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Simple and accurate quantification of odorous volatile organic compounds in air with solid phase microextraction and gas chromatography - mass spectrometry

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Simple and accurate quantification of odorous volatile organic compounds in air with solid phase microextraction and gas chromatography - mass spectrometry

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The student author and the program of study committee are solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

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TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

NOMENCLATURE

VOC	Volatile Organic Compound
SPME	Solid Phase Microextraction
GS-MS	Gas Chromatography and Mass Spectrometry
ppbv	Parts per billion volume
pptv	Parts per trillion volume
SIM	Selected Ion Monitoring
S-VOC	Sulfur Containing Volatile Organic Compounds
VFA	Volatile Fatty Acids
TWA	Time Weighted Average
GC	Gas Chromatography
LC	Liquid Chromatography
FID	Flame Ionization Detector
MS	Mass Spectrometry
MDL	Method Detection Limit
LOQ	Limit Of Quantification
EPA	Environmental Protection Agency
TWA	Time-Weighted Average
SD	Standard Deviation

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ABSTRACT

Finding rugged and farm-proven sampling methods for odor measurement and mitigation of emissions continues to be a challenge. The objective was to develop a new method to quantify odorous volatile organic compounds (VOCs) in air. The main goal was to transform a fragile lab-based technology into a sampler that can be deployed for longer periods of time in remote locations. The developed method uses improved solid-phase microextraction (SPME) for combined on-site air sampling and sampling preparation. No power source is needed, and the technique is solvent-less. SPME fiber is exposed inside a protective glass liner. Thus, extraction of odorants is controlled by diffusion. Gas chromatography coupled with mass spectrometry is used for sample analysis in the laboratory. Acetic acid was chosen as a model compound to prove the concept. In the new method, extraction of acetic acid had a linear relationship with extraction time ($R^2<0.99$). The Car/PDMS 85 µm fiber was shown to have better sensitivity for acetic acid. The effects of glass liner condition and diffusion path length on mass extraction were studied. The new method was evaluated under field conditions by comparing it to the standard method (sorbent tubes) in four different locations. This research shows that SPME fiber retracted into a glass liner is a low-cost, simple, yet accurate sampling technique for quantification of odorous VOCs.

CHAPTER 1. INTRODUCTION: ODOROUS VOLATILE ORGANIC COMPOUNDS

1.1 Motivation

Offensive odors dispersed from animal feeding operations are a common concern for neighboring communities. These odors originate mainly from manure and other organic matters in livestock operations and are a complex mixture of many gases, which the largest portion is volatile organic compounds (VOCs). VOCs are complex chemicals distinguished by their ability to evaporate easily at room temperatures. They can be found almost everywhere. VOCs originated from industry and transportation have been studied extensively, since VOCs coming from these sources have adverse effects on human health. Less attention has been focused on VOCs found in animal production systems. Similar to VOCs from industrial objects and transportation, those VOCs can have potential side effects on human health depending on the duration and intensity of exposure. However, the research in this area is limited [1, 2], and research interest has been focused mainly on odor nuisance.

Addressing public concerns about odorous emissions from livestock operations has always been problematic since many of these VOCs usually have a low odor detection threshold. Even at low concentrations (ppbv, pptv), they are potent odorants [3]. Even when each compound is present at very low levels, the synergistic effect of these compounds can cause offensive odors. Thus, sampling and analysis of VOCs generated from animal operations are still challenging.

Methods to detect and quantify VOCs from animal facilities are important to measure air quality and to develop and test technologies that can mitigate odorous emissions. Many approaches that have been used for sampling and analysis of VOCs

that are effective for qualitative analysis, but most of the methods are typically not sensitive enough to quantify low concentrations of some VOCs

1.2 Background

Numerous VOCs can be found at animal facilities. Starting from 1965 when stearic acid was first identified [4], the list of known VOCs at animal facilities has constantly been extending. The results of the most recent studies show that more than 512 VOCs in total have been found at swine facilities [4]. VOCs found in animal facilities can be classified into several groups. They are acids, alcohols, aldehydes, amines, hydrocarbons, indoles, nitrogen-containing compounds, phenols, sulfur-containing compounds, volatile fatty acids and others [5]. However, sulfur-containing VOCs (S-VOCs) and volatile fatty acids (VFAs) have been identified as the most dominant classes of VOCs at animal facilities which are responsible for those offensive odors [3]. A derivative of phenolics, *p*-cresol was reported to be one of the main compounds responsible for characteristic odor at swine barns [3, 6]. In order to test sampling methods, most studies have focused on 10-15 odorous VOCs were used to simulate air emission in typical livestock setting in a laboratory [3, 7, 8]. Some of the odorous VOCs include acetic, propionic, butyric, and isovaleric acids: methyl, ethyl, and butyl mercaptans; dimethyl sulfide, *p*-cresol and others.

Acetic acid is considered the most abundant VOC in any animal facility, including swine farms. It is a colorless liquid that can be easily evaporated, and it has a strong and distinct pungent and vinegar-like smell. It was reported that the concentration of acetic acid could range from 1-2 to 617 mg m^{-3} [8]. Due to its abundance, many research studies have used it as a model compound to validate new sampling methods.

1.3 Time-Weighted Average Analysis of VOCs

Due to the fact that many of the odorous VOCs are found at low concentrations, VOC quantification requires reliable air sampling techniques and analytical methods that effectively represent the air in the monitoring site. The time weighted average (TWA) approach can be useful in such cases. This approach is used to determine the average concentration of the analyte over time periods that extend from a few minutes to several weeks [9]. TWA concentrations are needed to know average exposure to a contaminant without adverse effect to human health as well as to the health of the animals. Due to longer sampling times, TWA approach can achieve part per trillion levels. A number of different sampling techniques have been introduced to obtain TWA concentrations of VOCs in the field. Some of the most popular of techniques are whole air sampling techniques and sorbent tubes [1, 10]. The choice of which air sampling technique to use depends on the chemical-physical properties of the VOCs of interest and on the preferences motivated by historical reasons in each country [6].

Whole air sampling tools come in two forms, the hard form and the flexible form. The hard form includes evacuated stainless steel canisters. In the US, evacuated canisters were introduced in the 1980s, and since then have been improved consistently [11]. Today canisters are applicable for a sampling of up to 150 polar and nonpolar VOCs [12]. Standard canisters are equipped with flow controllers, particulate matter filter, and vacuum gauge. For TWA sampling of VOCs in the field, flow controller should be pre-calibrated for a desired amount of time in the laboratory. Only then can the canisters be deployed to the monitoring site. There are two types of canisters depending on the wall coating. Canister walls, which are made from stainless steel, can modify the original content of sampled gas; that is why the walls are coated with a thin

layer of chromium and/or nickel oxides (Summa canisters) or molten silica to provide VOCs stability inside the canisters during sampling and storing [11]. However, it has been reported that the coating cannot provide absolute stability to some of the VOCs, for example, naphthalene [13].

The flexible form of evacuated canisters is air sampling bags– or inert bags. Sampling bags have been commonly used for sampling of gases with pungent odor [11]. Sampling bags are simple (consisting of the polymer film and a connector) and inexpensive to use. There are several commercially available suitable materials from which sampling bags can be made of, including Tedlar, Teflon FEP, and Nalophane. Despite to their simplicity and cost-effectiveness, there are several limitations to using each of the material. For example, Tedlar bags can desorb acetic acid and phenol, and absorb indole, p-cresol, nonanoic and octanoic acids and some other VOCs resulting in increased or decreased total mass of those VOCs in every sample [14]. Nalophane is the least expensive material; however, the material is not recommended for benzene and other petrochemicals and cannot be used for more than 6 hours [15] . Teflon FEP bags are considered most chemically inert among other bags, but they have a higher cost [16]. Canisters and inert bags are available in different sizes [1].

Both canisters and air sampling bags require special preparation before VOCs can be sampled in the field. The wall of whole air samplers can modify the original composition of samples. Thus, cleaning procedures should be taken to reuse the samplers. For example, the canisters should be cleaned first in the laboratory and, then, transported to the monitoring site for VOC collection [1]. The cleaning of canisters performed at elevated temperatures and pressure followed by immediate evacuation of

the canisters [12]. Due to their low cost sampling bags are often used only one time and then followed by disposal. However, to reuse a sampling bag, they need to be flushed with ultra-pure air or pure nitrogen, and checked for any residual compounds [11]. These procedures prior to actual sampling make whole air sampling techniques more laborious and time-consuming. For quantification of VOCs with low concentrations, larger volumes of air are required to improve detection limits. However, large volumes cannot be injected into GC column for analysis. Thus, the components of interest are preconcentrated (using cryogenic and sorbent traps) from large volumes of air for further separation, identification, and quantification. Despite their popularity and improvements, the methods are still quite laborious in operation and relatively expensive per sample due to equipment, transportation, and storage costs [1]. Large volumes of whole air samples are inconvenient in transportation and storage in a crowded laboratory.

The use of canisters and bags has recently declined shifting towards sampling with sorbent tubes. Sorbent tubes have become a good alternative to canisters and bags due to simpler operation in VOCs collection. In addition, it is applicable to a wider range of analytes and provides a wider range of air sample volumes. Unlike canisters, sorbent tubes are compact and are easier to transport and store. Moreover, sorbent tubes have greater stability to polar compounds. In this method, contaminated air passes through a tube containing sorbent material inside which absorbs VOCs. Usually, to facilitate this process the contaminated air passes through the tube at constant rate with the help of an air sampling pump. The cleaning of sorbent tubes is performed by using thermal desorption system, where the sorbent material inside a tube is flushed

with constant flow of N_2 at elevated temperatures. After thermal desorption, sorbent tubes are ready to be reused. Sampling with sorbent tubes has become one of the conventional sampling procedures for VOCs quantification in ambient air [1,10,17].

