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GENERATION AND CALIBRATION OF STANDARD GAS MIXTURES FOR VOLATILE FATTY ACIDS USING PERMEATION TUBES AND SOLID PHASE MICROEXTRACTION

Jarett P. Spinhirne¹ and Jacek A. Koziel¹

ABSTRACT

Volatile fatty acids (VFAs) are major components of odors associated with agricultural operations and livestock housing, solid waste processing and disposal, and industrial and municipal wastewater collection and treatment systems. Emissions estimation and assessment of odor control methods depend on reliable air sampling and analysis methods for VFAs. The objective of this research was to develop and test a method for continuous and reliable generation of standard gas mixtures for VFAs based on permeation tubes. Standard gas mixtures for acetic, propionic, isobutyric, butyric, isovaleric, valeric, and hexanoic acids were generated with permeation tubes and monitored for a 100-day period. The gravimetric loss of VFA from each tube was measured periodically and used to calculate the emission rate for each permeation tube. Emission rates were as high as 2,011 ng/(min·cm) for acetic acid to as low as 49 ng/(min·cm) for isovaleric and hexanoic acids, respectively. The emission rate was combined with the dilution flow rate to calculate standard concentrations. Five different concentrations for each VFA were obtained by adjusting dilution flow rate. Gas concentrations were monitored with DVB/Carboxen/PDMS 50/30 µm fibers using triplicate 1 min extractions. Maximum standard gas concentrations ranged from 21.9 ppmv for acetic acid to 0.22 ppmv for hexanoic acid. Minimum standard gas concentrations ranged from 3.0 ppmv for acetic acid to 0.03 ppmv for hexanoic acid. The relative standard deviations (RSDs) for all VFA concentrations ranged from $\pm 1.6\%$ to 7.56 %. Rapid SPME extractions were sufficient to preconcentrate significant amount of VFAs for separation on a GC-FID without derivatization. Dilution gas flow rate did not affect the emission rates from permeation tubes. In contrast, low acid levels affected permeation rates of the acids from the tubes. Methodology described in this research paper could be used to generate and test standard gas mixtures for other groups of odorous gases.

KEYWORDS: permeation tubes, standard gas generation, volatile organic compounds, volatile fatty acids, solid phase microextraction, gas chromatography, air sampling, odor

INTRODUCTION

Volatile Fatty Acids. Volatile fatty acids are flammable organic acids with pungent smell that contribute to nuisance odors surrounding agricultural feeding operations, concentrated animal feeding operations (CAFOs), solid waste processing and disposal facilities, and municipal solid and liquid collection and treatment disposal facilities. Volatile fatty acids are produced in the environment from the bacterial decomposition of organic materials. Problems with odors can arise when acidogenic bacteria produce VFAs faster than acetogenic/methanogenic species can consume the acids. Low molecular weight VFAs are important odor indicators in air surrounding agricultural facilities (Zhu *et al.*, 1999; Wiles *et al.*, 2000). To date, the majority of VFA emissions data from confined animal feeding operations (CAFOs) have been collected for

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swine facilities (Zhu *et al.*, 1999; Zahn *et al.*, 1997; Schiffman *et al.*, 2001; Bicudo *et al.*, 2001; Gralapp *et al.*, 2001). Municipal wastewaters also contain many low molecular weight VFAs (Hvitved-Jacobsen *et al.*, 1994). Light molecular weight VFAs such as acetic and formic acids are ubiquitous in the atmosphere and in precipitation, and can significantly contribute to free acidity in remote regions. Air sampling and analysis of VFAs may be used to characterize emitted odorous gases and evaluate efficiency of odor control and abatement. To date no standard method for air sampling and analysis of VFAs exists. This is partially due to the fact that VFAs are reactive and polar. Any analytical method for the measurement of VFAs in air should use a source of standard VFA gas for calibration of instruments and methods development. The properties of VFAs make the preparation of standard gas mixtures challenging. In this research, we show a reliable method for generating standard gas mixtures for VFAs based on permeation tube technology.

