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CHARACTERIZATION OF ODOROUS AND HAZARDOUS GASEOUS COMPOUNDS IN LIVESTOCK BUILDING AIR

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ABSTRACT

CHARACTERIZATION OF ODOROUS AND HAZARDOUS GASEOUS COMPOUNDS IN LIVESTOCK BUILDING AIR

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This study was conducted to develop methods for the characterization of odorous compounds in swine building air and to apply the methods developed to study the effect of ozone on odors in swine facilities.

Several methods for the determination of odorous compounds in swine building air were investigated. Conventional air sampling methods, such as sorbent trapping and impingers, and a Solid Phase Microextraction (SPME) method for the sampling VOCs in swine building air were studied. Two methods for the quantification of phenolic and indolic compounds (phenol, p-cresol, p-ethylphenol, indole and skatole) by SPME were investigated. These methods were based upon equilibrium theory and diffusion theory.

Without any further sample concentration, solvent desorption sorbent traps and impinger traps were not able to determine any volatile organics from the swine nursery housing air using a sample volume of up to 36L. Thermal desorption multi-bed tubes were able to collect volatile and some of semi-volatile compounds from swine building air, however the recovery of high boiling point compounds was not good. SPME air sampling method was the most efficient method for the collection of odorous volatile compounds in swine building air.

The efficacy of a commercial ozonation system to reduce odors was studied. In this system ozone was distributed throughout the animal housing facility using a manifold. In this study the VOCs in the air and the odor of the air were monitored. The VOCs were measured using thermal desorption tubes and SPME fibers with a PDMS/CAR coating. Ozone was effective in reducing odor detection threshold, but did not significantly reduce the odor intensity or odor offensiveness in the building. Sensory testing indicated that the characteristics of the air in the ozonated rooms were different from those in control room. Monitoring of the VOCs present in the air showed that ozonation reduced the levels of phenolic and indolic compounds in the swine building air, however, it did not reduce the level of volatile fatty acids in the air.

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PROBLEM STATEMENT AND SIGNIFICANCE

Modern swine production managements have changed to the larger populations of animals on production sites in an effort to improve animal production efficiency. These expansions of concentrated animal feeding operations (CAFO) have increased awareness by the public and government agencies for the potential impacts of these facilities on water and air quality. In spite of the increasing demands for odor and air quality control in livestock production facilities, researches related to odors have not been actively conducted in agricultural area.

A reason is that odorous compounds have not been regulated because odor is defined as a "nuisance", not as a "contaminant", in spite of the presence of toxic compounds in the livestock buildings, such as ammonia, hydrogen sulfide and other sulfide gases (Xue et al., 1998).

Regulation of the odor and/or odorants from the livestock building has been challenging, because monitoring the odorous compounds in the air of the livestock building is complicated for a number of reasons.

First, the concentration of the odorants is very low, and often is below the detection limits. Second, numerous compounds are present in the air of the livestock buildings. Many researchers have attempted to characterize the odor by analyzing the chemical compositions in the air. More than 30 odorous compounds have been found in the swine house air. Third, the analysis of the odorous compounds is difficult because of the wide range of physical and chemical properties of the odorous compounds found in the livestock wastes and air. Some of the compounds from livestock production units are gases such as hydrogen sulfide, ammonia, and methyl mercaptan. Other compounds found in the livestock facilities, such as indole and skatole, have boiling points more than in excess of 250 °C.

The government agencies such as, NIOSH, OSHA, and EPA have reported several methods for the determination of toxic organic compounds in ambient air. These methods were designed for the detection of specific compounds, such as aldehydes, phenols, or polycyclic aromatic hydrocarbons (PAHs) in the ambient air. A single method for the sampling of odorants from livestock facilities is not sufficient for the monitoring various volatile organic compounds (VOCs) in livestock building air.

Ozone has been widely used for indoor air control in recreational areas, such as casinos, offices and hotels. A recent study by Oehrl et al. (2000) showed that ozone was effective in decreasing the low molecular volatile fatty acids on the dust samples from swine house. The effectiveness of ozone for oxidizing odorous volatile compounds in swine slurry such as; phenol, p-cresol, p-ethylphenol, indole and skatole, in swine slurry have been proven (Wu nad Masten, 1999).

Human health effects from polluted livestock air have been a great issue. Most of gaseous compounds found in the livestock buildings are "hazardous pollutants" listed in Clean Air Act (CAA). Finding adequate air sampling and analytical techniques are the key points for successful air characterization in the livestock buildings.

This research proposes air sampling methods for odorous compounds in livestock facilities by testing some air sampling methods used by the US government agencies (NIOSH, OSHA, and EPA). This research also proposes the adaptation of the new air sampling method, such as solid phase microextraction (SPME), for the sampling of odorous compounds in livestock building.

This research will identify suitable air sampling and analytical techniques for compounds in swine houses.

CHAPTER 1. LITERATURE REVIEW

1.1 Odor characterization and quantification in swine waste and production facility

1.1.1 Odor

Odor is something that stimulates the olfactory systems or sense of smell. The perception of odor is due to the presence of volatile compounds in the inhaled air. Humans are known to be able to detect over 10,000 odors, despite being able to identify only a few of them. Human nose can detect and discriminate odors at concentrations even lower than those detectable by analytical techniques, such as gas chromatography (e.g. hydrogen sulfide) (Mackie et al., 1998). The minimum concentration required to detect an odor is termed the odor threshold values (OTV). The lowest toxic value (LTV) of these compounds in air may be at least a factor of 500 higher than OTV. In this case the odorous compound is detected long before it becomes a health risk (Tamminga, 1992).

There is no universally accepted definition of an objectionable odor, nor are there any legally defined conditions under which livestock producers become required to reduce odor emissions emanating from the animal facility (NPPC, 1995). No federal guidelines exist that regulate and control odors in the environment because of the technical difficulties of defining odor limits and their measurement and evaluation. In contrast to pollutants for which legal limits are set and enforced by federal agencies, odor is considered a nuisance and complaints are normally handled by state or local authorities (Mackie et al., 1998).

1.1.2 Odorous compounds in livestock slurries and buildings

An increase in the number of complaints from the public about odors from pork production units has stimulated interest in the measurement and reduction of odors at these facilities. Research has been conducted on qualitative and quantitative chemical characterization of odorants in livestock wastes, especially in swine slurries (Yasuhara et al., 1984; Ritter, 1989; Yu et al., 1991; O'Neill and Phillip, 1992; Hobbs et al., 1995; Zahn et al., 1997; Wu et al., 1998).

Yasuhara et al. (1984) identified approximately 30 organic compounds in fresh and rotten swine manure using vacuum distillation extraction, followed by the gas chromatography-mass spectrometry (GC/MS). The study suggested that the significant odorous compounds in the swine manure were alcohols, 3-hydroxy-2-butanone, fatty acids, aromatic carboxylic acids, phenols, and indoles.

Hammond et al. (1989) found the most important contributors to the odor in swine waste lagoons were dimethyl disulfide and dimethyl trisulfide. Indole, skatole and cresol made minor contributions to the odor.

O'Neill and Phillips (1992) identified 168 chemicals in livestock slurries and manures, of which 30 have odor detection thresholds lower than or equal to 0.001 mg/m^3. Sulfur containing compounds were the major group of the compounds with low odor detection threshold.

The research by Hobbs et al (1999) studied the average daily and annual emission rates for several gases and odorous compounds from pig slurry storage. Volatile fatty acids (C_2 to C_7), phenolics (phenol, p-cresol, p-ethylphenol) and indolics (indole and skatole) and the major by-product gases of the anaerobic storage; carbon dioxide, methane, ammonia, and hydrogen sulfide, were monitored. The authors mentioned that there was no relationship between the odor emission rate and that of H_2S, and other major odorants, nor was there any relationship between the odor concentration emission rate and the concentration of individual odorants in the slurry (Hobbs et al., 1999). This research suggests that the odor is not simply correlated to the individual odorants in the slurry.

O'Neill and Phillips (1992) compiled a list of the chemical compounds in livestock air and manure. The results of twelve studies were considered. The most frequently reported compounds were phenol, p-cresol, ammonia and the volatile fatty acids. They noted that nearly all workers have used gas chromatography (GC) for the odor analysis, even though this technique does not guarantee the identification of every compound present. The paper showed that the reported concentrations in air of the compounds showed wide variations. This review paper also showed the wide variations in the chemicals identified in air, depending upon the sampling and analytical methods used, suggesting that no single method is suitable for the identification of all chemicals in air.

Hobbs et al. (1995) investigated the odorous compounds in the air and slurries from livestock facilities. Silica and carbon based adsorbents were used for the sampling of air from the pig house prior to analysis by GC/MS. The results showed that the two different sampling methods (sorbent tube and liquid extraction of the slurry) gave different chemical profiles. Table 1-1 shows the chemicals that Hobbs et al. (1995) found in the air and swine slurries.

Table 1-1. Compounds found in air and a slurry from a swine facility.

Air (Silica sorbent - orbo 52)	**Slurry** (Liquid extraction with diethyl ether)
acetic acid	3-methyl butanoic acid
	2-methyl butanoic acid
Undecane	Phenol
4-methyl phenol	4-methyl phenol
4-ethylphenol	4-ethyl phenol
	Indole
Skatole	Skatole
	2,3-dihydro-4-methyl 1H indole
	2,3-dihydro-indole carboxyaldehyde

Source: Hobbs et al., 1995.

Zahn et al. (1997) studied the chemical composition of the swine slurry, sludge, and air in a swine facility. They used a multi-bed sorbent trap of Tenax TA and Carbotrap C or Carboxen-569 for the sampling of air. Thermal desorption followed by GC/MS was used to identify the trapped analytes. Solid Phase Micro Extraction (SPME) and conventional liquid extraction method were used to analyze the slurry samples. The results found for the air and slurry samples were different (see Table 1.2) and the compounds found were dependent upon the sampling procedures. This research showed that indole and skatole were present in high concentrations in the slurry, but rarely detected in the airborne emissions from the slurry basin. The study also showed that several compounds, including trimethyl dihydroindene and butylated hydroxytoluene, were present in air samples, but never detected in slurry samples. This research suggests that a number of compounds are concentrated at the air-solution interface (Zahn et al., 1997). Table 1.3 summarizes the chemicals found in air and swine slurries based on the literature previously cited.

Table 1-2. The chemicals founds in air and a slurry from a swine facility.