Methods for sampling and quantifying VOCs such as whole air samplers and sorbent tubes require specialized equipment (cleaning and evacuation of canisters, flushing air sampling bags with ultra-pure air or nitrogen, thermal desorption, air sampling pump) which makes the methods laborious to work with. Thus, simpler and more reliable methods to quantify VOCs at animal feeding operations are needed.

1.3.1 The TWA SPME approach

Solid phase microextraction (SPME) is a relatively new sampling method that has been applied in different applications. This method combines on-site air sampling and sampling preparation, so there is no need for pre-concentration of VOCs. SPME is a compact sampler that consists of a fiber that is kept inside a hollow metallic needle. During air sampling, VOCs are collected on a SPME fiber (Fig 2.A). SPME has shown to be a very sensitive instrument that can measure at parts per trillion levels. After sampling, SPME fiber is injected into gas or liquid chromatography (GC or LC) coupled with flame ionization (FID) or mass spectrometry (MS) for further separation, identification and quantification of VOCs. After analytes were transferred to GC, the fiber is free of VOCs and can be reused. Thus, SPME eliminates the need for solvents, and it works with existing analytical technologies.

SPME is applicable for grab and continuous sampling. TWA concentrations can be obtained by averaging the results of several short grab samples by exposing the SPME fiber outside of the protective needle. In continuous sampling mode, an SPME fiber is retracted into the needle for a known distance during the desired sampling

period. The latter approach is less laborious. In contrast to exposed fiber where the analyte reaches an equilibrium with the matrix, extraction of VOCs by retracted fiber is controlled by diffusion. Since fiber is kept inside the needle and extraction of VOCs is controlled by diffusion, the extraction rates are slower. Thus, the fiber can be used for longer periods of time before the sorptive capacity limit of the fiber is reached. Accumulated analytes on the fiber give the measurement of the average concentration to which the fiber was exposed to [18].

The TWA sampling technique with a retracted SPME fiber follows Fick's first law of diffusion: the mass extracted on the fiber is proportional to (1) the diffusion coefficient of the analyte, (2) the concentration of the analyte in the gas phase, (3) sampling time, (4) cross-sectional area of the SPME needle opening; and it is inversely proportional to diffusion path length. The formula for Fick's first law of diffusion is shown below:

$$n = D_g \frac{A}{Z} \int Cg\,(t)dt$$

where n - a mass of extracted analyte; D_g – the diffusion coefficient; A – the opening area of the SPME needle; Z – the length of diffusion path; C_g – concentration of the analyte in the gas phase; t- extraction time.

1.3.2 Application of the TWA SPME approach

Despite the advantages of the TWA SPME approach, comparatively few studies have been conducted to bring the approach to the field. The studies [9, 19-25] have shown that SPME devices could be used as TWA samplers to access occupational exposure to different volatile and semi-volatile organic compounds [9]. The approach has been tested for measuring indoor concentrations of VOCs such as dodecane [19], hydrocarbons and formaldehyde [18, 20, 21], and n-alkanes [22]. The TWA-SPME

method tested in these studies followed Fick's first law of diffusion and some of these studies [??] have shown a good correlation with traditional methods. Additionally, the TWA-SPME approach has shown a great potential to be applied in the measurement of chlorinated semi-volatile compounds in an outdoor setting [9], where retracted SPME fibers were deployed for sampling of the VOCs for several days.

The previous studies have developed the TWA SPME approach in static environments (i.e., no air exchange). However, the most recent studies related to the TWA SPME approach have used dynamic environments which more closely represent typical moving air conditions in the field. These studies include VOC quantification from process streams in fast moving environments at elevated temperatures such as syngas stream [23, 24] and idling vehicle exhaust [25]. In two of these studies [23, 24], Woolcock et al. have used retracted SPME fiber with Carboxen/PDMS coating for identification and quantification of light tar compounds such as benzene [23]. After proving the concept of using retracted SPME fiber for quantification of benzene, the number of target VOCs was expanded to include benzene, toluene, styrene, indene, and naphthalene [24]. In this latter study, Woolcock et al. [24] compared their new TWA method to the traditional method and concluded that their method proved to be an effective substitute to the traditional method for light tar quantification. In another study, Baimatova et al. [25] developed the TWA SPME approach for quantification of benzene, toluene, ethylbenzene and o-xylene (BTEX) in vehicle exhaust gases. In their work they found that the metallic surface of the SPME needle ("broken fiber") had absorptive properties as well as the fiber itself. Thus, one of the main suggestion was that before using the TWA approach for quantification of VOCs, the contribution of mass extracted

by “broken fiber” should be accounted for. Thus, the contribution to extraction of VOCs by metallic surfaces varied from 10% to 13% for benzene, from 22% to 26% for toluene, from 33% to 41% for ethylbenzene, from 29% to 41% for o-xylene. Based on this finding (i.e., contribution of the “broken fiber’), in the study of Koziel et al. [26] the contribution of mass extracted by metallic surfaces was accounted for quantification of five biomarker VOCs such as DMDS, DMTS, pyrimidine, phenol, and p-cresol that are emitted during aerobic digestion of animal tissue. However, no research has been reported for quantification of major VOCs that are responsible for characteristic offensive odor downwind from animal feeding operations using TWA SPME approach.

1.3.4 Research objectives

Reliable and cost efficient methods to quantify VOCs at animal feeding operations are needed especially in the current scenario where the demand for animal products is increasing with the growing population. This means that the problem related to odorous emissions from animal facilities tends to be exacerbated in the future. Thus, it is desired that the new method has low detection limits, operates with no electricity source and without need to bring odorous samples to the analytical laboratory. To address this problem, the current research is devoted to developing an effective method for collection, identification and quantification of odorous VOCs in the air of livestock operations using SPME technology for simplified, yet accurate sampling and sample preparation.

The goal of this work is to develop a method for quantification of target odorous VOCs with TWA SPME approach that is low-cost, accurate and less laborious. Unlike the previous TWA SPME approaches where a SPME fiber is retracted into a metal needle, this research proposes to use a SPME fiber that is exposed inside the GC glass

liner to achieve the effect of a traditional retracted fiber. The opening on the glass liner serves as a diffusion path. Thus, extraction of VOCs is controlled by diffusion which provides longer sampling times and potentially can be used for sampling of VOCs in remote locations. The method utilizes GC glass liners that are readily available in many analytical laboratories. As the most abundant VOC in livestock operations, acetic acid was chosen as a model compound to prove the concept. Thus, the specific objectives of this research were to (1) build and verify a gas generation system that simulates typical dynamic animal facility air in the lab; (2) test the efficiency of an SPME fiber retracted into a glass liner in the gas generation system; (3) test the new method for quantification of acetic acid on a typical Iowa swine facility and evaluate its feasibility and (4) compare the developed method to a standard method under field conditions.

CHAPTER 2. METHODS

2.1 Chemicals and materials

Chemicals used in this study included acetic acid and helium. Acetic acid, glacial (Certified ACS ≥ 99.7%) was purchased from Fisher Chemical (Fair Lawn, NJ, USA), and helium (≥99.99%) was purchased from Air Gas (Des Moines, IA, USA). Car/PDMS 85 µm and 50/30 µm DVB/CAR/PDMS SPME fibers and manual SPME holders were obtained from Supelco (Bellefonte, PA, USA).

2.2 Standard gas generation and sampling system

The standard gas generation and sampling system were built to simulate typical air flow rates through swine facilities (Figure 1).

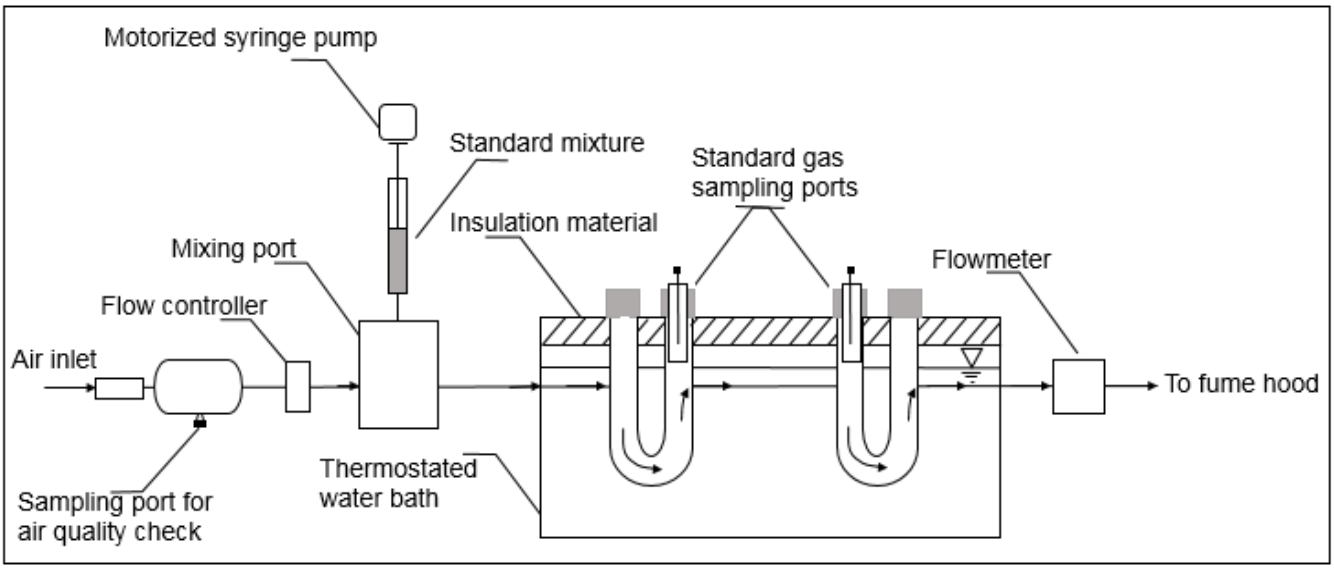

Figure 1 Schematic of standard mixture flow in the system. Passive gas sampling was completed with SPME retracted inside a GC injector glass liner.