Generation of Standard gases: Dynamic Methods. Dynamic standard gas generators that produce a steady stream of standard gas are sometimes better than “static “ or “batch” methods and can be used for repetitive calibrations and QA/QC checks without depleting (via extractions) the source. Dynamic generators also have the advantage of producing a continuous stream of gas that initially coats absorption sites on “wet” surfaces of connecting transfer lines and sampling chambers. This allows for a semi steady-state adsorption/desorption equilibrium and minimization of wall effects (Martos and Pawliszyn, 1997). This effect can be further minimized by passivation of “wet” surfaces. Stainless steel can be deactivated with pretreatment of a 5-10% nitric acid wash. Alternatively, treated stainless steel lines can be purchased commercially. Active sites on glass surfaces can be eliminated by treatment with dimethyldichlorosilane in a silanization process. Standard gas sources that can be coupled with dilution gas flow include: (1) syringe injection, (2) capillary tube diffusion, (3) thermal degradation of polymer, and (4) liquid or gas-filled permeation tubes.

Permeation Tubes. The use of permeation sources for the production of environmental standards is not new. O’Keeffe and Ortman (1966) first suggested and tested the use of permeation tubes in the mid-1960’s for propane, butane, SO₂, NO₂, and several aromatic and halogenated VOCs. Since then permeation sources have been used for a wide variety of standards including: SO₂, NO₂, NH₃ (Scaringelli *et al.*, 1970), vinyl chloride (Cedergren and Fredriksson, 1976), halocarbons (Crescentini *et al.*, 1981), formaldehyde (Dong and Dasgupta, 1986), acetaldehyde and acetone (Mangani and Ninfali, 1988), thiols (Choi and Hawkins, 1997), p-xylene, carbon tetrachloride, chlorobenzene, toluene, n-decane, n-undecane, and benzene (Namiesnik *et al.* 1999; Couret, 2002). The advantage of permeation sources over static and diffusive techniques is that generated concentrations are lower and more stable over time. The basic design of a permeation source is a liquid or gas-filled tube of PTFE or other semi-inert permeable material that is placed inside a temperature-controlled flow-through container. At constant temperature, liquid analytes permeate (diffuse) through the tube wall at a rate directly proportional to the length of the exposed tube (Nelson, 1992). To date, there is no data in the literature related to the generation of VFAs with permeation tubes for the calibration of analytical instruments or analysis of ambient air.

The purpose of this research was to develop and test a method for continuous and reliable generation of standard gas mixtures for VFAs based on permeation tubes and calibration with SPME. Specific tasks included construction of an air sampling chamber and assembly of permeation tubes for each VFA, adjusting and monitoring dilution gas flow rates and VFA emission rates to obtain a wide range of standard gas concentrations, and monitoring gas concentrations with SPME.

MATERIALS AND METHODS

Standard Gas Generator and Permeation Tubes

Standard gas concentrations of VFAs were made using a Model 491B standard gas generator (Kin-Tek, LaMarque, TX). The heart of the generator is the oven (**Figure 1**), which holds a sealed glass bulb at a controlled temperature. Inside the oven bulb were 7 permeation tubes that contained one analyte, i.e., acetic, propionic, isobutyric, butyric, isovaleric, valeric, and hexanoic acids, respectively. Seven permeation tubes were made using small amounts (1 to 1.5 mL) of pure acid placed in 6.35 mm OD $\times$ 0.51 mm wall thickness ($\frac{1}{4}$ " OD $\times$ 0.020") tubes fabricated from PTFE tube stock (Supelco, Bellefonte, PA). The ends of the tubes were sealed with 12 mm length $\times$ 6 mm dia. ($\frac{1}{2}$ " $\times$ $\frac{1}{4}$ " dia.) plugs made from extruded virgin PTFE rod (Enflo, Bristol, CT) that were beveled on one end to aid in insertion into the tubing and sealed in place with 8 mm (5/16") stainless steel crimp clamps. The effective length of each tube measured as the distance between the interior surfaces of the end plugs varied from 79 to 85 mm depending on the acid.

All 7 VFAs can be purchased commercially. However, tubes were made at a cost of approximately \$1 each compared with \$200 to \$400 for commercial tubes. In addition, the design of the permeation tubes in this research allowed the metal sealing bands to be cut and replaced with new bands and the tubes to be refilled without damaging the PTFE tube walls. Ultra high pure (UHP) N₂ was used to dilute the oven bulb headspace and transport the acids. Standard gas leaving the oven was then diluted with more N₂ in its base unit for up to a 1:20 dilution.