Air (Tenax TA + Carbotrap, thermal desorption)	**Slurry** (liquid extraction, SPME liquid, SPME head space)
VFAs	**VFAs**
acetic acid	acetic acid
propanoic acid	propanoic acid
butanoic acid	butanoic acid
pentanoic acid	pentanoic acid
hexanoic acid	hexanoic acid
octanoic acid	octanoic acid
nonanoic acid	nonanoic acid
benzoic acid	benzoic acid
dodecanoic acid	
Phenols	**Phenols**
phenol	phenol
4-ethylphenol	4-methylphenol
4-(1,1-dimethylpropyl) phenol	4-ethylphenol
	4-(1,1-dimethylpropyl) phenol
Others	**Others**
2-butanol	2-butanol
1-decanol	1-decanol
1-dodecanol	1-dodecanol
1-bromodecane	benzyl alcohol
butylated hydroxytoluene	1-bromodecane
1,1,3-trimethyl-dihydroindene	butylated hydroxytoluene
hexadecanoic acid methyl ester	1,1,3-trimethyl-dihyroindene
2-amino acetophenone	hexadecanoic acid methyl ester
bis (2-ethylhexyl) phthalate	2-amino acetophenone
	bis (2-ethylhexyl) phthalate

Source: Zahn et al., 1997

Table 1-3. Compounds found in swine wastes and gases

Carboxylic acids	Alcohols	Aldehydes & ketones	Nitrogen heterocycles
formic acid	methanol	formaldehyde	indole
acetic acid	ethanol	acetaldehyde	skatole
propanoic acid	n-propanol	propionaldehyde	pyridine
n-butyric acid	n-butanol	acrolein	3-aminopyridine
I-butyric acid	2-butanol	butylaldehyde	2-methylpyrazine
n-valeric acid	2-methyl-1-propanol	iso-butyraldehyde	methylpyrazine
I-valeric acid	3-methylbutanol	2-butenal	trimethylpyrazine
2-methylbutanoic acid	hex-3-ene-1-ol	pentanal	tetramethylpyrazine
2-methyl-2-butenoic acid	2-methyl2-pentanol	3-methylbutanal	2,3-dihydro-4-methyl-1H-indole
n-caproic acid	1-heptanol	hexanal	
2-methylpentanoic acid	I-heptanol	2-heptenal	**Others**
heptanoic acid	2-ethylhexanol	octanal	methane
octanoic acid	2-methoxyethanol	nonanal	ammonia
decanoic acid	2-ethoxy-1-propanol	2-nonenal	hydrogen sulfide
undecanoic acid	2,3-butanediol	2,4-nonadienal	sulfur dioxide
dodecanoic acid	2-phenylethanol	decanal	pentane
tridecanoic acid	1-decanol	2,4-decadienal	hexane
tetradecanoic acid	1-dodecanol	benzaldehyde	octane
benzenecarboxylic acid	Benzyl alcohol	2-propanone	benzene
phenylethanoic acid		2,3-butanedione	toluene
phenylpropanoic acid		methylethylketone	xylene
hydrocinnamic acid	**Amines**	3-hydroxy-2-butanone	indane
	methylamine	diethylketone propione	naphthalene
Esters	ethylamine	cyclopetanone	methylnaphthalene
methylformate	n-propylamine	2-methyl cyclopentanone	chloroform
methylacetate	iso-propylamine	2-octanone	hydrazine
ethylformate	pentylamine	amylvinylketone	2-methylfuran
ethyl acetate	trimethylamine	acetophenone	2-pentylfuran
propylacetate	triethylamine		2-methylthiophene
I-propylacetate		**Phenolics**	2,4-dimethylthiophene
butylacetate	**Sulfides**	Phenol	diethyl ether
I-butylacetate	carbon disulfide	p-cresol	1-bromodecane
I-propylpropionate	carbonylsulfide	m-cresol	butylated hydroxytoluene
hexadecanoic acid methyl ester	dimethylsulfide	o-cresol	1,1,3-trimethyl-dihydroindene
	diethylsulfide	o-methoxyphenol	2-amino acetophenone
Thiols	dimethyldisulfide	2.6-dimethylphenol	bis(2-ethylhexyl) phthalate
methanethiol	dimethyltrisulfide	3,4-dimethylphenol	benzisothiazole
mropanethiol	diethyldisulfide	p-ethylphenol	benzthiazole
2-propanethiol	dipropyldisulfide	p-(1,1-dimethylpropyl)phenol	2,3-dihydro-indole-carboxyaldehyde
	diphenylsulfide		

1.1.3 The effect of dust on odor

The effect of dust on odors in swine houses has been investigated (Hammond et al, 1979). Many swine production facilities use high ventilation rates to remove the odorants in livestock house resulting in high dust emissions. Dust in livestock buildings is mainly composed of organic material originating from feed, skin, and bedding and dried feces (Harry, 1978). Dust can adsorb and concentrate the odorants. Hammond et el. (1979) showed that odorous compounds in livestock building air were adsorbed onto particles of dust, as well as being molecularly dispersed. In this report, nineteen compounds were identified in the dust collected from air in a swine housing facility. Aldehydes, acids, phenolics, skatole, and sulfur compounds were identified. The authors also conducted odor tests with a panel of eight observers by exposing them to the filtered air and unfiltered air. The filtered air was odorless, while the unfiltered air had an intense odor (Hammond et al., 1979). This result supports the role of dust in the odor of swine facilities.

Oehrl et al. (2000) conducted an analysis of odorous compounds in swine house dust using gas chromatography. Dust samples were taken from the exhaust fans of the swine house and extracted with methanol at 60 °C and analyzed by the GC. Ten of volatile fatty acids (C_2, C_3, C_4, iso-C_4, C_5, iso-C_5, C_6, C_7, C_8, and C_9) and p-cresol were found in the dust samples.

Despite efforts to establish a relationship between dust and odor intensity, no relationship has been determined. Williams (1989) tried to correlate the dust particle numbers and concentration in terms of mass and surface area of dust particles with odor concentration, however it was not successful.

In a review paper, Carpenter (1986) quoted unpublished data claiming that particles in 5-20 μm diameter size range are the mainly responsible for transporting odors. However, the threshold of dust or particle concentration below which odor would be effectively eliminated was not indicated. This paper also showed that the complexity of particle penetration and deposition in the respiratory tracts make it difficult to define the dust size ranges where particles may be trapped in the nasal passage. No sharp demarcation exists, but it is generally accepted that the particles with diameter > 10 μm are deposited in the nasal passages, particles with a diameter 5 to10 μm are deposited in the upper respiratory tract and particles with a diameter < 5 μm are deposited in the lungs themselves (Hayter and Besch, 1974).

The concentration of particles and implication of dust on human health has been reported (Donham, 1986). The threshold limit value (TLV) for inert mineral total dust for humans is 10 mg/m^3, and for respirable dust, 5 mg/m^3 for 8-hour worker exposure (ACGIH, 1993). According to Maghirang et al. (1997), the overall mean total dust concentration in an enclosed swine nursery was 0.72 mg/m^3, and the dust concentration ranged from 0.12 to 2.14 mg/m^3. The overall mean respirable fraction was 11% with a range from 2 to 30% (Maghirang et al., 1997).

1.2. Odor measurement: quantification and qualification

1.2.1. Sampling of volatile organics in the air

As described above, the chemical composition of the volatiles in livestock facilities is variable and the results found are highly dependent on the analytical and/or sampling methods. The analysis of odorous compounds in the air found in the livestock facilities is particularly challenging, as a wide range of volatile compounds are found in this environment.

The Environmental Protection Agency (EPA) has compiled methods for the determination of toxic organic compounds in ambient air. There are 17 compendium methods in the EPA for the determination of toxic organic compounds in ambient air (Air Toxic Methods, 2001).

Harper (2000) has summarized information for the sorbent trapping of volatile organic compounds from air. This article has information for the trapping methods (sorbent trapping and reaction trapping) and desorption methods (solvent desorption, thermal desorption) for various volatile compounds in air. The sorbents, such as silica gel, activated charcoal, Anasorb 747, carboxens, porous polymers and carbon molecular sieves are discussed.

The Solid Phase Microextraction (SPME) method has been widely used for the determination of volatile organics in foods and for flavor analysis (Yang and Peppard, 1994; Ng et al., 1996; Clark and Bunch, 1997; Song et al., 1997). SPME methods have been used mostly for the sampling of volatiles in liquid phases. A recent study showed that this method was able to detect benzene, toluene, ethylbenzene and xylene (BTEX) compounds in the air with a relatively short sampling period (Koziel and Pawliszyn, 2000).

Based on a review of the literature, the following sampling methods were chosen for further evaluation: solvent desorption sorbent tubes, impinger, active multi bed sorbent tubes and SPME.

1.2.1.1. Sorbent trap with solvent desorption

Many NIOSH, OHSA, and EPA methods use the sorbent trapping with solvent desorption for the determination of the volatile organics from the ambient air. More than 30 different sorbent tubes are commercially available. Based on a review of the literature, the following sorbent materials were chosen for evaluation. This choice is based on whether the sorbent is suitable to adsorb the compounds found in the air of livestock facility and whether the sorbent material is able to adsorb wide range of volatile compounds.

1.2.1.1.1. Activated Charcoal

Activated charcoal is commonly used as a sorbent. Coconut shell charcoal and petroleum charcoals have been most widely used. Coconut shell charcoal is used by NIOSH for the analysis of acetic acid, aromatic hydrocarbons, ketones, and esters (NMAM methods 1603, 1501, 1300, and 1450 respectively). It is an inexpensive adsorbent, however, water uptake is a problem with an activated charcoal. When the relative humidity is greater than about 50%, water molecules are adsorbed onto the surface of the charcoal (Harper, 2000). Since the relative humidity in the swine facilities is often greater than 50%, charcoal may be unsuitable for the air sampling in these facilities.

1.2.1.1.2. Silica gel

Silica gel has been used for the determination of polar hydrocarbons in air. Silica gel is used for the detection of aliphatic and aromatic amines (NIOSH, 1994). Due to the sorption of water, the silica gel may have a reduced capacity at high humidity (Harper, 2000).

1.2.1.1.3. Carbon Molecular Sieves

Molecular sieves are substances that have discrete pore structures that discriminate between molecules on the basis of size. Molecules that are small enough to enter the pores of sieves are retained. Carbon molecular sieves are made from polymers, such as polyvinylindene and polyacrylonitrile. Molecular sieve materials such as Carboxieve® S-III and Carboxen® 1000 can be used for the trapping of low-boiling popint compounds (-60 to 80 °) in the C_2 through C_5 range. Molecular sieves can be used for the sampling of small volatile molecules, such as methyl ethyl ketone, vinyl acetate, methyl chloride, dichrolomethane (NIOSH 1453, 2500 and 2549; Rosell, 1991).