The standard gas generation system included sampling ports for air quality check, a mass flow controller (Aalborg, Orangeburg, NY, USA), a motorized syringe pump (KD Scientific, Holliston, MA, USA), a 50 µL gastight syringe (Hamilton, Reno, NV, USA), a mixing port, PTFE tubing (Thermo Scientific, Rochester, NY, US) and

compression fittings. After the clean compressed air was introduced into the standard gas generation system, it flowed through the air quality check to be purified. Airflow was managed by a mass flow controller. The rate of the target compound injection was controlled by a motorized syringe pump. Known volumes of the target compound were introduced to clean air in a heated mixing port to produce the desired concentrations. After standard gas (Cgas) was generated, it passed through the gas sampling system.

The gas sampling system consisted of two U-shaped gas bulbs submersed inside of a thermostated water bath. Gas bulbs were filled with solid glass balls to help evenly distribute acetic acid in clean air. Both sides of bulbs were sealed with lids. A sampling port was installed on one of the lids of a bulb. Sampling ports included SPME fiber enclosed in a glass liner (Figure 2). The distance between the opening of the liner and the tip of the fiber was fixed at 1.75 cm. As it can be seen in the inset in Fig. 2 A, a glass liner was inserted into the gas bulb. The PTFE tubing was slid around the top of the glass liner. A septum was inserted into the PTFE tubing to close the top of the glass liner and for SPME needle insertion. The water bath was covered with insulation material to avoid excessive water evaporation. The temperature of the water in the bath was held at 25 °C. After passing through the gas sampling system, airflow was checked with a volumetric flowmeter (Bios Defender 520, MesaLabs, Butler, NJ, USA) to detect possible leaks in the system, and then exhausted to the fume hood.

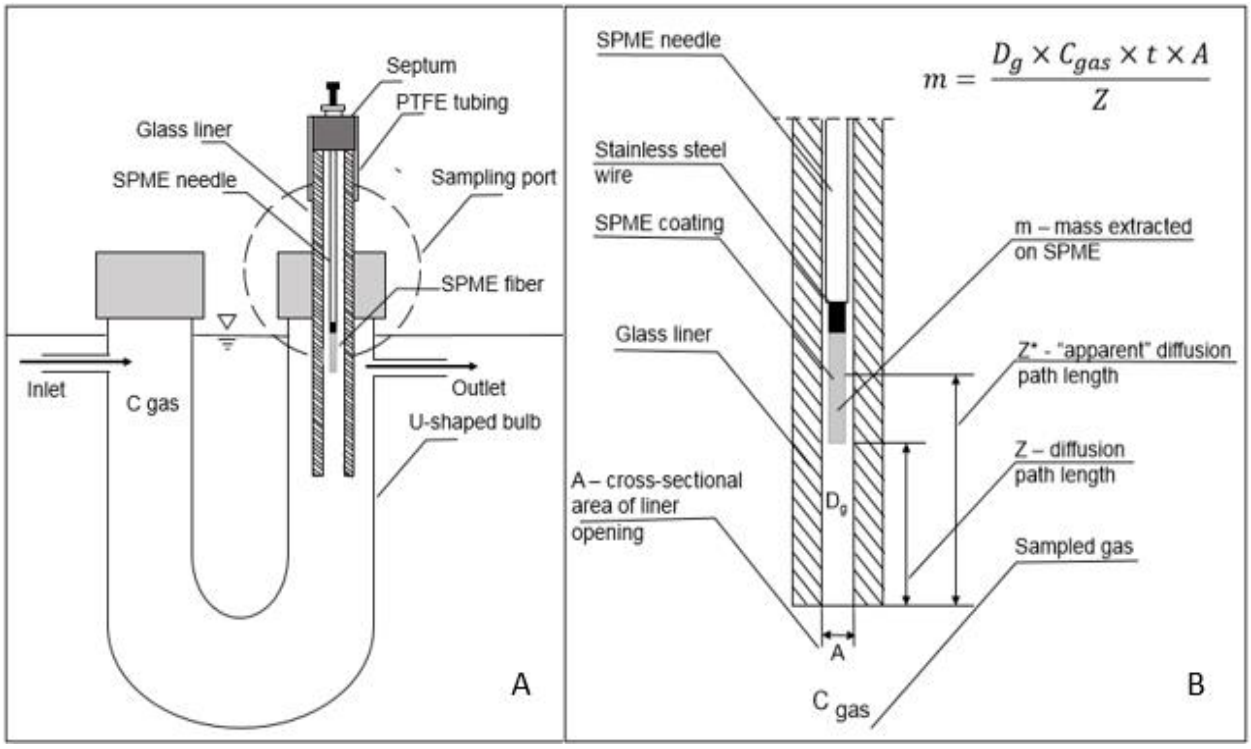

Figure 2 Passive gas sampling with SPME fiber retracted inside a GC injector glass liner. Part A shows the design of sampling port in the standard gas generation system. Part B represents the terms in the Fick's first law of diffusion. The SPME fiber is exposed inside of a GC glass liner; thus, the walls of the liner serve as a protective needle in traditional retracted mode.

The mass flow controller and the motorized syringe pump were used to produce the desired concentration of acetic acid in the gas generation system. The maximum concentration of acetic acid (617 µg m^{-3}) which was reported by Cai et al. [8] was chosen in our research to assess the method. To achieve the desired concentration, the rate of acetic acid injection into a heated mixing port was calculated using equations (4), (5), and (6) described in the study by Baimatova et al. [25]. Since the calculated injection rate to generate 617 µg m^{-3} of acetic acid in the system was small (0.0053 µg/h), it was decided to dilute acetic acid with distilled water at the ratio of 5 to 100, respectively. The syringe with the 5% acetic acid solution was refilled every day. The dilution with water also helped to avoid big fluctuations in the concentration of acetic acid since the dilution increased the number of solution injections into the system.

2.3 Liquid injection and flow rate verification

Since the motorized syringe pump and the mass flow controller were key instruments to generate the concentration of acetic acid in the standard gas generation system, reliability of those instruments was verified. The results of acetic acid injection can be found in Appendix B (Table 1A). To verify that the motorized syringe pump provided a correct rate of injection, a known volume of water was injected into the empty vial. The mass of the vial was weighed before and after injection. The results of the mass of injected liquid and the set point were compared, and the difference between them did not exceed 3%. The rate of injection was constantly verified visually during the experiments.

A similar verification for flow rate was completed to assure that the system did not leak (Table 2A). Measurements for three different flow rates were compared with the mass flow controller and the flowmeter. The difference between readings on the flow controller and the flowmeter depended on the flow rate. Smaller flow rates yielded a higher difference between readings on the two instruments.

2.4 MS detector calibration with acetic acid standard solution

To convert the peak area count of acetic acid extracted from the SPME fiber, we needed to know the response factor. The response factor was obtained by preparing a solution of 50 µL of acetic acid to 10 mL of hexanes. Then, 0.1, 0.3, 0.5, and 1 µL of the prepared solutions were injected directly into GC injection port to determine corresponding peak area counts. Direct injections were conducted in triplicate. A splitless mode on GC-MS was used. From the known volume, the mass of acetic acid was obtained by multiplying the volume by the density (1.049 gm L^{-1} at 25 °C).

Response factor was calculated from the average mass injections, and corresponding

$$RF = \frac{PA}{m} \quad (2)$$

peak area counts (Equation 2).

Where RF is the response factor, PA is the peak area counts and m is the known mass. Response factor is equal to 1.37E+04 (Appendix C).

Knowing the response factor, the quantification of acetic acid mass extracted on SPME fiber was done using the same equation.

2.5 SPME fibers conditioning

A new SPME fiber was thermally cleaned in a heated GC injection port according to the manufacturer's instructions. Before each sampling, an SPME fiber had to be cleaned in the GC injector port. This was done by holding, the SPME fiber in the heated GC injection port at 240°C for 3 min. Then, the fiber was injected into the glass liner at the sampling port. After adsorption of the target compound, the SPME fiber was quickly transported to the GC injection port, where it was kept for 3 min for desorption. Between injections, the SPME fiber was kept in aluminum foil to avoid absorption of VOCs in the laboratory air.