Figure 1. Schematic of gas standard generator and air sampling system.

Estimation of Emission Rates and Standard Concentrations

Emission rate from each tube was determined by massing it 3 times periodically approximately every 2 weeks during dilution gas cylinder exchanges. In this research, tubes were massed with a scale that had 0.0001 g resolution. More frequent measurements were not necessary and feasible. Longer times between massing allowed for the measurement of larger mass changes from the permeation tubes and therefore higher accuracy of the measurement. The emission rate of each tube was determined using the following equation:

$$E_{\text{acid}} = \frac{\Delta m}{t} \quad (1)$$

where: E_{acid} = emission rate for the compound of interest (ng/min), Δm = average of triplicate measurement of mass change of the tube (ng), and t = time between tube massing (min).

The emission rate was then used to estimate the concentration of the VFA in the standard gas, using the following equation:

$$C_{\text{gas}} = \frac{E_{\text{acid}}}{Q_{\text{gas}}} \quad (2)$$

where C_{gas} = concentration of compound of interest in standard gas mixture (ng/L) and Q_{gas} = carrier gas flow rate (L/min). C_{gas} can be converted to mixing ratio's units using the following equation:

$$C_{\text{ppm}} = C_{\text{gas}} \frac{RT}{MW \times p \times 1000} \quad (3)$$

where C_{ppm} = concentration in parts per million (ppmv), R = ideal gas law constant = 0.08206

$\left(\frac{\text{L} \times \text{atm}}{\text{mol} \times \text{K}} \right)$, T = temperature of standard gas (K), MW = molecular weight of the acid (g/mol),

and p = atmospheric pressure (atm). The outlet of the standard gas generator was connected with 6 mm (1/4") stainless steel tubing to a 1L glass flow-through sampling bulb (Supelco, Bellefonte, PA). The bulb sampling port was fitted with a Thermogreen LB-1 half-hole septum (Supelco, Bellefonte, PA) for insertion and sampling with SPME. A circulating heating/cooling bath (New Brunswick Scientific Co., Edison, NJ) held the temperature of the standard gas at 28.3 °C.

Monitoring of Standard Gas

Sampling bulb temperature, room temperature, barometric pressure, dilution gas flow, and concentration measurements were taken as part of a weekday QC/QA protocol to test the ability of the standard gas generator to maintain a stable concentration over the effective life of its permeation tubes. The flow through the sampling bulb was also measured with a 1 L bubble flow meter (Supelco, Bellefonte, PA) and a NIST-traceable timer (VWR, Suwanee, GA) in three replicate measurements on each day samples were taken. The flow meter temperature and the barometric pressure were used to correct the flow to standard temperature and pressure, defined here as 273 K and 1 atm. Air samples from standard gas in the chamber were collected in triplicate using 1 DVB/Carboxen/PDMS 50/30 μm SPME fiber (Supelco, Bellefonte, PA) and a 1 min sampling time. Earlier tests indicated that this fiber coating was the most efficient for isovaleric, valeric, and hexanoic acids, and the second most efficient (after Carboxen/PDMS 75 μm) for acetic, propionic, isobutyric, and butyric acids (Spinhirne et al., 2002).

Sample Analysis

All SPME samples were analyzed on a Varian 3900 GC- FID. The low partitioning constant at high (250°C) temperatures in the injector caused compounds to desorb from the fiber. The injector was held in the splitless mode for the entire run. The column (HP-FFAP, 25 m $\times$ 0.20 mm $\times$ 0.33 μm) was initially at 60 °C, ramped to 110 °C at a rate of 60 °C/min, ramped to 170 °C at a rate of 10 °C/min, and finally ramped to 250 °C at a rate of 60 °C/min with a holding time of 3 min. A constant 2.0 mL/min of UHP grade He was maintained through the column at all times. The FID detector was supplied with 25 mL/min UHP helium makeup flow, 30 mL/min UHP hydrogen flow, and 300 mL/min zero grade air flow. Both the injector and the detector were kept at 250 °C. SPME fibers were desorbed in the injector for the entire 11.7 min GC run. The response factors (RFs) for the acids were used to calculate the mass of analyte extracted

from 1 min SPME samples during calibration and QC/QA. RFs for the 7 target VFAs on the FID were estimated from 1 μ L injections of ethanolic standard.