1.2.1.1.4. Porous polymers

Microporous polymers can be used as sorbents. The degree of porosity is controlled by the amount of cross-linking. Water adsorption on the polymer surface is not significant and the surface is inert. Tenax, Chromosorb 106, Amberlite XAD-4, and Porapak Q are micoporous polymers. Tenax is useful for the high boiling compounds (EPA CM TO-1, 1999; Martin et al., 2000; Tsai and Hee, 2000; Paustenbach et al., 2001). It has been used with thermal desorption, as Tenax is incompatible with many solvent systems solvent extraction is rarely used for the recovery of the compounds sorbed on Tenax.

Amberite XADs and Chromosorbs are mesoporous polymers with moderate surface areas, they are used for the trapping of large, semi volatile molecules such as polycyclic aromatic hydrocarbons (PAHs) and pesticides. XAD-4 resin is able to adsorb phenols under acidic conditions, where the molecular phenol species is predominant (Ku and Lee, 2000). XAD-2 adsorbent has been used for the collection of sulfur compounds in the work place and carbon tetrachloride was used for the solvent desorption (Suryanayarana et al., 2001). A glass fibre prefilter XAD-2 sampling methods was used by Kontsas et al. (1993) for the collection of airborne chlorophenol.

1.2.1.2. Impinger traps

The midget impinger is another way to trap the VOCs in the ambient air. NIOSH methods use the midget impingers for the trapping of monomethylamine, aminoethanol, formaldehyde, hydrazine, and keptone. Before NIOSH changed the method for phenol and cresol to a method based on sorbent trapping, an impinger trap with 0.1 N NaOH was used. The major advantage of using impingers for air sampling is the ease of sample delivery to the analytical instrument. Since the impinger traps the analytes in solution, the sample can be introduced to the analytical systems, such as a gas chromatograph, without further sample treatment. A disadvantage is that longer sampling times are required than for other sampling methods. Normally, a sampling volume at least 10 times larger than that used sorbent traps is required to obtain similarsensitivity..

1.2.1.3. Sorbent trap with thermal desorption

A major advantages of the sorbent trap-thermal desorption method over sorbent trapping-solvent desorption or impinger methods are that:

a) thermal desorber can transfer the entire sample to the analytical instrument, so lower sampling volume is needed. As the sorption capacity of the sorbent trap is limited, reduced sampling volumes not only save time, but reduce the chances of interferences due to competitive interactions between the anlayte and other chemicals present in the air, e.g., water.

b) as the analyte is not dissolved in a solvent in GC the problem of interference between the solvent and early eluting compounds is avoided.

Multi-bed thermal desorption tubes are useful when the sample contains compounds with a wide range of boiling points. The first bed in the tube is for the collection of compounds with higher boiling points (semi-volatiles) and the second bed is for the collection of the more volatile compounds present in the air. In desorption process, sorbed chemicals are desorbed by heating the tubes. The carrier gas transfers them to the analytical instrument.

Many types of sorbent materials are used in air analysis. Some of the commonly used sorbents are discussed below. Tenax TA is a hydrophobic, macroporous, a semi-crystalline polymer made with diphenyl-p-phenylene oxide. It is relatively inert, granular and available in a wide range of mesh sizes. Due to the relatively low surface area (about 15 m^2/g), the adsorption capacity is low. However, it has an ability to have a very low background (less than 1 ng per component) when it is conditioned and also it is stable at high temperature, so that it allows the recovery of many semi-volatile compounds (Harper, 2000). It is useful for the collection of the multiple analytes present at low concentrations. Some of oxidizing gases, such as ozone and nitrogen oxides, can degrade Tenax.

Chromosorb 106 is very hydrophobic and relatively unaffected by ozone (Harper, 2000). It has a greater capacity than Tenax but it's thermal stability is lower than Tenax, so it is not suitable for analysis of semi-volatile compounds.

Carbotrap B and Carbotrap C are graphitized carbons and are made from carbon black. They do not react with ozone and are relatively hydrophobic and adsorb little water. Carbotrap B, often known as Carbotrap or Carbopack, has a higher surface area (100 m^2/g) than Carbotrap C (10 m^2/g). These sorbents are good for the collection of low boiling point compounds and are rarely used for a single bed. However they are commonly used as the last trap in multi-beds.

1.2.1.3.1. Multi-bed sorbent traps

When the analyst wishes to determine a wide range of analytes, more than one sorbent materials may be required. Multi-bed thermal desorption tubes consist of two or three different sorbent materials. The direction of sample flow in the multi-bed tubes is critical, since the sorbents have different sorption strength. Sample flow should always be from least sorbing material to material with the maximum sorbent strength. Recent US government agency methods have used the mixed sorbents for the air sampling (e.g., EPA Method TO-17, NIOSH Method 2549). The advantage of a multi-bed tube over the single bed tube is sorbents can be chosen to collect a broad range of chemical present in the sample. In NIOSH method, a ¼" stainless steel tube packed with Carbopack Y, Carbopack B, and Carboxene 1003 (Supelco, Inc.) is used. The amount of packing for each sorbents was 90, 115, and 150 mg, respectively. All packing materials should be 40/60 mesh.

EPA suggests that three different types of multi-bed thermal tubes may be used for air sampling. The Type 1 tube is packed with 30mm Tenax and 25mm Carbopack B, the Type 2 tube is packed with 35mm Carbopack B and 10mm of Carbosieve S III or Carboxene 1000, and the Type 3 tube is packed with 13mm Carbopack C, 25mm

Carbopack B, and 13 mm Carbosieve S III or Carboxene 1000. As shown in Table 1-4, three types may be used for trapping analytes of different volatility.

Table 1-4. Multi-bed sorbent materials and sampling methods used in EPA TO-17.

Compounds	Trap packing	Sampling
n-C_6 to n-C_{20}	Tenax(30mm) plus Carbopack B(25mm)	2L at any humidity
n-C_3 to n-C_{12}	Carbopack B(35mm) plus Carboxen 1000(10mm)	2L at relative humidity below 65% and temperature below 30°C 0.5L at RH above 65%
n-C_3 to n-C_{12}	Carbopack B(35mm) plus Carbosieve SIII(10mm)	2L at relative humidity below 65% and temperature below 30°C 0.5L at RH above 65%
n-C_3 to n-C_{16}	Carbopack C(13mm) plus Carbopack B(25mm) plus Carboxene 1000(13mm)	2L at relative humidity below 65% and temperature below 30°C 0.5L at RH above 65%

1.2.1.4. Solid Phase Microextraction

Solid phase microextraction (SPME) was developed by Pawliszyn's group (Arthur and Pawliszyn 1990, Zhang and Pawliszyn 1993). It is a solventless extraction method from gaseous and liquid phases. This method has been utilized widely for the food/flavor analysis (Yang and Peppard, 1994; Ng et al., 1996; Clark and Bunch; 1997; Song et al., 1997). It saves time and labor for the sample treatment and also makes it possible to use aqueous samples for GC/MS without further treatment. The coated silica fiber adsorbs/absorbs the polar and/or non-polar compounds from the sample and it can be thermally desorbed in the GC injector. The length of the SPME fiber coating is typically 10 mm and the polymer thickness ranges from 7 to 100 μm.

Traditional air sampling methods involve drawing air through a sorbent or impinger trap, followed by solvent or thermal desorption into an analytical instrument. These methods require the use of expensive equipment and/or the use of toxic solvents for analysis. Since SPME sampling methods does not use solvent, solvent peaks can be eliminated. Another advantage of the SPME sampling over the conventional air sampling methods is the re-use of the fiber without further cleaning.

Several different types of polymer-coated fibers with different polarities are commercially available. The following SPME fibers are most popular for air or headspace sampling applications; poly dimethylsiloxane (PDMS), PDMS/Carboxen (CAR/PDMS), and PDMS/divinylbenzene (PDMS/DVB).

The partitioning of the analytes of interest between the sample matrix and the polymer film depends on the properties of the SPME coating (Louch et al., 1992). Each coating material has a different selectivity for a particular compounds. The selectivity of these coating materials for specific volatile compounds in the air has not been well documented, however, suitable coatings may be selected based upon the general properties of the anlaytes.

The PDMS coating is a nonporous, amorphous polymeric phase, so the analyte uptake in PDMS is via absorption. The PDMS coating is the one of the most widely used coatings for extracting volatile analytes from environmental samples (Koziel et al., 2000). The theory behind the equilibrium and non-equilibrium extraction process for absorptive PDMS coatings is well described (Wercinski and Pawliszyn, 1999).

PDMS and Divinylbenzene (PDMS/DVB) and PDMS and carboxen (Carboxen/PDMS) are porous solid-phase fibers. The Pores in the fiber have the ability to adsorb analytes and physically retain them, which results in tighter retention of the analyte molecules that are small enough to fit into the pores in the sorbent (Shirey, 1999). Fibers containing porous materials are generally better for trace level analytes (ppt or ppb) with low distribution constants. Therefore, the PDMS/DVB and PDMS/CAR coatings can extract greater amounts of VOCs than the PDMS coating. However, competitive adsorption and displacement effects make mass calibration and quantification partially challenging. Koziel et al. (2000) have described a method based on diffusion controlled extraction for the quantification of SPME measurements. This research also showed that temperature and humidity affect the adsorption process. High humidity in the ambient air had a negative effect on the adsorption, but short sampling times can minimize this effect.

Headspace SPME has been investigated for the analysis of flavor volatiles using two types of fiber coatings (PDMS and Polyacrylate (PA))(Steffen and Pawliszyn, 1996). This research showed that a PA coated fiber extracted polar volatile compounds more efficiently than a PDMS coated fiber.

Pan et al. (1997) documented the analysis of amines in gaseous and aqueous matrices using SPME-derivatization. Three types of the fiber coatings were tested; Carboxen/DVB, Polyacrylate (PA) and PDMS. The results showed that the amines had a high affinity for the polar Carboxen/DVB and PA coatings. This research also showed that hydroxyl groups on a Carboxen/DVB coating interacted more strongly with amines than is the case with the PA coating. Derivatization coupled with SPME significantly improved the sensitivity over direct SPME. The derivatizing reagents used were 2,3,4,5,6-pentafluorobenzylaldehyde (PFBAY) and p-nitophenyl trifluoroacetate (NPTFA).

Air sampling and the analysis of volatile organic compounds with SPME were investigated by Koziel and others (Koziel and Pawliszyn, 2001). This research showed that air sampling with SPME devices is an alternative to NIOSH field sampling methods for VOCs, semi VOCs, and formaldehyde. The paper also showed that the PDMS coating was more suitable for the sampling of semi-VOCs and that the PDMS/DVB coating was more suitable for VOCs and was more efficient in retaining VOCs over a longer period of time.