2.6 Conditions of GC-MS

A gas chromatograph (6890N/5975C, Agilent, Santa Clara, CA, USA) coupled with a mass spectrometer was used in this study. Helium was selected as a carrier. The constant flow of helium in the column was 7.5 µL min^{-1}. Temperatures of the ion source, quadrupole and MS interface were 230°C, 150°C and 240°C, accordingly. Splitless mode on the GC injection port at 240°C was used. The oven temperature was initially

set at 40°C for 3 min, followed by heating rate increments of 7°C up to 125°C, and by the heating rate increments of 30°C up to a final 240°C (held for 2 min). Total GC run time was 29.41 min. Retention time for acetic acid was 12.7 min. The MS detector was autotuned daily.

2.7 Standard gas stability check

The standard gas that was generated by the gas generation system was checked for stability. For this purpose, the standard gas was checked for several times for 3 consecutive days. The standard gas was sampled with SPME fiber every hour after injection with an exposed Car/PDMS 85 µm fiber. A sampling time of 20 sec was sufficient. Simultaneously, the concentration of acetic acid was monitored with the same type of fiber, but in a “retracted” position. The sampling time for the “retracted“ fiber was 1 h. This stability check provided the information that the system was capable of producing stable responses over time and the data which was going to be collected in the future would be reproducible. Further, before starting a new set of experiments, the concentration of acetic acid was verified with an exposed fiber. At the same time, the standard method (sorbent tubes) was used to verify the concentration of acetic acid in the system. After 24 h, the syringe was refilled with an acetic acid solution (50 µL).

2.8 Experimental design

Calibration of SPME fiber was conducted by exposing the fiber inside a glass liner to the air with an acetic acid concentration of 617 µg m^{-3} at 25°C generated by the standard gas generation system. Retraction depth was fixed at 1.7 cm (Z in Fig. 1B). The inner diameter of the glass liner was measured using a digital microscope (CC-HDMI-CD1, New Haven, CT, USA) and was equal to 0.8438 mm. As an adsorptive fiber [27], SPME fiber required testing of different sampling times to make sure that the fiber

did not reach its sorptive capacity. Thus, the sampling time of 1, 4, 8, and 12 h were examined to determine the longest sampling time before the sorptive capacity limit of the fiber was reached. All experiments were completed in triplicates. To improve noise-to-signal ratio, quantification of acetic acid was performed using SIM mode at mz^{-1} 60.00.

Method detection limit (MDL) and limit of quantification (LOQ) were calculated as described on the Detection Limit Guidance by the U.S. Environmental Protection Agency (EPA) [28]. To calculate the MDL, the sample standard deviation (S) was multiplied by the Student t-value (Equation 3):

$$\mathrm{MDL} = \mathrm{S} \times \mathrm{t}_{(\mathrm{n}-1,1-\mathrm{a})} \quad (3)$$

Where n is the number of replicates.

Further, LOQ was calculated using Equation 4:

$$\mathrm{LOQ} = 10 \times S \quad (4)$$

For eight replicates of 1 h acetic acid sampling and seven degrees of freedom (with 95% confidence interval) $\mathrm{t}_{(\mathrm{n}-1,1-\mathrm{a})}$ equals to 2.998.

2.9 SPME fiber selection

Two commercially available SPME fibers, Car/PDMS 85 µm and 50/30 µm DVB/CAR/PDMS, were tested to select the most suitable fiber for extracting the target compound. Two SPME fibers were inserted in each sampling port (Fig. 1) and exposed inside a glass liner. Before every SPME fiber injection, glass liners were washed and baked overnight. Extractions of acetic acid with two different fibers were conducted simultaneously. Three replicate samples were taken with each fiber. Sampling times

between 1 to 12 h were examined. Constant dry airflow at 150 mL min^{-1} with a diluted acetic acid injection rate of 0.53 µg was used to generate the desired concentration.

2.10 Effect of a glass liner

The effect of a glass liner was examined because of the previous study of Baimatova et al. (2015). In their work, SPME needle assembly has shown to extract a significant portion of VOCs [25]. For this reason, exposed SPME fiber was inserted into a glass liner. Two different conditions of a glass liner were tested. In the *cleaned* condition, glass liners were washed and baked overnight to evaporate all remaining VOCs. *Cleaned* liners were inserted into the sampling port in the standard gas generation system immediately before the SPME fiber insertion. In the e*quilibrated* condition, glass liners remained in the sampling port of the standard gas generation system for at least an hour prior to SPME fiber insertion. A *t*-distribution was used to test the null hypothesis that the two population means (mass extracted on SPME fiber exposed into a *cleaned* and e*quilibrated* liners) were equal at the 95% CI (two-tailed test).

2.11 Sorbent tubes

Sorbent tubes packed with Tenax TA 65 g were used to compare the results of exposed SPME fiber inside a glass liner. The procedure of sampling with sorbent tubes was completed as described in the work of Zhang et al. [7]. First, sorbent tubes were thermally cleaned at 260°C under a 100 mL min^{-1} of N_2 flow for 5 h., and, then, before following uses, were pre-conditioned at 260°C under a 100 mL min^{-1} of N_2 flow for 30 min. In the field, sorbent tubes with two sections, sampling and breakthrough (against saturation), were connected to an air sampling pump (SKC Inc., Eighty Four, PA, USA) at a 50 mL min^{-1} set flow rate. The sampling flow rate was monitored with a flow meter.

2.12 Application in the field

After validating the described method in the lab, a sampling of acetic acid was performed in indoor and livestock settings. Indoor air sampling included two sites: a manure treatment laboratory and an office space at Iowa State University. In livestock setting, sampling of acetic acid was carried out inside of the barns. Livestock air samples were taken at two swine farms: a typical swine farm located in Central Iowa (Farm 1) and a new farm with air scrubber and filtration technology for odor reduction (Farm 2). Both the new method (i.e., “retracted” SPME fiber) and the traditional method (i.e., the sorbent tubes) were used at sampling sites. The samplers were placed on the wooden floors upstream of exhaust fans. The opening of the “retracted” fibers and sorbent tubes were pointed in the direction of the exhaust fans.

Three 85 mm CAR/PDMS fibers were used at each site. Every fiber was thermally cleaned in GC injector port as described in Section 2.5. Then, the fiber was assessed for residuals. For a SPME fiber protection in the field, a “retracted” SPME fiber was placed inside of 40 ml thermally cleaned vial. Thus, only the opening of the glass liner was exposed to the environment. Vials with a “retracted” SPME fiber was kept in thermally clean aluminum foil to prevent any interaction with environment before actual sampling. Depending on anticipated concentrations at each monitoring site, the sampling time for a “retracted” SPME fiber was adjusted. For quantification of acetic acid in indoor settings, a sampling time of 12 h was used. For testing the method in the livestock settings, the sampling time of 40 min was sufficient.

Quantification of acetic acid was also performed with Tenax sorbent tubes. The sorbent tubes were thermally cleaned as described in section 2.11. Multiple air samples were taken with two adjacent sorbent tubes and the results were averaged for the

indoor setting. Sampling time was 20 min. For the livestock setting, sampling time of 40 min was used.

SPME fibers and sorbent tubes were analyzed within 5 h after sample collection.

A *t*-distribution was used to test the null hypothesis that the sample means received with the two methods were equal at the 95% CI (two-tailed test).

CHAPTER 3. RESULTS AND DISCUSSION

3.1 Standard gas stability check

Stability of standard gas generated by the standard gas generation system is shown in Figure 3. For the purpose of checking stability, the standard gas was simultaneously measured with exposed, and “retracted” SPME fibers and sorbent tubes for several times per day for three consecutive days.

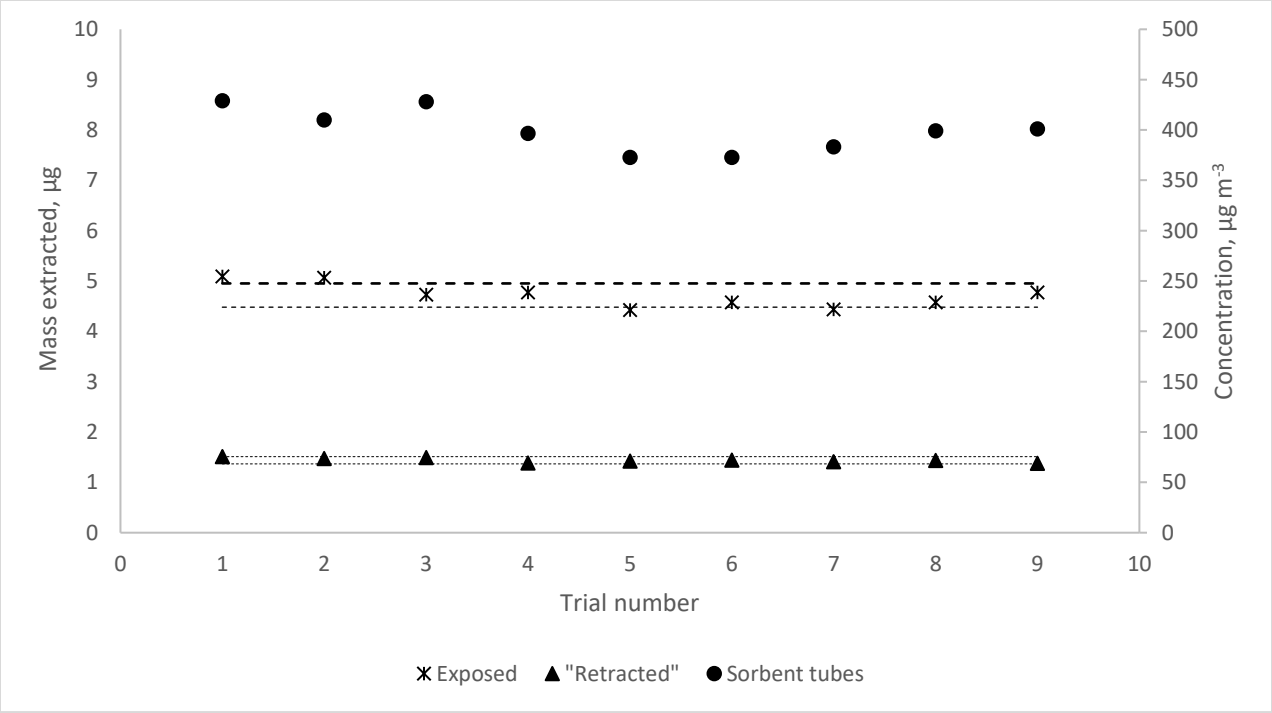

Figure 3 Standard gas stability check. Extraction conditions: two 85 µm CAR/PDMS SPME fibers (one retracted, and one exposed). Both were exposed to the standard gas (acetic acid, Cg=617 µg m^3). Retraction depth was 1.75 cm. Gas sampling was performed every hour for 3 consecutive days. Sampling times were 20 sec. for the exposed SPME fiber, and 1 hour for the retracted SPME fiber. The dashed lines on the graph indicate a +/-5% band from the average. The concentration of acetic acid was verified with sorbent tubes. SIM mode at mz^{-1} 60.00 was used for acetic acid detection and quantification.