RESULTS AND DISCUSSIONS

Emission Rates for Permeation Tubes

Table 1 lists the emission rates (E_{acid}) calculated using Equation 1 for the permeation tubes throughout the experiment. Average emission rates varied from as much as 16,149 ng/min for acetic acid to 421 ng/min for hexanoic acid. The RSDs for emission rates were less than 8 % for all 7 VFAs. High RSDs for valeric (4.8 %), hexanoic (6.9 %), and isovaleric (7.8 %) were likely caused by the uncertainty in measuring their relatively small mass changes between measurements (71 to 95 mg). Acetic acid had a mass loss during the 2 weeks between weightings of about 3,000 mg and a lower RSD (3%). The acetic and propionic acid levels inside their tubes dropped below $\frac{1}{4}$ full and were refilled once during the experiment at day 30. It is important to notice that refilling both the acetic and propionic tubes did not change the emission rate of the tubes more than 2.8% which is very similar to the variance of both tubes for the whole study (Table 1). The effective lifetime before refilling one full tube was about 1 month for acetic acid and 24 months for hexanoic acid based on the emission rates for the respective tubes. The liquid level in the acetic acid tube was allowed to fall a second time below 25% of the total volume of the tube and was not refilled after the weighing on day 68. The emission rate for the acetic acid permeation tube decreased during the time between day 15 and 29 and between day 55 and 100 after more than 75% of the liquid was emitted. However, the small fluctuations in the emission rate for the propionic acid tube were not affected by fluid level. Emission rates for the propionic acid actually increased about 20 ng/min between days 15 through 29 at a time the tube had less than $\frac{1}{4}$ of its maximum capacity. Emission for propionic acid decreased slightly (-74 ng/min) in the period immediately following its refill yet reached numbers similar to previous emission rates in the subsequent measurement periods.

Table 1. Emission rates (E) for permeation tubes (ng/min) estimated using Equation 1 and average emission rates per tube length E_L (ng/(min·cm)). These emission rates were used to calculate standard gas concentrations using Eq. 2 and 3.

Acid	Emission rate E (ng/min) for permeation tubes								Avg E_L (ng/(min·cm))
	Day 0-14	Day 15-29	Day 30-40	Day 41-54	Day 55-68	Day 69-82	Day 83-100	Average E (ng/min)*	
Acetic	16,701	15,234	16,290	16,293	16,228	16,150	15,748	16,149 $\pm$ 2.7%	2,011
Propionic	6,162	6,186	5,988	6,323	6,210	6,283	6,199	6,192 $\pm$ 1.6%	772
Isobutyric	1,100	1,090	1,090	1,093	1,045	1,013	1,083	1,072 $\pm$ 2.8%	128
Butyric	2,042	2,123	2,036	2,056	1,973	2,008	1,979	2,040 $\pm$ 2.4%	250
Isovaleric	396	398	409	434	328	408	418	395 $\pm$ 7.8%	49
Valeric	761	787	762	829	696	774	786	768 $\pm$ 4.8%	97
Hexanoic	420	447	442	447	359	412	412	421 $\pm$ 6.9%	49

*Note: Values for E are shown with relative standard deviation.

Emission rates for isobutyric and isovaleric acids were approximately half the rate of their respective straight-chained isomers of the same carbon number. This could be caused by slower diffusion of the branched isomers through the PTFE wall. Table 1 summarizes emission rates per unit of tube length (E_L) in ng/(min·cm). Values of E_L were estimated by dividing E_{acid} by respective effective length of permeation tube. Diffusion through PTFE plugs was assumed negligible and not accounted for in the estimate of E_L . Emission rates ranged from 49 ng/(min·cm) for isovaleric and hexanoic acids to 2,011 ng/(min·cm) for acetic acid, respectively,

and were inversely proportional to molecular weight. Considering that average emission rates presented in Table 1 are strongly correlated with molecular weight, and it is possible to design desired ratios of new standard gas concentrations. For example, much longer tubes for VFAs with high MW and much shorter tubes for VFAs with low MW should be used to achieve concentrations within the same order of magnitude. Alternatively, less permeable tube material, replacement of a PTFE tube with metal, or use of multiple tubes in place of a tube plug as the only permeation source for the same analyte could be used to achieve the same concentration.