1.2.1 Analytical method for the characterization of the odorous compounds

Most researches involving air analyses in livestock houses have used gas chromatography, however, the analytical conditions and sampling procedures are varied. The selection of columns, injection, detector and sampling techniques are very important in GC. Helmig (1999) summarized 17 research papers which used gas chromatography for air analysis. In this review paper, he summarized the columns, carrier gases, detectors, and sampling techniques used (Helmig, 1999). Capillary columns were widely used for air analysis. For mass spectrometric detection, columns with an inside diameter of 0.32mm or less were preferred.

1.2.3 Odor measurement: Olfactometry and GC/Sensory

There are four terms (frequency, intensity, duration and offensiveness) that describe the severity of odor. Frequency and duration depend on wind direction and the footprint of the odor source, as it affects those in the path. There is no measurement tool available for these two terms. In general, if several complaints have occurred within a few years, then there may be an odor problem.

Several methods are used to define odor intensity. The human nose is the most accepted standard measurement. Olfactometry is commonly used to measure the odor intensity and odor offensiveness in air. Olfactometry is a psychophysical method based upon the responses of individuals sniffing diluted odors presented by an olfactometer. Olfactometry can provide an effective approach to the measurement of the odor concentration of complex odors.

In the testing procedure, a diluted odorous mixture and an odor-free gas (as a reference) are presented separately from two sniffing ports to a group of panelists. In comparing the gases emitted from each port, the panelists are asked to report the presence of odor together with a confidence level, such as guessing, inkling, or certainty. The gas dilution ratio is then decreased by a factor of two (i.e., chemical concentration is increased by a factor of two). The panelists are asked to repeat their judgment. This continues for five - six different dilution levels, resulting in a total of up to 8x6x2 = 96 judgments (sniffings) from eight panelists. Using the panelists responses over a range of dilution settings, odor concentration, expressed as odor unit (OU) per cubic meter, can be calculated from the individual threshold estimates. The OU is used interchangeably with the term dilution to threshold (DT). The dilution to threshold can be calculated using the following equation.

$$DT = \frac{V_o + V_A}{V_o}$$

DT = dilution to threshold (volume/volume)

V_o = volume of odorous air,

V_A = volume of fresh air

where V_o and V_A are determined at the dilution threshold.

The typical standard for the olfactometry is 1-butanol because of its stability, low toxicity, and generally agreeable smell.

CHAPTER 2. MATERIALS AND METHODS

This chapter describes the sampling and analytical methods that have been used in the work described in this dissertation.

2.1. Sampling methods

2.1.1. Solvent Desorption Sorbent Tubes

Table 2-1 shows the sorbent tubes used in this research.

Table 2-1. Sorbent tubes used for the sampling of VOCs.

Packing material	Supplier[1]	Part No.	Dimensions D , L (mm)	Amount of packing material (mg)	Plug material[2]
Amberlite XAD-7	Supelco	ORBO 615	6, 70	50/100	GW
Anasorb CSC	SKC Inc.	226-01	6, 70	50/100	F, GW
Silica gel	Supelco	ORBO 52	8, 110	150/150	GW
Silica gel	SKC Inc.	226-10	6, 70	75/150	GW
Tenax	SKC Inc.	226-35	6, 70	15/30	F, GW

[1]Supelco, Bellefonte, PA; SKC Inc., Eighty Four, PA

[2]This is the material used in the plugs that retain the packing in the tubes (see Figure 2.1) F: foam, GW: glass wool

Figure 2-1 shows the sampling train used. A SKC (Aircheck sampler 224-PCXR8) pump was used for air sampling and the sample flow rate was measured both before and after sampling using a mass flow meter.

The sampling conditions used are listed in the Table 2-2. The sample flow rates and the total sample volumes for the tubes chosen were based on the manufacturer's recommendations.

Table 2-2. Sampling flow rates and volumes used for the collection of VOCs on solvent desorption sorbent tubes.

Sorbent tube	Flow rate (ml/min)	Total Volume (L)
Amberite XAD-7	100	24
Anasorb CSC	200	24
Silica gel (large)	200	36
Silica gel (small)	100	18
XAD	100	24
Tenax	100	6

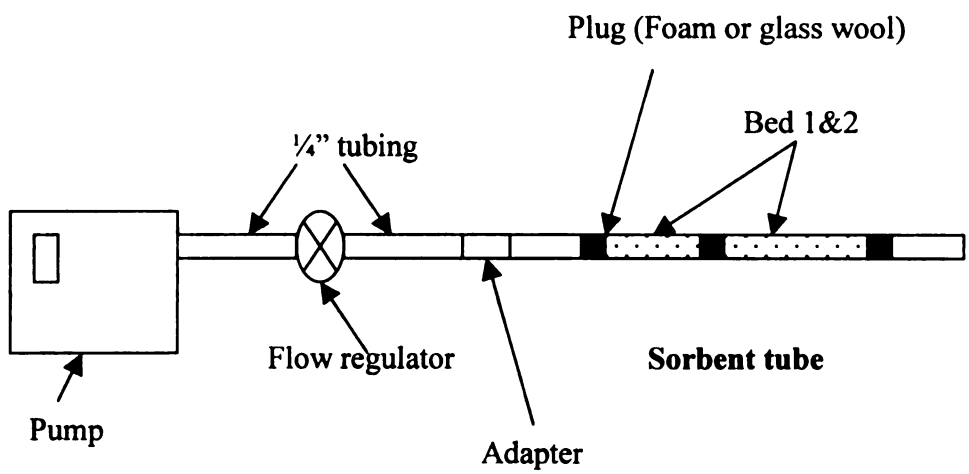


Figure 2-1. Sampling train for ORBO tubes

2.1.2. Sample Preparation

2.1.2.1. Charcoal

The glass wool and foam plugs were removed from the tubes and the sorbent materials from the first and second beds were transferred to separate 2 mL GC auto-sampler vials. One mL of formic acid and CS_2 were added to each GC vial to desorb VOCs from the sorbent. The injection volume to the GC was 5 μL.

2.1.2.2. Silica gel

Two types of silica gel tubes were used. For the large silica gel tube, 95% ethanol was used for the desorption of VOCs. For the small tube, dilute H_2SO_4 in 10% (v/v) aqueous methanol was used for the desorbing solvent.

For the large ORBO 52 tubes, the beds were transferred to separate 2 mL vials and 1 mL of 95% ethanol was added to each vial. The vial then was capped and placed in an ultrasonic bath for 1 hour. The vials were allowed to sit for another 30 minutes, to allow the particles to settle. The supernatant was then transferred to a 2 mL vial. Five μL of the sample was injected into the GC.

For the SKC silica gel tube, the beds were transferred to separate 2mL vials and 1mL of dilute H_2SO_4 in 10% (v/v) aqueous methanol was added to each vial. The vials were then allowed to sit for 30. A 500 μL aliquot was transferred to a clean 2 mL vial and 500 μL of 0.3 M KOH was added to the vial to neutralize the sample. The samples were then immediately analyzed. Five μL of the sample was injected into the GC.

2.1.2.3. XAD

Three types of solvents were used for the desorption of VOCs from XAD tubes: methanol, CS_2, and methylene chloride. The front and back beds of the sorbent tubes were transferred to separate 2mL vials and 1mL of the desorption solvent was added to the vials. The vials were then capped and placed in an ultrasonic bath for 30 minutes. The vials then allowed to sit for 30 minutes to allow the particles to settle. The supernatant in each vial was transferred to 2mL septum vial. The injection volume to the GC was 1 μL.

2.1.2.4. Tenax

Three types of solvents were used for the desorption of VOCs from Tenax tubes: methanol, CS_2, and methylene chloride. The glass wool and the foam were removed from the tube and the sorbent materials in the first and second beds were transferred to separate 2 mL vials. Five hundred (500) μL of solvent was added to the vial and it was capped. The vial then was placed in an ultrasonic bath for 30 minutes. The vials were allowed to sit for 30 minutes to allow the particles to settle. The supernatant was then transferred to a 2mL septum vial. An injection volume of 5 μL was used for GC analysis.

2.1.3 Sampling using a midget impinger

Two 25 mL midget impingers (SKC Inc., 225-36-2) were attached to the sampling pump as shown in Figure 2-2. Fifteen (15) mL of trapping solution was placed in each impinger. A flow rate of 700 mL/min was used for sampling and total of 42L of air was collected. The sample solution was injected to GC/FID or GC/MS without any further treatment. An injection volume of 5μL was used for GC analysis.

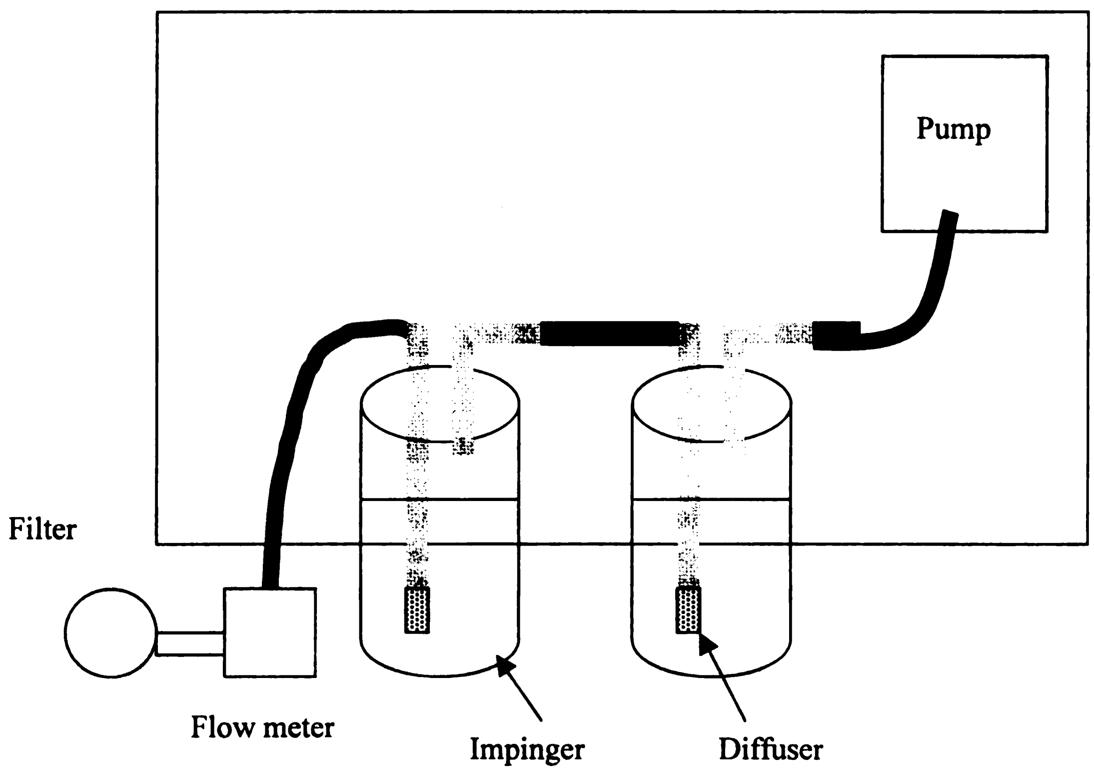


Figure 2-2. Sampling diagram for the impingers

2.1.3. Sampling on thermal desorption sorbent tubes

Quarter inch diameter (¼") and 7" long stainless steel multi-bed sorbent tubes were used. The pre-packed tubes were purchased from Supleco. Figure 2-3 shows the construction of the thermal tube. The tubes contained 30mm of Tenax TA and 30 mm of Carboxen or 30 mm of Tenax TA and 30mm of Carbosieve SIII. The two sorbent materials were separated by unsilanized glass wool. Prior to sampling, the tubes were conditioned at 280°C for 30 minutes to remove any contaminants on the sorbent material. Three liters (3 L) of high purity helium was passed through the tube during conditioning. The conditioned tube was sealed with a Teflon plug and wrapped with aluminum foil and placed in the opaque clean container and stored in a refrigerator at 4°C until it was used.