The result of daily extractions with exposed and “retracted” SPME fibers and sorbent tubes shows that the standard gas generation system was successfully generating a continuous supply of acetic acid. As can be seen in Figure 3, the exposed

SPME fiber responses were more variable than the “retracted” SPME fiber in terms of extracted mass The RSD of extracted mass associated with the exposed fiber was 5.61%. Whereas, the RSD of extracted mass associated with the “retracted” fiber was 3.25%. Because the exposed SPME fiber was fully in contact with the environment, its extracted mass was more than two magnitudes higher than the mass extracted with the “retracted” SPME fiber. These results are consistent with the findings from Baimatova et al. (2015). The sampling of standard gas with sorbent tubes showed that the average concentration of acetic acid in the system was 400 µg m^{-3}, which is 35% lower than what was expected in the experimental design described in section 2.8.

MDL and LOQ were calculated based on 8 replicates. MDL and LOQ were equal to 21.76 µg m^{-3} and 72.22 µg m^{-3} (8.90 and 29.52ppbv) for acetic acid, respectively.

3.2 SPME fiber selection

Comparison of acetic acid extractions with two fibers, Car/PDMS 85 µm and 50/30 µm DVB/CAR/PDMS, is shown in Figure 4.

During the experiments two fibers have shown to effectively extract acetic acid. Mass extracted on the fibers showed a linear response with sampling time (R^2>0.99). However, the results show that the average mass extracted on two SPME fibers were higher than the theoretical value (Equation 1) by 63.5%, and 53% on average for Car/PDMS and DVB/CAR/PDMS fibers, respectively.

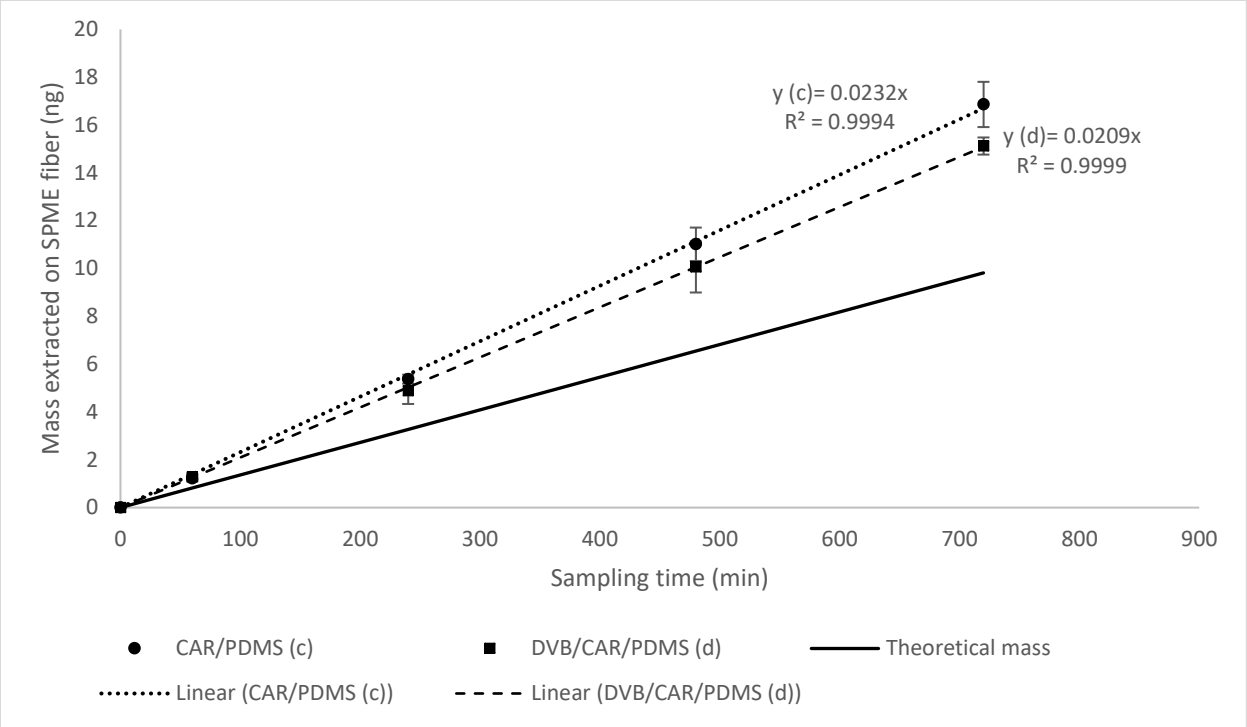

Figure 4 Comparison of extraction efficiency of acetic acid by Car/PDMS 85 µm and 50/30 µm DVB/CAR/PDMS SPME fibers. The theoretical mass on the SPME fiber (shown as a solid line) was calculated using Equation 1. The experimental masses (shown as doted and dash lines for Car/PDMS and DVB/CAR/PDMS fibers, respectively). Extraction conditions: 85 µm Carboxen/PDMS fiber exposed inside a glass liner, standard gas (acetic acid, Cg=617 µg m^{-3}). Retraction depth was 1.75 cm. SIM mode at mz^{-1} 60.00 was used for acetic acid detection and quantification. Experiments were completed in triplicates.

The Car/PDMS 85 µm fiber revealed a higher response than the DVB/CAR/PDMS fiber. The results were consistent with the study of Bayona et al. [29]. The total mass extracted on the SPME fibers was reproducible. The RSDs of MS responses with Car/PDMS (ranging from 2.3% to 12.2%) were lower in comparison with DVB/CAR/PDMS fiber (ranging from 3.2% to 14.7%). A linear regression model with a log-transformed response showed that masses extracted were not significantly different between the two SPME fibers (p=0.54) as well as between both fibers and theoretical values (p=.0.14). The differences in mass extracted with 50/30 µm DVB/CAR/PDMS at every sampling time were 9% less than the mass extracted with Car/PDMS 85 µm,

respectively. Log-transformation of mass extracted on SPME fiber was performed because there was non-constant variance in the residuals.

3.3 Effect of the glass liner

TWA sampling of acetic acid using exposed SPME fiber inside a glass liner is show in Figure 5.

