings from this study could be used to develop sampling and quantification methods for other volatile organic compounds of the mortality composting operations. Other potential compounds of interest may include dimethyl sulfide, methanethiol, and ethanethiol.

ABBREVIATIONS USED

CAR/PDMS, Carboxen/polydimethylsiloxane; DMDS, dimethyl disulfide; DMTS, dimethyl trisulfide; GC, gas chromatography; MS, mass spectroscopy; PA, polyacrylate; PDMS, polydimethylsiloxane; PDMS/DVB, polydimethylsiloxane/divinylbenzene; PTFE, polytetrafluoroethylene; SPME, solid phase microextraction; VFA, volatile fatty acids; VOC, volatile organic compound.

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LITERATURE CITED

(1) Wilkinson, K. G. The biosecurity of on-farm mortality composting. *J. Appl. Microbiol.* **2007**, *102*, 609–618.

(2) Spencer, J. L.; Rennie, B.; Guan, J. Emphasis on biosecurity for composting poultry and manure during an outbreak of highly pathogenic *Avian influenza* in British Columbia. *Can. Anim. Health Net Bull.* **2004**, *9*, 21–23.

(3) Bendfeldt, E. S.; Peer, R. W.; Flory, G. A. In-house composting as a rapid response to avian influenza. *Biocycle* **2006**, *47*, 38–43.

(4) Day, M.; Shaw, K.; Krzymien, M. Composting odors: what can chemistry tell us? *Proceedings of the International Composting Symposium*, Halifax/Dartmouth, NS, **1999**.

(5) Romain, A. C.; Godefroid, D.; Kuske, M.; Nicolas, N. Monitoring the exhaust air of a compost pile as a process variable with an e-nose. *Sens. Actuators, B* **2005**, *106*, 29–35.

(6) Akdeniz, N.; Koziel, J. A.; Ahn, H. K.; Crawford B. P.; Glanville, T. D. Qualitative characterization of volatile compound emissions during biological decomposition of plant materials using SPME-GC-MS. *ASABE Annual International Meeting*, ASABE Paper 074041, Minneapolis, MN, June 2007.

(7) Akdeniz, N.; Koziel, J. A.; Ahn, H. K.; Crawford B.; Glanville, T. D. Stability evaluation of simulated plant and animal composts utilizing respiration rates and VOC emissions. *ASABE Annual International Meeting*, ASABE Paper 074155, Minneapolis, MN, June 2007.

(8) Akdeniz, N. *Identification, evaluation, and quantification of VOCs as biosecure markers of swine carcass degradation*. Ph.D. Dissertation Thesis, Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA, **2008**.
(9) Epstein, E. *The Science of Composting*; Technomic Publishing: Lancaster, PA, 1997; pp 487.
(10) Koziel, J. A.; Jia, M.; Khaled, A.; Noah, J.; Pawliszyn, J. Field air analysis with SPME device. *Anal. Chim. Acta* **1999**, *400*, 153–162.
(11) Wercinski, S. A. S. *Solid Phase Microextraction*; Dekker: New York, 1999; pp 93−94.
(12) Jia, M.; Koziel, J.; Pawliszyn, J. Fast field sampling/sample preparation and quantification of volatile organic compound in indoor air by solid phase microextraction and portable gas chromatography. *Field Anal. Chem. Technol.* **2000**, *4* (2−3), 73–84.
(13) Augusto, F.; Koziel, J.; Pawliszyn, J. Design and validation of portable SPME devices for rapid field air sampling and diffusion-based calibration. *Anal. Chem.* **2001**, *73*, 481–486.
(14) Koziel, J. A.; Pawliszyn, J. Air sampling and analysis of VOCs with solid phase microextraction. *J. Air Waste Manage. Assoc.* **2001**, *51*, 173–184.
(15) Pacolay, B. D.; Ham, J. E.; Wells, J. R. Use of solid-phase microextraction to detect and quantify gas-phase dicarbonyls in indoor environments. *J. Chromatogr., A* **2006**, *1131*, 275–280.
(16) Wright, D.; Nielsen, L.; Eaton, D.; Kuhrt, F.; Koziel, J. A.; Spinhirne, J. S.; Parker, D. B. Multidimensional GC-MS-olfactometry for identification and prioritization of malodors from confined animal feeding operations. *J. Agric. Food Chem.* **2005**, *22*, 8663–8672.
(17) Koziel, J. A.; Cai, L.; Wright, D.; Hoff, S. Solid phase microextraction as a novel air sampling technology for improved GC-olfactometry-based assessment of livestock odors. *J. Chromatogr. Sci.* **2006**, *44*, 451–457.
(18) Kim, H.; Nochetto, C.; McConnell, L. L. Gas-phase analysis of trimethylamine, propionic and butyric acids, and sulfur compounds using solid-phase microextraction. *Anal. Chem.* **2002**, *74*, 1054–1060.
(19) Davoli, E.; Gangai, M. L.; Morselli, L.; Tonelli, D. Characterization of odorants emissions from landfills by SPME and GC/MS. *Chemosphere* **2003**, *51*, 357–368.
(20) Kim, K. H.; Choic, Y. J.; Jeon, E. C.; Sunwoo, Y. Characterization of malodorous sulfur compounds in landfill gas. *Atmos. Environ.* **2005**, *39*, 1103–1112.
(21) Kim, H.; McConnell, L. L.; Millner, P. Comparison of odorous volatile compounds from fourteen different commercial composts using solid-phase microextraction. *Trans. ASABE* **2005**, *48*, 315–320.
(22) Koziel, J. A.; Martos, P. A.; Pawliszyn, J. System for the generation of standard gas mixtures of volatile and semi-volatile organic compounds for calibrations of solid-phase microextraction and other sampling devices. *J. Chromatogr., A* **2004**, *1025*, 3–9.
(23) Lide, D. R. *Handbook of Chemistry and Physics*, 85th ed.; CRC Press: New York, 2004−2005.
(24) EPA. U.S. Environmental Protection Agency. Method detection limit (MDL) procedure found in title 40 code of Federal Regulations (40, CFR 136, Appendix B, revision 1.11).
(25) Ahn, H. K.; Glanville, T. D.; Crawford, B. P.; Koziel, J. A.; Akdeniz, N. Evaluation of the biodegradability of animal carcasses in passively aerated bio-secure composting system. *ASABE Annual International Meeting*, ASABE Paper 074037, Minneapolis, MN, June **2007**.
(26) Glanville, T. D.; Ahn, H. K.; Koziel, J. A.; Akdeniz, N.; Crawford, B. P. Performance evaluation of a passively aerated plastic wrapped composting system designed for emergency disposal of swine mortalities. *ASABE Annual International Meeting*, ASABE Paper 074155, Minneapolis, MN, June **2007**.
(27) Haug, R. T. *The Practical Handbook of Compost Engineering*; Lewis Publishers: Boca Raton, FL, 1993; 718 pp.
(28) Pawliszyn, J. SPME method development. In *Solid Phase Microextraction—Theory and Practice*; Pawliszyn, J., Ed.; Wiley-VCH: New York, 1997; pp 97−140.
(29) Mani, V. Properties of commercial SPME coatings. In *Applications of Solid Phase Microextraction*; Pawliszyn, J., Ed.; The Royal Society of Chemistry: Cambridge, U.K., 1999; pp 57−108.

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