The sample was taken using a portable and programmable air sampling pump (SKC Inc.). Figure 2-4 shows the sampling diagram for the thermal desorption tubes. The sampling time was 30 minutes. A flow rate of 200 mL/min was used for sampling.

2.1.4. Sampling for the particulates

For sampling dust, a 37mm cassette filter holder (225-3, SKC, Inc.) with a membrane filter (pore size of 1.0 µm, SKC Inc. 226-7) and a support pad (Metricel, Gelman Lab.) was used. The three-piece cassette filter and filter holder were connected to the air sampling pump. A flow rate of 200 mL/min was used for the dust collection. The total sampling time was 30 minutes. Samples were carried in an ice-box to the laboratory and stored in a refrigerator (4 °C) until they were analyzed.

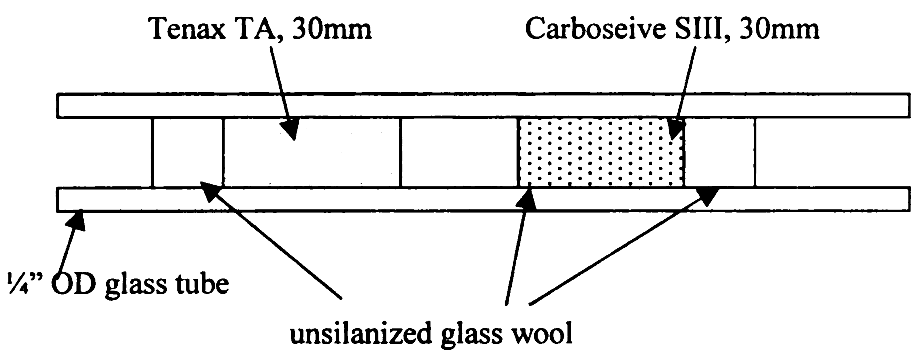


Figure 2-3. Construction of the thermal desorption tube

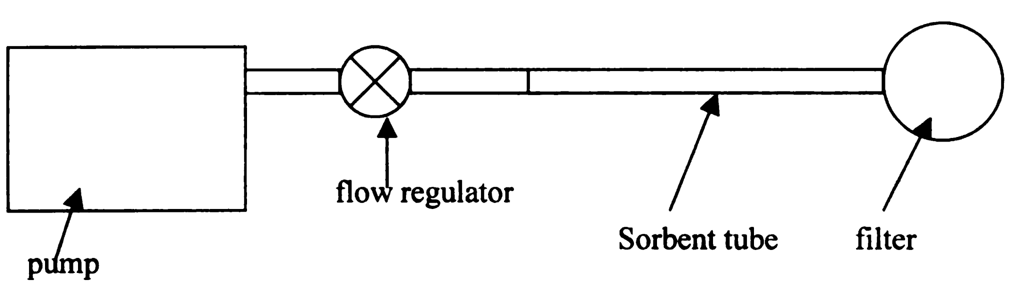


Figure 2-4. Sampling diagram for the thermal desorption tube

2.1.6 Sampling using Solid Phase Microextraction fibers

Three different fibers were evaluated to determine which fiber has the greatest efficiency for extraction of the odorous volatile compounds from the air of the swine building. Table 2-3 shows the fibers used.

Table 2-3. SPME Fiber coatings used for the study

Fiber	Phase	Film thickness (μm)
PDMS	Polydimethylsiloxane	100
PDMS/CAR	PDMS and Carboxen (porous carbon)	75
PDMS/DVB	PDMS and divinylbenzene	65

A Supelco field SPME sampler (504831) was used to collect the VOCs. New fibers were conditioned prior to use according to the manufacturers specifications, so as to remove any contaminants on the fiber coatings. The temperature and times used for conditioning were as follows: PDMS, 250°C for 1 hour; PDMS/DVB, 260°C for 30 minutes, and PDMS/CAR, 280°C for 30 minutes. The conditioned samplers were wrapped in aluminum foil and stored in the refrigerator until they are used.

The grab sampling method was used for SPME air sampling. For the sampling of VOCs, the fibers were exposed to the ambient air of the swine building for the required sampling time. After sampling, SPME fibers were carried in an ice-box to the laboratory and the sample was stored in the refrigerator until they were analyzed.

2.2. Analytical Instrumentation

2.2.1. Thermal desorber

An Aerotrap 6000 (Tekmar) was used for the thermal desorption of the sorbent tubes. A cryo-trap in the Aero trap concentrates the volatiles in –165 °C with liquid nitrogen. The instrument contains a moisture trap to remove water from the sample.

The conditions used for the thermal desorber are as follows; trap cool at -165°C, sample desorption at 250°C for 20 minutes, trap desorb preheat at 200°C. The traps weredesorbed for 5 minutes at 250°C. High purity helium was used for the carrier gas and carrier gas flow rate of 20 mL/min was used.

2.2.1.1. Desorption of VOCs from particulates

An empty ¼" tube was used for desorption of VOCs from the filter. A filer was placed in the empty tube. Other conditions were same as the normal thermal desorption mode.

2.2.2. Gas chromatography and mass spectrometry

A Varian 3800 gas chromatograph (Varian Chrompack, GC-3800) with a programmable injector (1079) was used for the analysis of volatile compounds. The GC was connected to a Saturn 2000 Mass Spectrometer (Varian Chrompack). The GC also had a flame ionization detector , FID. High purity hydrogen and air were used for the combustion gases for the FID, and high purity helium was used for the make up gas for the FID.

A DB-5MS (60m, 0.25mm ID, 0.25μm film thickness) capillary column was used for the separation of the analytes. High purity helium (99.9995%) was used as a carrier gas. The column flow was held at 1 ml/min. The GC oven temperature program was; 35°C for 5 minutes, ramped to 100°C for 5°C/min and ramped to 220°C for 20°C/min. The operating conditions for the mass spectrometer were: trap temperature 150°C, transfer line temperature 120°C, scan range 40 to 200 m/z, scanning speed 1 second/scan. A Varian 8200 autosampler was used to inject the liquid samples.

CHAPTER 3. A COMPARISON OF SAMPLING METHODS FOR THE CHARACTERIZATION VOLATILE ORGANIC COMPOUNDS IN LIVESTOCK FACILITIES USING GAS CHROMATOGRAPHY - MASS SPECTROMETRY.

3.1. Introduction

As described previously, the characterization of odorous compounds in air in an around livestock facilities is difficult for a number of reasons. First, numerous compounds are present in the air. O'Neill and Phillips (1992) reported that 168 compounds have identified in livestock wastes or in the air around livestock facilities. Many other compounds present have not been identified. Compounds found in livestock air and livestock wastes include VFAs, phenolics, indolics, amines, and sulfides. Another problem is that many odorous compounds may be present at very low concentrations. O'Neill and Phillips (1992) found that at least thirty of the compounds found in the livestock wastes had odor thresholds lower than or equal to 0.001 mg/m^3. Other difficulties are posed from the analytical standpoint, due to the very wide range of physical and chemical properties of the odorous compounds found in livestock wastes. Some odorous compounds (e.g., hydrogen sulfide, methyl mercaptan and ammonia) are gases, whereas, as others have boiling points in excess of 250°C (e.g., indole , skatole).

Gas chromatography (GC) has been widely used for the analysis of odorous compounds in air. Due to the very low detection limits required to identify some odorous compounds, it is necessary to concentrate the compounds present in the air. Two concentration methods, sorbent trapping and impinger trapping, have been widely used in standardized methods published by the EPA, NIOSH and OSHA. Thermal or solvent desorption may be used to transfer the analytes trapped on a sorbent tube to the analytical instrument. The impinger solution can usually be transferred directly into the analytical instrument. Recently another sample concentration method for air analysis, Solid Phase Microextraction (SPME), has been investigated. Several researchers have investigated the applications of the SPME for air and headspace analyses (Arthur and Pawlizyn, 1990; Zhang and Pawliszyn, 1993; Koziel and Pawliszyn, 2001).

3.2. Objectives

The main objective of this research were to determine the most effective air sampling method for the odorous volatile organics in swine building air.

3.3. Materials and methods

3.3.1. Swine housing

The sampling was conducted in a nursery room in the Michigan Sate University Swine Teaching and Research Farm. The nursery has 30 pens with eight pigs in each pen. The temperature in the nursery room was maintained at about 24°C (76°F) by mechanical ventilation. The sampling was done every day at 4 PM. Temperature and relative humidity in the room were measured.

3.3.2. Samplings

Four sampling methods were used; solvent desorption sorbent trapping, thermal desorption sorbent trapping, impinger trapping, and SPME. Table 3-1 shows the sorbent tubes and desorption solvents that were chosen for the study. Desorption solvents were varied to see the effect of the solvent types on the results. Some of sorbent tubes were specially designed for the certain solvent, in that case only the specified solvent was used.

Table 3-1. Summary of sorbent tubes and desorption solvents chosen for the collection of various VOCs in livesotk building air.