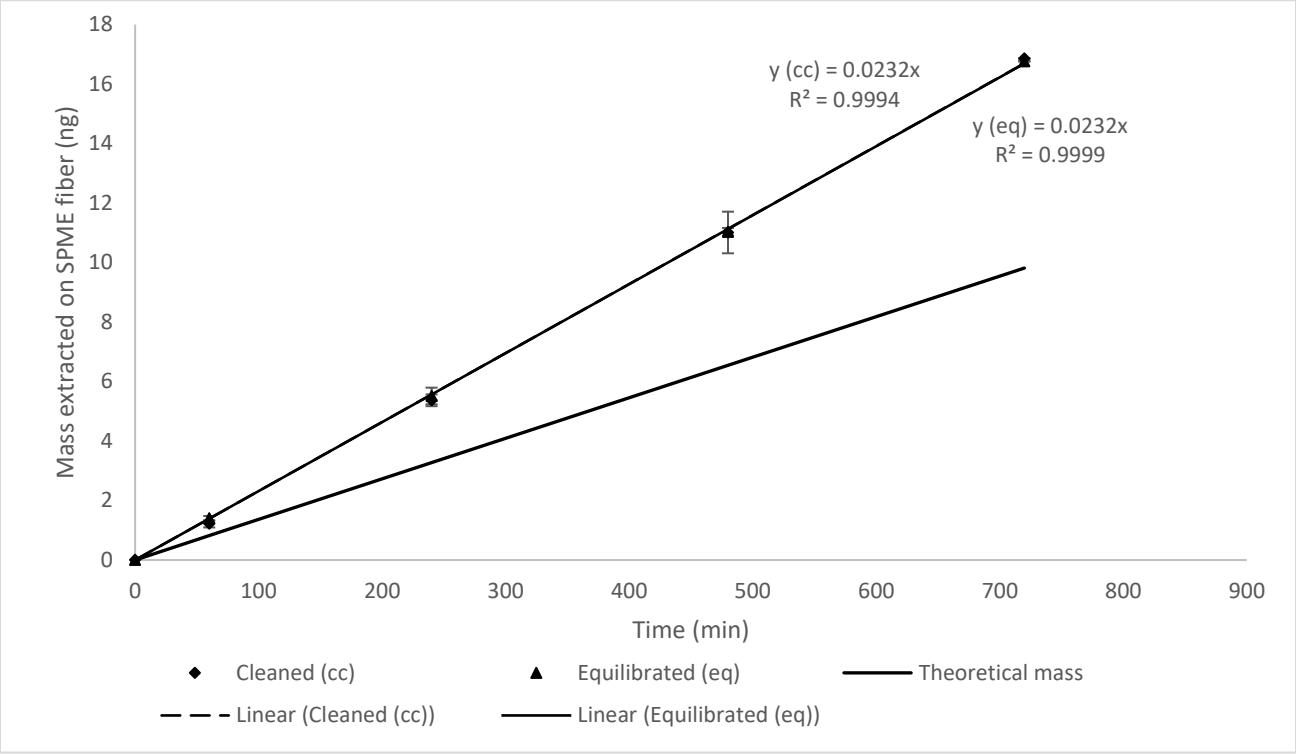

Figure 5 Effect of extraction time on mass extracted (ng). Extraction conditions: 85 µm Carboxen/PDMS fiber exposed inside glass lines, standard gas (acetic acid, Cg=617 µg m^{-3}). Retraction depth was 1.75 cm. SIM mode at mz^{-1} 60 was used for detection and quantification of a target compound. Dashed lines represent the experimental masses extracted on the SPME fiber with *cleaned* and e*quilibrated* glass liners.

The total mass extracted on SPME fiber was reproducible. RSDs (%) ranged from 4.3% to 8.2% with *cleaned* and from 1.6% to 7.9% with e*quilibrated* liners. A two-sample t-test did not show a statistically significant difference in mass extracted on the SPME fiber exposed inside a *cleaned* and e*quilibrated* liners. To see if the rate of increase were different, a linear regression model with a log-transformed response was

used. Log-transformation of masses extracted on SPME fiber was performed because there was non-constant variance in residuals. Fitting of the model showed no significant difference in interaction between the condition of a glass liner and time (p=0.74). Looking at the means of mass extracted on a SPME fiberwith different glass liners at each time point, the P values were not significant (from 0.68 to 0.93 for each time point respectively). However, one of the interesting finding was that the percent difference between two glass conditions was the highest at sampling time of 1 h (15.0%). Then, the percent difference decreased up to 2.6% at sampling time of 4 h and continued to decrease at longer sampling times. After 12 h sorptive capacity of the fiber was not found to reach its limit.

Figure 6 summarizes the result of previous experiments with two SPME fibers, and two glass liners conditions (*clean* vs. e*quilibrated*)

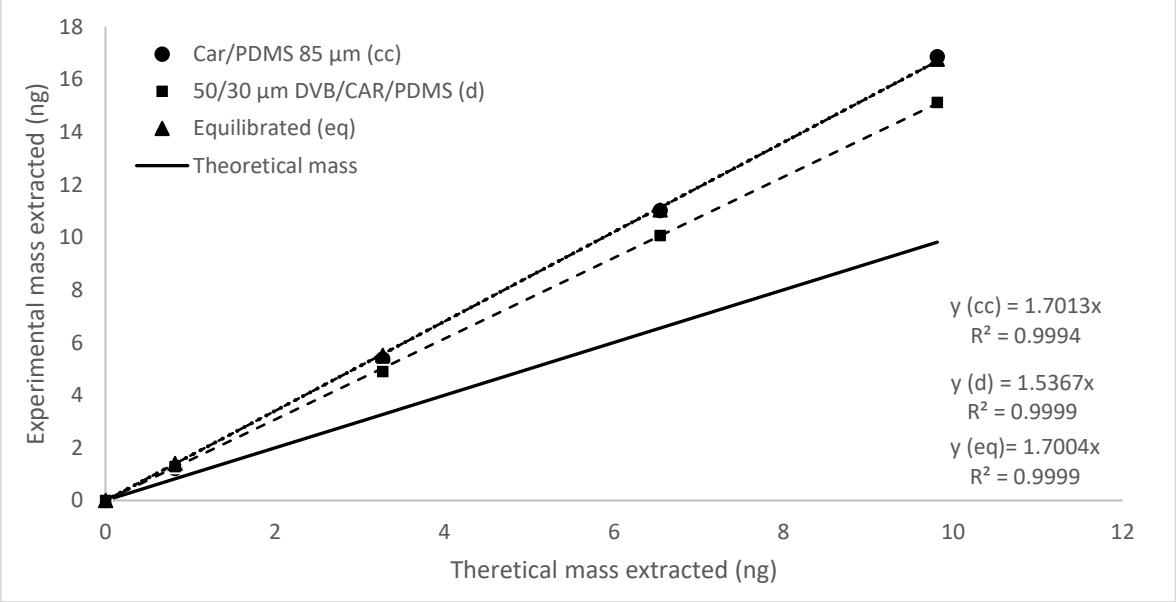

Figure 6 Relationship between theoretical and experimental masses extracted in ng. The results of previous experiments were taken to compare the theoretical mass with the experimental masses extracted using Car/PDMS 85 µm (with clean and saturated glass liners) and 50/30 µm DVB/CAR/PDMS fibers. The theoretical mass extracted was calculated using Fick's first law of diffusion (Equation 1).

The result of previous research shows that SPME fibers extracted reproducible amounts of the target compound. Thus, the theoretical mass extracted on the fiber was proportional to the diffusion coefficient of the acetic acid, the concentration of the acetic acid in the gas phase, sampling time, cross-sectional area of the glass liner opening and inversely proportional to diffusion path length.

The discrepancy between the values of experimental and theoretical extracted masses provided insight on the possible influence of SPME fiber retraction depths on extracted masses. To investigate this possibility, several retraction depths (0.5, 1.0, 3.0 and 3.5 cm) were tested and compared to the fixed retraction depth of 1.7 cm that was used in the previous experiments. The aim of these new tests was to identify if different retraction depths would indicate the same concentration of acetic acid and, if not, which retraction depth could more efficiently lessen the discrepancy between the experimental and theoretical values. The results of the effect of retraction depth is shown on Figure 7:

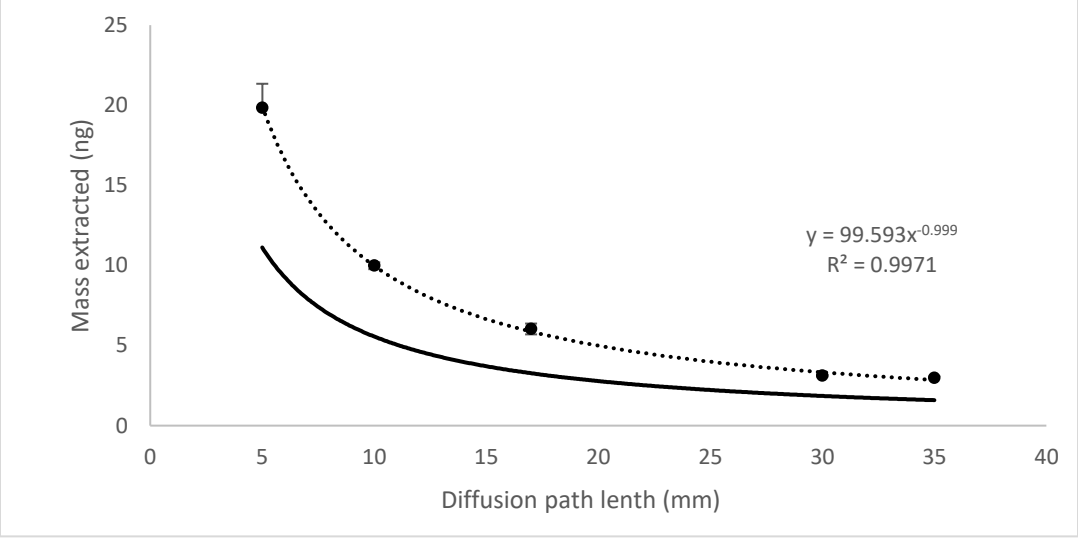

Figure 7 Effect of diffusion path length on mass extraction. Extraction conditions: “retracted” Car/PDMS 85 µm, standard gas (acetic acid, Cg=617 µg m^3). SIM mode at mz^{-1} 60 was used for detection and quantification of a target compound. Solid line represents the theoretical mass for different diffusion path length (Equation 1). Sampling time of 4 h was used.

Extracted masses at the diffusion path lengths followed power-law distribution (R^2<99.7%). RSDs for extracted masses did not exceed 10.0% (5.8%, 2.2%, 2.7%, 1.7% and 5.8% for 5, 10, 17, 30 and 35 mm, respectively). Percent difference between experimental and theoretical masses slightly decreased with increasing diffusion path length until a certain point. For example, percent difference between theoretical and experimental values decreased from 87.0% to 67.0% at the lengths of 5 to 3.0 mm, and at the length of 3.5 mm it increased from 67% up to 87%. Thus, the Figure 7 suggests that the diffusion path length could affect mass extraction process inside a glass liner, however, it does not fully explain those large discrepancies between theoretical and experimental values.