Figure 2. Concentrations for VFAs in sampling bulb were calculated using Eq. 2 and 3. Dotted lines signify exchanges of dilution gas cylinders.

Standard Gas Concentrations

Standard gas concentrations were obtained by changing dilution gas flow rate. The measured flow of UHP nitrogen was steady at 506 ± 4.4 mL/min (standard deviation $n = 50$) for the initial 82 day test period. Next, the nitrogen flow was adjusted to 795 ± 4.8 mL/min ($n = 3$), $2,857 \pm 24$ mL/min ($n = 5$), $1,528 \pm 6$ mL/min ($n = 4$), and 397 ± 3.2 mL/min ($n = 3$) and kept there for several days at a time. The concentrations were estimated using Equation 3. Minimum and maximum concentrations ranged from 2.98 ppmv to 21.89 ppmv for acetic acid, 0.72 ppmv to 5.25 ppmv for propionic acid, 0.11 ppmv to 0.77 ppmv for isobutyric acid, 0.19 ppmv to 1.41 ppmv for butyric acid, 0.03 ppmv to 0.26 ppmv for isovaleric acid, 0.07 ppmv to 0.48 ppmv for valeric acid, and 0.03 ppmv to 0.22 ppmv for hexanoic acid. The RSDs for calculated concentrations of VFAs ranged from 1.6% for propionic acid to 7.8% for isovaleric acid. The range of obtained concentrations from a single permeation tube could be significantly extended in several ways, e.g., using a secondary dilution loop. Concentrations can also be adjusted by changing the oven temperature and thus changing permeation rate.

SPME Calibrations

VFA mixtures were sampled in triplicate every weekday, except for days when the compressed gas cylinder of nitrogen was changed, for the duration of the experiment with one DVB/Carboxen/PDMS 50/30 μm SPME fiber for 1 min. The RSDs for area counts for acetic, propionic, isobutyric, butyric, isovaleric, valeric, and hexanoic acids from SPME samples never exceeded 1% within each triplicate sample. VFA gas concentrations were adjusted and stable after 1 day (or less) after the flow rate adjustment. This result suggests that VFAs were adsorbed or desorbed to/from “wet” surfaces, i.e., surfaces that are in contact with the gas mixture, to reach new equilibrium. Thus, the time to reach a desired concentration for VFAs was likely much longer than 3 to 4 system residence times.

CONCLUSIONS

A new method for reliable and continuous generation of standard gas mixtures for VFAs including acetic, propionic, isobutyric, butyric, isovaleric, valeric, and hexanoic acids based on permeation tubes was developed and then tested with SPME. Refillable permeation tubes were made from PTFE and placed in a standard gas generator. Emission rates were very consistent over the duration of the experiment and ranged from as low as 1.6% (propionic acid RSD) to as high as 7.8% (Isovaleric acid RSD) from their individual average emission. Low acid levels (less than $\frac{1}{4}$ full) inside tubes decreased permeation rates. In contrast, dilution gas flow rate did not affect the tube permeation rates. Dilution flow rate was adjusted from 397 mL/min to 2,857 mL/min and the concentrations of generated mixtures were estimated based on emission rates and the measured dilution flow rate. Five different standard gas concentrations for each VFA were obtained. Maximum standard gas concentrations ranged from 21.9 ppmv for acetic acid to 0.22 ppmv for hexanoic acid. Minimum standard gas concentrations ranged from 3.0 ppmv for acetic acid to 0.03 ppmv for hexanoic acid. Permeation tubes provided very stable source of standard gas concentrations.

SPME was used to monitor standard gas concentrations for the duration of the project (100 days). Rapid SPME extractions (1 min sampling time) were sufficient to preconcentrate significant amount of VFAs for separation on a GC-FID without derivatization. Methodology described in this research paper could be used to generate and test standard gas mixtures for other functional groups of odorous gases including volatile amines, mercaptans, alcohols, n-alkanes, aldehydes, phenols, ammonia and hydrogen sulfide. These mixtures could be used for instrument calibration and quality control/quality assurance (QC/QA) in agricultural engineering and air quality research.

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