ORBO tube	Analyte/Sampling	Solvent
ORBO 608 (Amberlite XAD-2)	Volatile organics	Methanol, CS_2, methylene chloride.
ORBO 615 (XAD-7)	Phenol, p-cresol	Methanol
	Other volatile organics	CS_2
Tenax	Volatile organics	Methanol, CS_2, methylene chloride
ORBO 32S (coconut charcoal)	Acetic acid	1mL formic acid
	Esters	1mL CS_2
	Ketones	1mL CS_2
	Aromatic hydrocarbons	1mL CS_2
ORBO 52S (Silica gel)	Amines (aliphatic and aromatic)	Aromatic: 95% ethanol (1h ultrasonic bath) Aliphatic: 1 mL dilute H_2SO_4 in 10% (v/v) aqueous methanol (3 h in ultrasonic)

For the experiments used in impingers, the trap solution and conditions were chosen based on the previous researches. Table 3-2 shows the trapping conditions for the various organic compounds.

Table 3-2. Liquid trap solutions for impinger air sampling method for the collection of VOCs in the livestock building air.

Compounds	Solvent	Injection
Acids and neutrals (Phenol, p-cresol, VFAs, etc.)	0.1N NaOH	Neutralize with 5% sulfuric acid before inject
Bases (amines, etc.)	5% sulfuric acid	Neutralize before inject

Sampling and conditioning methods for the tubes and SPME fibers are described in section 2.1.

3.2.3. Analytical instrument

Two identical GC columns, DB-5MS columns, were connected to the switching valve and TD and GC injector. The switching valve was used to switch the TD or GC injector to MS.

An Aerotrap 6000 thermal desorber was used for the thermal desorption. The conditions for the desorber are described in the section 2.2.1. Varian 3800 GC and 2000 MS were used for the analysis of VOCs from various samples. The analytical conditions used for GC/MS analysez are described in the section 2.2.2.

3.4. Results

3.4.1. Solvent desorption sorbent traps and Impinger traps

The solvent desorption methods lacked the sensitivity necessary to determine the odorous compounds. Figure 3-1 shows the chromatograms obtained with samples collected on a charcoal trap. As shown in this Figure, only a few small peaks are observed in the chromatogram.

The impinger traps also lacked the sensitivity necessary to determine the odorous compounds using the sample volume of up to 72 L.

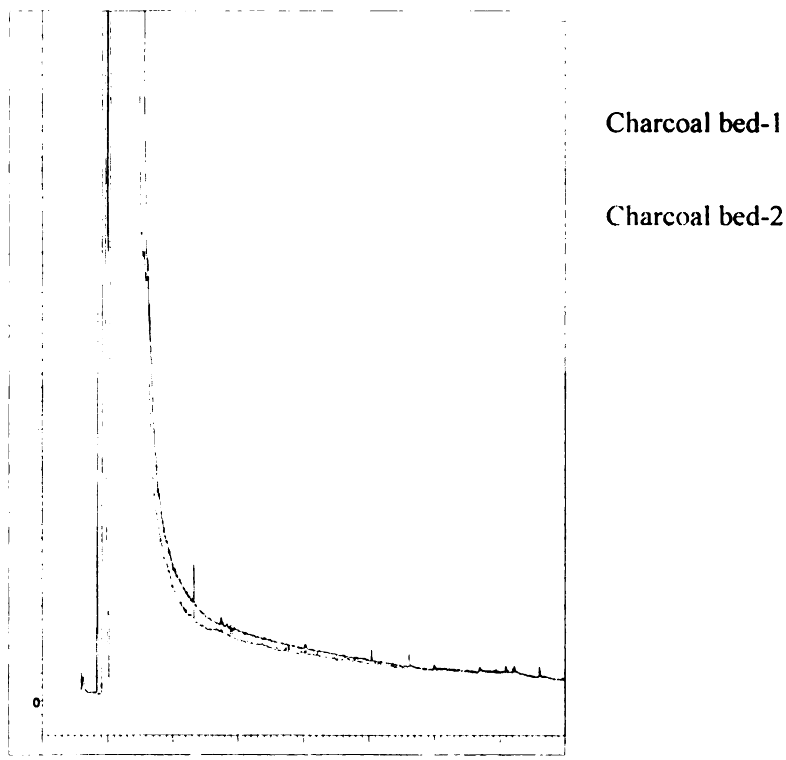


Figure 3-1. Chromatograms for air samples which were collected on charcoal tubes.

3.3.2. Thermal desorption sorbent traps

Figure 3-2 shows typical chromatograms for air samples that were trapped on a thermal desorption tubes. A larger number of volatile organics were found. Figure 3-2 showed that the Tenax TA – Carbosieve SIII tubes were able to collect the volatile (early eluting) organic compounds more effectively than the Tenax TA – Carboxen tubes. The recovery of compounds in the mid-boiling point range was better with the Tenax TA – Carboxen tubes. The recovery of high boiling point compounds, such as indole and skatole, were poor with both types of sorbent tubes. The major compounds found in swine house air were hydrocarbons and the substituted benzenes (mono, di and tri substituted alkyl benzenes). Sulfur compounds such as 1,2-ethanthiol, dimethyl disulfide and dimethyl trisulfide were also present.

Table 3-3 and 3-4 lists of the compounds which were detected from the swine nursery air by thermal desorption sorbent tubes and GC/MS. The compounds were found by matching the spectrum of the compound with the library provided with the Saturn instrument (NIST/EPA/NIH Mass Spectral Library '98). The matching threshold was set to 700.

Polar biogenic VOCs such as alpha-pinene, beta-pinene, limonene, 3-carene were also found. These compounds have been identified and quantified in air in rural area (Ciccioli et al., 1993). These compounds were not confirmed by comparing the retention time and spectra with those of standards. Isomers were not determined. The stereo-chemical information for the compounds is not available at this stage.

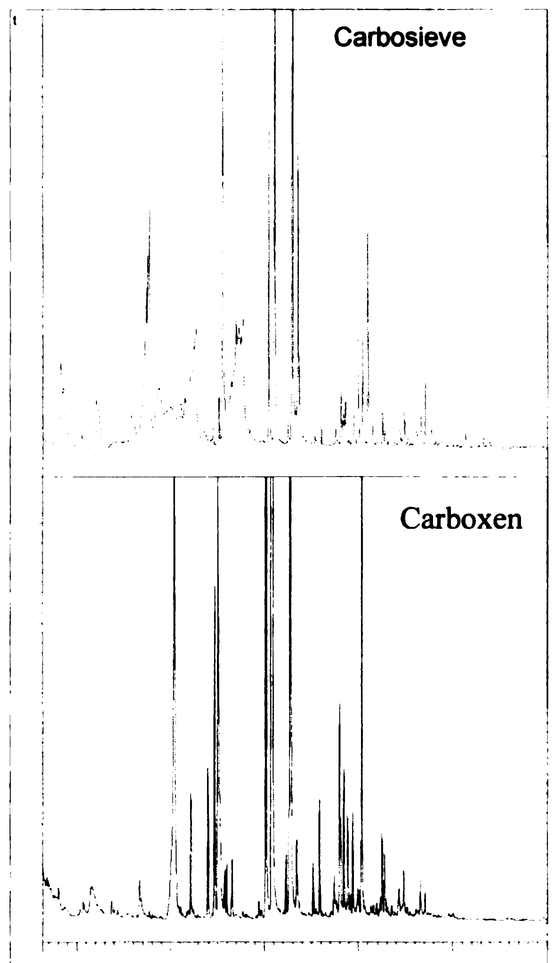


Figure 3-2. Chromatogram for air sample which were sorbed on thermal desorption tubes.

Table 3-3. Compounds found in swine house using the thermal desorption method (Tenax TA and Carbosieve SIII)

Tenax TA + Carbosieve SIII		
Retention Time (min)	**Compounds**	**Molecular Weight**
5.427	1-propanol	60
6.098	2-butanol	74
7.945	1-butanol	74
8.871	acetic acid	60
9.38	dimethyl disulfide	94
11.294	propanoic acid	74
12.752	Hexanal	100
13.728	butyric acid	88
15.528	p-xylene	106
16.485	m-xylene	106
16.78	heptanal	114
19.971	unknown	
20.23	1,2,3-trimethylbenzene	120
20.733	2-ethyl-2-hexanal	126
21.281	1,2,4-trimethylbenzene	120
21.427	limonene	136
23.562	decane	142
23.865	nonanal	142

Table 3-4. Compounds found in swine house using the thermal desorption method

Texax TA + Carboxen		
Retention Time (min)	**Compounds**	**Molecular Weight**
5.795	Benzene	78
8.395	acetic acid	60
10.177	dimethyl disulfide	94
11.06	1,6-heptadiene-3-yne	92
11.984	4-octene	112
12.329	2,4-dimethylhexane	114
12.511	hexanal	100
12.955	2-octene	112
13.279	unknown	
15.066	ethylbenzene	106
15.444	p-xylene	106
16.316	m-xylene	106
16.707	heptanal	114
17.578	1-methylethyl benzene	120
17.917	pinene	136
18.705	propylbenzene	120
18.982	1-ethyl-2-methylbenzene	120
19.23	1,2,3-trimethylbenzene	120
19.425	dimethyltrisulfide	126
19.685	1-ethyl-3-methylbenzene	120
20.172	1,2,4-trimethylbenzene	120
21.386	limonene	136
22.167	1-methyl-3-propylbenzene	134
22.398	1,2,3,5-tetramethylbenzene	134
23.545	2-methyl-1-octanol	

3.3.3. Solid Phase Microextraction

Figure 3-3 shows chromatograms for air samples which were taken with three different types of the SPME fibers. The PDMS coating was not effective for the collection of the volatile organics in the air. The PDMS/CAR coating was the best for the extraction of the compounds of intermediate volatility, such as acetic acid, propionic acid, butyric acid, and hexanoic acid. In general the PDMS/DVB coating permitted the best recovery of the high boiling point compounds, such as phenol, p-cresol, p-ethylphenol, indole, and skatole, in swine building air. The recovery of low boiling point compounds was not good for all three types of fibers.

Tables 3-5, 3-6, and 3-7 show the compounds found in swine nursery using the three types of SPME fibers. p-cresol and skatole were found using all three types of the fibers. VFAs were found using PDMS/CAR and PDMS/DVB coatings.The recoveries of the VFAs were higher in PDMS/CAR coating. Phenol was only detected using the PDMS/DVB coating in the experiment. Indole was not detected usingany of the fibers, however, in the experiments described in Chapter 5 indole was detected in swine building air.