To understand the nature of those large discrepancies, it was decided to look closer at the mass extraction process inside of a glass liner. Mass extraction processes inside a glass liner and a metallic needle is shown in Figure 8. As it can be seen in the figure, with the opening of a glass liner almost twice more than the opening of the needle in a traditional retracted fiber, Fick's first law of diffusion had some limitations. In the law, mass extraction occurs only on the tip of the fiber; thus, diffusion path was equal to the distance between the opening of the needle to the tip of the fiber. However, the extraction of the VOC was occurring not only on the tip, but also on the surface of the SPME coating. Thus, the large discrepancies between theoretical and experimental values could be explained by the "apparent" diffusion path Z^*. If in the case of a traditional retracted mode, where a fiber is retracted into a metallic needle, the effect of "apparent" diffusion path Z^* was much smaller, therefore, the discrepancies were much

smaller. For example, Baimatova et al. [26] reported that the differences between theoretical and experimental values for BTEX could go up to 45.0%.

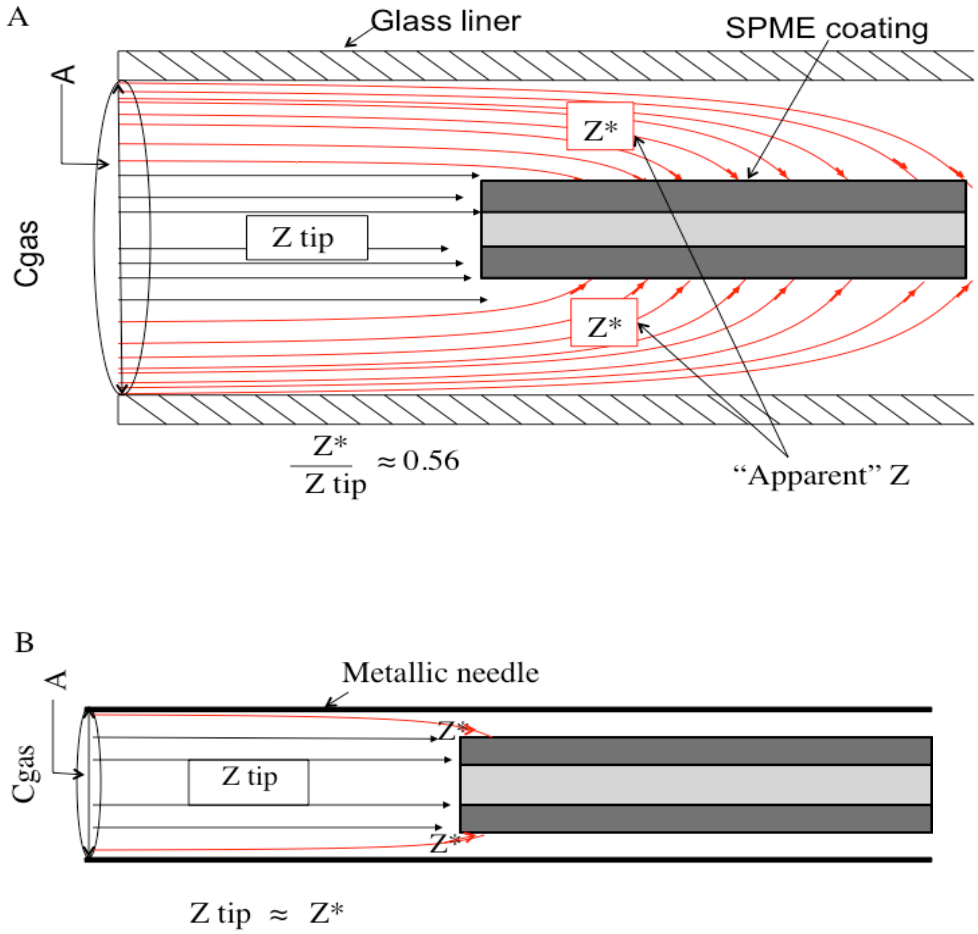

Figure 8 Mass extraction process. Part A represents mass extraction inside of a glass liner. Part B represents mass extraction in inside of a traditional retracted fiber. Black arrows represent modeled diffusion path or Z tip. Red arrows represent the "apparent" diffusion path.

Later, when the method was applied in the field the effect of Z* were substracted.

3.4 Application in the field. (Comparison of Sorbent tubes vs. SPME)

The new method was compared with sorbent tubes (a conventional method). Table 1 shows the result of measured concentrations of acetic acid in indoor (laboratory, office) and livestock air. Masses extracted with "retracted" fibers were adjusted considering the existing discrepancy between SPME fibers and sorbent tubes. Background masses were subtracted. Triplicates were taken at each sampling site.

Simultaneous analysis with the two methods showed that the results of the SPME fibers were comparable to the result of the sorbent tubes. The difference between those methods varied depending on the sampling site. For example in indoor setting, the differences between the two methods in resulting concentrations of acetic acid were 26.6 % and 2.4% in the office and the laboratory, respectively. However, the differences between the two methods in indoor setting were not statistically significant ($p>0.10$).

The TWA concentration of acetic acid in indoor setting were significantly lower than the TWA concentration in livestock settings (approximately 5-80 times lower). Two indoor sampling sites had nearly similar concentrations of acetic acid. The small difference could be explained with more efficient ventilation system in the laboratory that helped to keep the concentration of the compound low. Whereas the doors of the office were kept closed during the sampling, so there is no air intensive exchange between the office and the hallway.

Sampling of acetic acid in Farm 1 for two days revealed large differences in results produced by “retracted” SPME and sorbent tubes. The differences were statistically significant ($p<0.01$). During the first day of sampling, the SPME fibers were placed in the wrong direction facing the airflow. Therefore, the differences between the two methods were the highest (54.9%). Next day, when SPME fibers were placed pointing in the direction of exhaust fans, the discrepancies decreased (by nearly 11%), but still remained high. Interesting fact that the concentrations measured by the two methods were higher than it was previously reported.

In the Farm 2, the two methods showed a good correlation. The differences between them did not exceed 5.0%. RSD of masses extracted for both methods were under 11.0%. In the Table 1, at Farm 2, Day 1 only one sample with sorbent tubes was taken, so SD could not be calculated.

Table 1 Comparison of acetic acid concentrations in different locations using 85 μm CAR/PDMS and sorbent tubes with Tenax TA.

Location	Concentration (μg m^{-3})		% difference	p-value
	SPME	Sorbent Tubes		
Office	7.10 (±1.17)	9.68 (±0.99)	26.60	0.10
Laboratory	6.80 (±0.39)	6.64 (±0.72)	2.41	0.70
Farm 1, Day 1	1672.93 (±80.63)	753.80 (±18.22)	54.94	0.0006
Farm 1, Day 2	1091.17 (±88.58)	753.80 (±177.31)	44.75	0.01
Farm 2, Day 1	328.61 (±24.25)	339.51	3.21	0.57
Farm 2, Day 2	389.21 (±40.95)	372.52 (±18.11)	4.48	0.28

Generally, the masses extracted by the SPME fibers were reproducible. In comparison with sorbent tubes, SPME fibers were much simpler to operate, and did not require thermal desorption system and additional instruments (a flowmeter and a pump) for VOC sampling. It was also convenient to use in quite places such as an office: the noise of a running pump caused a little discomfort to graduate students.

CHAPTER 4. SUMMARY AND CONCLUSIONS

A novel and simple TWA SPME-based method for quantification of acetic acid in ambient air was developed. The method demonstrated relatively simple on-site air sampling and sampling preparation, reusable, with low cost per sample without the need for any power source, sophisticated and expensive instrumentations.

- An SPME fiber exposed inside a glass liner acted as a zero sink sorbent. There was a linear relationship between extraction time and mass extracted up to 12 h (R^2<0.99). The amount of VOC adsorption on the fiber SPME was reproducible.
- The Car/PDMS 85 µm fiber revealed a higher response than the DVB/CAR/PDMS fiber. The mass extracted by Car/PDMS was 8.9% higher than the mass extracted by DVB/CAR/PDMS fiber
- There was no statistically significant difference between *cleaned* and *equilibrated* glass liners.
- Generally, Fick's first law of diffusion could describe the analyte extraction process; however, the law had limitations and required some improvements to be applied for VOC quantification.
- The new method was evaluated under field conditions by comparing it to the standard method (sorbent tubes) in four different locations. The "retracted" SPME fiber showed to have a reasonable match with sorbent tubes. The differences between the two methods did not exceed 26.6%. However, at high acetic acid concentrations, the difference could reach up to 44%.

The method has shown is a low-cost, simple, yet accurate sampling technique for quantification of acetic acid that poses no discomfort or health risk to workers. The method is reusable and the cost per sample is almost negligible. Further research should be done to extend the number of VOCs that can be used with this method.

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APPENDIX A: COMPARISON OF SAMPLING METHODS FOR QUANTIFICATION OF ODOROUS VOCS

Table 1A Comparison of sampling methods available for VOCs sampling

Sampling technique	Whole air sampling (sampling bags and canisters)	Active sorbent tubes sampling	SPME in grab sampling mode	SPME in continuous sampling mode
Measurements in TWA mode	Possible	Possible	Possible	Possible
Advantages	Simple, accurate,	Simple, accurate,	Simple, accurate, fast, no preconcentration and pump needed, low detection limits	Simple in operation, reusable, low cost, no preconcentration and pump needed,
Disadvantages	Relatively high cost; difficulties in transportation and storage; pump and preconcentration required; need for evacuation and cleaning in lab prior sampling; problematic to reuse bags	Pump and thermal desorption system required	Several grab samples needed for TWA concentration; mass extracted greatly affected by environmental variables.	Complicated standard gas generation system and calibration required

APPENDIX B: LIQUID INJECTION AND FLOW RATE VERIFICATION

Table 2A Results of trials for liquid injection rate verification.Duration of each trial was 24 h.