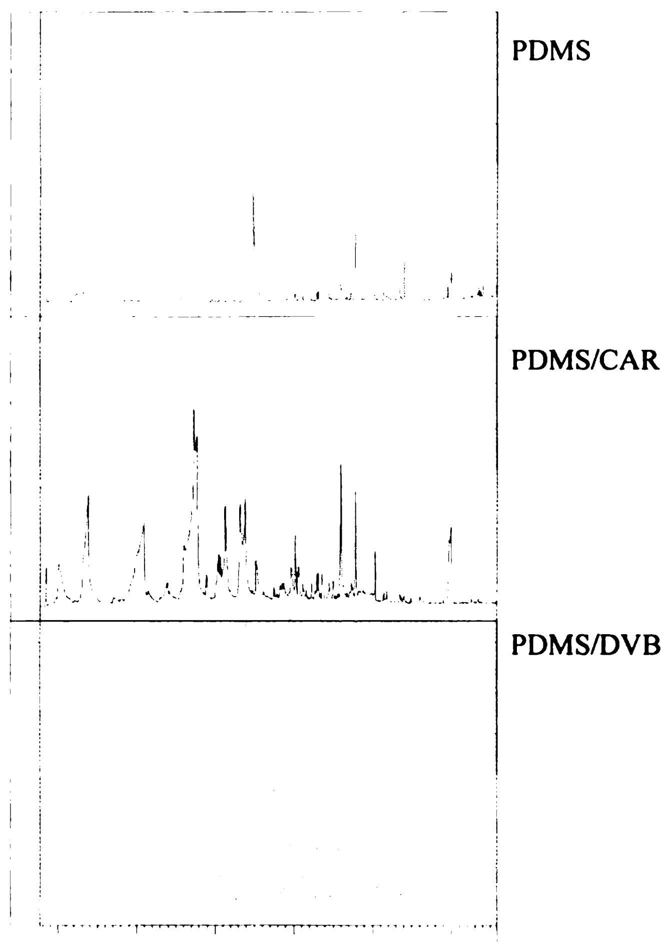


Figure 3-3. Chromatogram for air sample which were extracted by SPME fibers.

Table 3-5. The compounds found in swine housing air using SPME fiber with a PDMS coating.

R.T. (min)	Compound	Molecular Weight.
17.411	Amylamine	87
21.119	2-methyl-1-butanol	88
22.978	p-cresol	108
23.908	1,8-octanediol	146
25.87	p-ethylphenol	122
27.016	2-decanol	158
29.774	Undecanal	172
31.835	Skatole	131
32.002	Dodecanal	184

Table 3-6. The compounds found in swine housing air using SPME fiber with a PDMS/CAR coating.

Retention Time (min)	Compound	Molecular Weight
6.887	Acetic acid	60
10.253	propionic acid	74
11.88	isobutyric acid	88
13.491	butyric acid	88
15.233	isovaleric acid	102
15.629	p-xylene	106
16.558	m-xylene	106
16.908	hexanoic acid	116
19.232	1-methylethyl benzene	120
19.81	heptanoic acid	128
20.126	4-methylvaleric aicd	116
20.292	trimethlbenzene	120
21.802	benzylclcohol	108
22.976	p-cresol	108
23.922	nonanal	142
25.87	p-ethylphenol	122
26.987	methyl salicylate	152
31.857	skatole	131
33.446	diethyl ester	146

Table 3-7. The compounds found in swine housing air using SPME fiber with a PDMS/DVB coating.

Retention Time (min)	Compound	Molecular Weight
6.6	acetic acid	60
9.496	propionic acid	74
11.644	isobutyric acid	88
13.213	butyric acid	88
14.954	isovaleric acid	102
15.37	valeric acid	102
15.636	p-xylene	106
16.583	m-xylene	106
16.75	hexanoic acid	116
19.14	ethylmethylbenzene	120
19.24	benzaldehyde	106
19.805	phenol	94
20.288	trimethylbenzene	120
20.577	octanal	128
21.495	limonene	136
21.772	benzyl alcohol	108
23.019	p-cresol	108
23.914	nonanal	142
25.705	2-nonenal	140
25.872	p-ethylphenol	122
31.826	skatole	131
32.228	3-methyl-benzoxazolimine	148

Table 3-8. Compounds found in TD tubes and SPME fibers.

TD			SPME		
Retention Time (min)	Compound	Molecular Weight	Retention Time (min)	Compound	Molecular Weight
5.427	1-Propanol	60			
5.795	Benzene	78			
6.098	2-Butanol	74	6.887	Acetic acid	60
7.945	1-Butanol	74			
8.871	Acetic acid	60			
9.38	Dimethyl disulfide	94			
11.294	Propanoic acid	74	10.253	Propanoic acid	74
11.984	4-Octene	112	11.88	Isobutyric acid	88
12.752	Hexanal	100			
13.728	Butyric acid	88	13.491	Butyric acid	88
15.066	Ethylbenzene	106	15.233	Isovaleric acid	102
15.528	Xylene	106	15.629	Xylene	106
16.78	heptanal	114	16.908	Hexanoic acid	116
17.578	Methylethyl benzene	120			
			19.81	Heptanoic acid	128
17.917	Pinene	136	19.805	Phenol	94
19.425	Dimethyltrisulfide	126	20.126	Methylvaleric acid	116
20.23	Trimethylbenzene	120	20.288	Trimethylbenzene	120
20.733	Ethyl-2-hexanal	126	20.577	Octanal	128
21.427	Limonene	136	21.802	Benzyl alcohol	108
	Methyl-3-		22.976	p-Cresol	108
22.167	propylbenzene	134			
23.562	Decane	142	23.922	Nonanal	142
23.865	Nonanal	142	25.87	p-Ethylphenol	122
			31.857	Skatole	131
			33.446	Diethyl ester	146

3.4. Conclusion and Discussions

Without any further sample concentration, solvent desorption sorbent tube was not able to determine any volatile organics from the swine nursery housing air using a sample volume of up to 36 L. This method also required handling of hazardous organic solvent for the sample treatment. As sample concentration would be time consuming and there is a risk that analytes may be lost during this step, this method was deemed to be less suitable than the thermal desorption or SPME methods.

The impinger trap was also unsuitable for the determination of VOCs from the swine housing air, even using sample volume as large as 72 L.

Thermal desorption has been widely used for desorption of sorbent tubes. The major advantage of the thermal desorption method over solvent desorption is that the entire sample can be introduced into the analytical instrument. Also, as no solvent is used to desorb the analytes, there is no interference due to the solvent. The principal disadvantages of thermal desorption are a thermal desorber is required to desorb the sorbent tubes and the recovery of high boiling point or reactive compounds can be poor as they may be sorbed to or degraded within the thermal desorption instrument.

This research showed that the multi-bed thermal desorption method can be used for the sampling of VOCs from livestock building, however the recovery of high boiling point compounds was not good.

SPME air sampling method showed the good recovery of the high boiling point compounds, however this method was not good for the recovery of the low boiling point compounds.

Table 3-8 shows the major compounds found in swine nursery using TD tubes and SPME fibers. Table shows that the TD was able to collect more early eluting compounds (low boiling point compounds) and SPME was able to collect high boiling point compounds.

The SPME air sampling methods, has the following advantages over other sampling techniques:

- Sampling device is lightweight and compact.
- Reagents are not required for desorption.
- Sensitivity is good.
- Response is linear with concentration.
- Generally independent of humidity (except at very high humidities).
- Expensive cryotraps or thermal desorbers are not required.

The major drawbacks of SPME includes:

- Analytes of low volatility do not reach partition equilibrium quickly
- Samples are not time-integrated

It is apparent from research that no single methods for air sampling appears to be satisfactory. For the determination of high boiling point compound such as phenolics and indolics, SPME air sampling method offered the best results. The combination of SPME and collection on a Tenax TA – Carboxen sorbent tube followed by thermal desorption seems to offer the best results. For the low to mid boiling point compounds, recoveries were good using the thermal desorption sorbent tubes. For the high boiling point compounds, such as phenolics and indolics, SPME seems to be the most effective method.

CHAPTER 4. QUALITATIVE AND QUANTITATIVE ANALYSIS OF ODOROUS COMPOUNDS IN LIVESTOCK BUILDING WITH SOLID PHASE MICROEXTRACTION AIR SAMPLING METHOD

4.1 Introduction

Solid Phase Microextraction (SPME) is a relatively new sampling technique. It can be used for sampling liquids or air. Due to the simplicity and ease by which it can be used for sampling air, along with its sensitivity and specificity, SPME fibers have been used widely for the determination of volatile organics in food and flavor analysis (Yang and Peppard, 1994; Ng et al., 1996; Song et al., 1997; Sostaric et al., 2000; Vianna and Ebeler, 2001).

Supelco Co. (Bellefonte, PA) supplies SPME field samplers that are suitable for field use. SPME field sampler consists of SPME fiber and a fiber holder. A septum in front of the holder protects the fiber from contaminations. Figure 4-1 shows the SPME field sampler. Several different types of polymer-coated fibers with different polarities are commercially available. The different fibers are used for various needs. For example, polar fibers are useful for sampling of polar compounds.

Two sampling modes can be used for air sampling using SPME. In grab sampling, the fiber is said to be "exposed" when it is outside of the needle for sampling period. In this mode, the fiber is exposed to the ambient air. The fiber is said to be "retained" when it is inside the needle for sampling period. The second term is called "time weighted average (TWA)" sampling. (Koziel and Pawliszyn, 2001). In

TWA method, the fiber is retained inside of the fiber holder and VOCs slowly diffuse onto the fiber inside of the fiber holder.

Figure 4-1. SPME field sampler.

SPME (grab samples) have been widely used for relatively short sampling periods. Time integrated sampling with SPME has been challenging. Martos and Pawliszyn (1999) studied time-weighted average (TWA) sampling using a SPME air sampler in an attempt to enhance personal exposure monitoring to airborne pollutants. This research used SPME TWA sampling method to collect VOCs in work environment and compared with the conventional air sampling method (NIOSH method 2541). Martos and Pawliszyn (1999) showed that the commercially available SPME device could be successfully used as a TWA diffusive sampler for both hydrocarbons and formaldehyde.

The major disadvantage for SPME air sampling method is the difficulty in quantifying the analytes. SPME fibers are not uniformly sensitive to all compounds and therefore, relative GC peak areas for an SPME sample do not properly reflect the true proportions of the components in the sample to which they are exposed. Furthermore, other environmental/physical factors such as sampling time and temperature and humidity can affect the uptake of the contaminant on the fiber.