Trial #	Mass (g)			H_2O volume injected (µL)	RSD (%)	Set point for volume injected (µL)	% difference (injected vs. set point)
	Empty vial (± st.dev.)	Vial with injected H_2O (± st.dev.)	H_2O injected				
1	2.36×10^{0} ($\pm1.25\times10^{-4}$)	2.43×10^{0} ($\pm4.71\times10^{-5}$)	7.52×10^{-2} ($\pm1.33\times10^{-4}$)	75.20	1.93×10^{-3}	76.03	1.10
2	2.33×10^{0} ($\pm4.71\times10^{-5}$)	2.41×10^{0} ($\pm4.71\times10^{-5}$)	7.39×10^{-2} ($\pm6.6\times10^{-5}$)	73.97	1.95×10^{-3}	76.03	2.71
3	2.39×10^{0} ($\pm1.25\times10^{-4}$)	2.47×10^{0} ($\pm2.94\times10^{4}$)	7.49×10^{-2} ($\pm3.20\times10^{-4}$)	74.93	1.19×10^{-2}	76.03	1.46

Table 3A Results of trials for flow rate verification.

Trial #	Flow controller	Flowmeter (± st.dev.)	% difference (flow controller vs flowmeter)	RSD (%)
1	150	140.69 (± 0.23)	6.41	0.16
2	100	93.18 (± 0.49)	7.06	0.52
3	75	67.42 (±0.80)	10.65	1.18

APPENDIX C: MS DETECTOR CALIBRATION WITH ACETIC ACID STANDARD

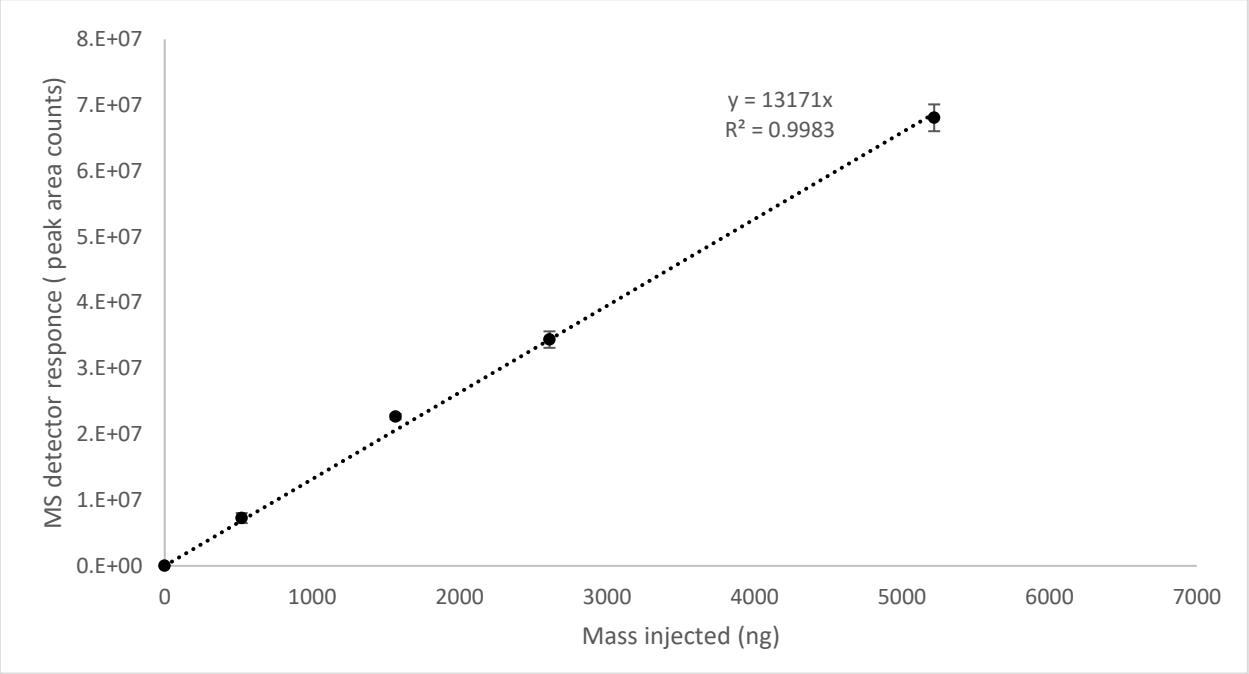

Figure 1A Calibration of MS detector response to acetic acid. SIM mode at mz^{-1} 60 was used for detection and quantification. Tests were conducted in triplicate

APPENDIX D: TEMPERATURE CHANGE INSIDE OF A GLASS LINER

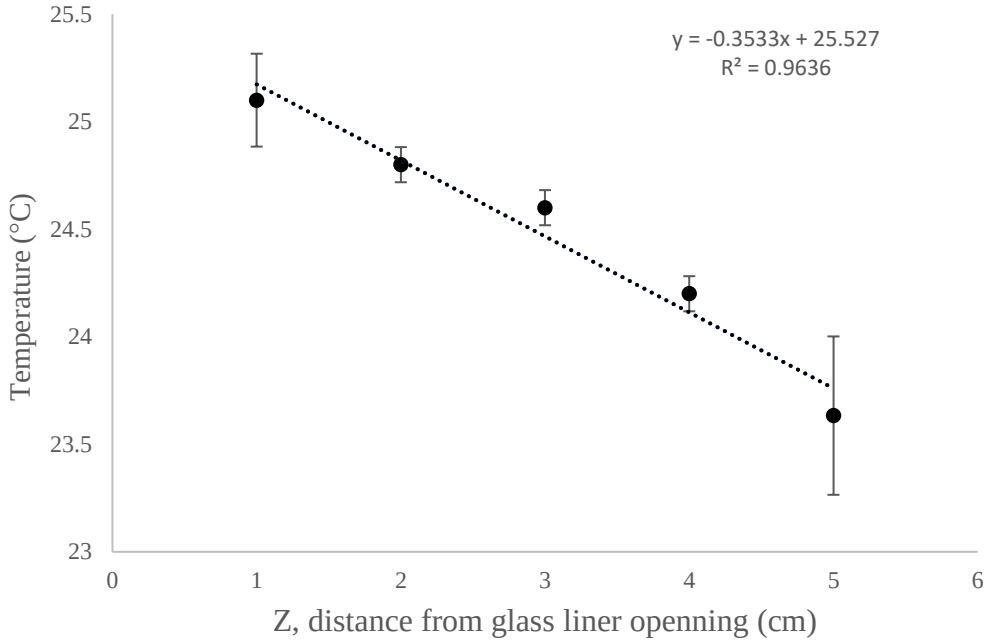

Figure 2A Temperature change inside of a glass liner

APPENDIX E: PHOTOS FROM FARM 1

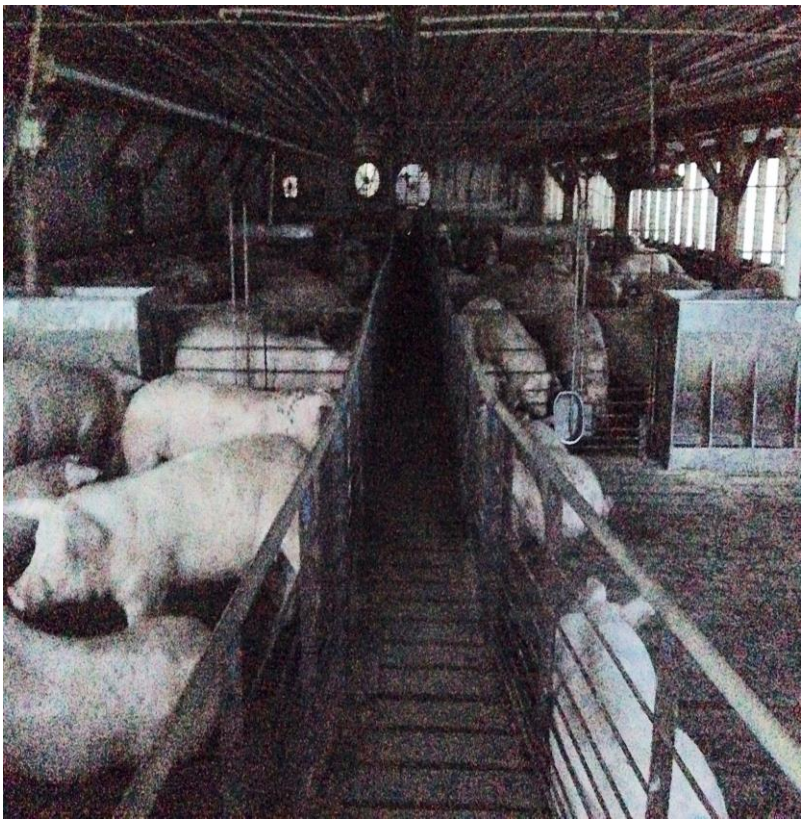

Figure 3A Farm 1: ISU Ag 450 Farm.

APPENDIX F: PHOTOS FROM FARM 2

Figure 4A Farm 2: A collective work of Reicks View Farms and Iowa State University for odor reduction.

Figure 5A Placement of the SPME fibers and the sorbent tubes in Farm 2.