Equilibrium theory has been widely used for the SPME quantification and has been described by several researchers (e.g., Martos and Pawliszyn, 1997; Koziel and Pawliszyn, 2001). However, it is generally believed that equilibrium theory cannot be used for the quantification of the compounds on the mixed porous fibers that are most widely used for air sampling (Koziel and Pawliszyn, 2001). The diffusion-based calibration method for rapid air sampling using SPME has been recently studied by several researchers (Ai, 1997; Koziel and Pawliszyn, 2000; Augusto et al., 2001). These researchers showed that SPME with mixed porous fiber coatings could be used for the rapid air sampling. Quantification methods also have been described by these researchers.

4.1.1 Equilibrium theory

Equilibrium theory assumes that the concentration of an analyte in the fiber coating is directly proportional to its concentration in the headspace.

$$K = \frac{C_{fiber}}{C_{air}} \quad \dots\dots\dots\dots\dots (1)$$

where C_{fiber} is the concentration on fiber
C_{air} is the concentration in the headspace and K is the equilibrium constant.

Because the volume of the fiber is constant (uniform SPME fibers are now commercially available), the equation simplifies to the mass of analyte absorbed by the fiber being directly proportional to the headspace concentration (Bartelt, 1997). The proportionality constant, K', (referred to as the calibration factor through this paper) is;

$$K' = \text{mass on fiber} / C_{air} \quad \dots\dots\dots\dots\dots\dots (2)$$

$$\text{and } K' = K \times V_{fiber}$$

Once the proportionality constants, K' has been defined, the concentration of the analyte in the air (C_g) can be calculated from the mass (n). The calibration factors, K', are different for different analytes and different fiber types. In general, high boiling point compounds tend to have low K' values.

The mass on SPME fiber coating can be measured by calibrating against direct standard injection and by calculating the response factor of the compound. The response factor can be determined by on-column injection of the analyte. It is calculated as nanograms of analyte per unit instrumentation response (unit area) by dividing the injection mass (ng) by area.

Response factor (RF) = mass (ng) /area ....(3)

The mass of analyte absorbed on the fiber, n_{fiber} (ng), is calculated by multiplying the GC peak area by the measured response factor.

n_{fiber} = RF factor x GC area .... (4)

A calibration curve can be constructed using the serially diluted standard solutions. A working stock solution was made from stock solution by dilution with methanol. The working stock solution was serially diluted to have final concentrations of 0.001 PPM for each compound. Curves for each compound have been constructed (see Appendix B). In this research, the mass (n) was measured using a calibration curve.

4.1.2 Non-equilibrium theory

The quantification of analytes on mixed phases coatings, such as PDMS/CAR and PDMS/DVB has been difficult because of the competition between analytes for the adsorptive sites available in the fiber and the inter-analyte displacement. In a recent study, Koziel and Pawliszyn (2001) presented an alternate methodology to overcome this problem. When a fiber is exposed to a gaseous sample moving perpendicularly to the fiber axis for a period of time much smaller than the equilibration time, the coating behaves as a perfect sink and all analyte molecules reaching the fiber surface are immediately adsorbed. As a large number of non-occupied adsorptive sites are available in these conditions, interanalyte competition and displacement are minimized and can be disregarded. The extracted amount of an analyte (n) depends on its concentration in the gaseous matrix C_g, its diffusion coefficient in air D_g; the fiber's length L; radius b; respectively, the thickness of the effective static boundary layer surrounding the fiber δ; and the sampling time t as shown:

$$C_g = \frac{n \ln\left(\frac{b+\delta}{b}\right)}{2\pi D_g L t} \qquad \text{........................(5)}$$

Several models are available to estimate diffusion coefficients in air. The Fuller-Schettler-Giddings model (Schwarzenbach et al., 1993) which is the most adequate model for a large number of analytes in normal sampling conditions, the diffusion coefficient, D_g, can be calculated by following equation:

$$D_g = \frac{0.001 T^{1.75} \sqrt{\frac{1}{M_{air}} + \frac{1}{M_{voc}}}}{p\left[\left(\sum V_{air}\right)^{1/3} + \left(\sum V_{voc}\right)^{1/3}\right]^2} \qquad \text{..................(6)}$$

where D_g is the diffusion coefficient (cm^2/s)

T is the absolute temperature (K)

M_{air} is the apparent molecular weight of air (g/mol)

(i.e. the weighed average of the molecular weights of the components of air)

M_{voc} is the molecular weight of the analyte (g/mol)

p is the ambient pressure (atm)

V_{air} is the molar volume of air (cm^3/mol)

V_{voc} is the molar volume of the analyte (cm^3/mol)

The thickness, δ, of the effective static boundary layer surrounding the fiber can be calculated from equation 7, where Re is the Reynolds number ($\mathrm{Re} = 2ub/\bar{v}$; u is the linear velocity of the air and v is the kinematic viscocity of air) and Sc is Schmidt number ($\mathrm{Sc} = v/D_g$)

$$\delta = 9.52b/\mathrm{Re}^{0.62}\,Sc^{0.38} \quad \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Using these equations, the concentration of analyte can be directly calculated from the chromatographic peak area, given the sampling conditions (sampling time, air velocity, temperature, and pressure) and constants (diffusion coefficient and fiber conditions) are known.

In this research, SPME quantifications with equilibrium theory and rapid non-equilibrium theory have been demonstrated. CAR/PDMS coating has been used for this research since this is the generally used mixed porous fiber coating for air sampling.

4.2 Hypothesis

1. The mass of volatile organic compounds sorbed on SPME fiber coating will be time dependent and will eventually reach an equilibrium.
2. The mass of sorbed on SPME fiber coating with CAR/ODMS coating will depend linearly on the concentration of the analyte in the gas phase at any particular sampling time.

3. The concentrations of odorous compounds in the livestock facility can be quantified using SPME CAR/PDMS coating.

4.3 Objectives

The main objectives of this research are

- To demonstrate the adsorption equilibrium time on SPME fiber for odorous compounds in livestock building air using CAR/PDMS coatings.
- To demonstrate the quantitative analysis of SPME air sampling for odorous compounds using equilibrium theory.
- To demonstrate the quantitative analysis using fast SPME air sampling technique for odorous compounds in livestock building air.

4.4 Materials and Methods

4.4.1 SPME fibers

A SPME field sampler (Supleco Co.) with 75 μm CAR/PDMS coating was used in this experiment. Conditions for the conditioning the new fibers are given in the section 2.1.1.4. The dimensions of the fiber coatings were: fiber length of 1 cm and the film thickness was 75 μm.

4.4.2 Test Mixtures

The mixture contains phenol, p-cresol, p-ethylphenol, indole and skatole. Table 1 lists concentrations of the compounds in the test mixture stock solution. The stock solution was made with methanol and the total volume was 25 mL. The stock solution was been stored in the refrigerator and working stock solution was made by dilution of the stock solution whenever it was needed.

Table 4-1. Stock solution of test mixture used for the SPME air sampling methods. (Total volume was 25 mL and the solvent was methanol.)

Compound	Amount
Phenol	1.07 g
p-Cresol	1.034 g
p-Ethylphenol	1.0247 g
Indole	1.028 g
Skatole	1.0335 g

4.4.3 Air sampling

One or two micro liters of stock solution were injected into the 1L gas standard bottle. Because the mixture was made with methanol, the phenolic compounds were quickly evaporated in the gas standard bottle (1 L, gas sampling bottle with septum purge). To prevent the sorption of analytes on to the glass sampling bottle, 100 μL of water was injected to the gas sampling bottle after all samples were evaporated. The water vapor did not affect sorption of the analytes on the SPME fiber, since the PDMS/CAR fiber coating is a non-polar material. Research has shown that humidity does not greatly affect on SPME sorption, since the mass loading on the fiber decreased by 10% at relative humidities greater than 90% (Martos and Pawliszyn, 1997).

For sampling, a freshly conditioned fiber was passed through the septum into the gas sampling bottle. Sampling times were varied from 5 seconds to 420 minutes according to the test objectives. Triplicate samples were taken for the same sampling period and averaged. All sampling was conducted in the static condition without disturbing the air flow in the gas sampling bottle. Fibers were not agitated during the sampling. Figure 4-2 illustrates the sampling procedure using SPME fibers and the gas standard bottle.

4.4.4 Calibration curve

A calibration curve was prepared by direct injection of serial dilutions of the test mixture. A Varian 8200 autosampler was used for the injection of liquid standards.

4.4.5 Gas chromatography and mass spectrometry

GC/MS was used for the analysis of SPME samples. The SPME field sampler was introduced into the GC injector. The analytical conditions are given in Section 2.2.2.

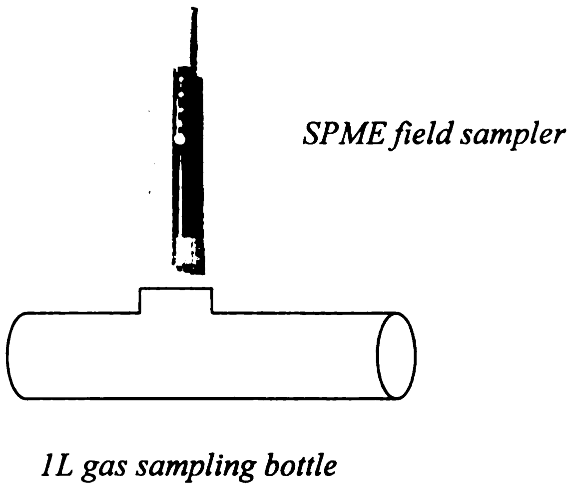


Figure 4-2. SPME air sampling system.

4.5 Results

4.5.1 Adsorption Time Profile for phenolic compounds on SPME CAR/PDMS coating

Sorption time profiles for phenolic compounds on SPME CAR/PDMS are shown in Figure 4-3. The figure shows that the mass of chemical adsorbed on SPME CAR/PMDS coating increased as sorption time increased. The increase in sorbed mass of the phenolic compounds can be described by a linear relationship for times up to 30 minutes. When the sorption time exceeded 30 minutes, the mass adsorbed on SPME coating increased in a non-linear relationship with time. None of chemicals, p-cresol, p-ethylphenol, indole and skatole, reached equilibrium within the course of the experiment (420 minutes).

4.5.1.1 Relationship between the amount adsorbed on SPME and the sampling times.

Based on the results mentioned in the previous section, a linear line for time versus adsorbed masses was constructed for sorption times less than 30 minutes. Figure 4-4 shows the linear relationship between the mass of phenol adsorbed on SPME coating and sampling times when the sampling time was less than 30 minutes. Similar results were observed for p-cresol, p-ethylphenol, indole and skatole (Figures 4-5, 4-6, 4-7, and 4-8).

The effect of concentration on SPME sorption behavior was studied. A standard mixture containing 0.43, 0.41,0.41, 0.41, and 0.41 μg/L of phenol, p-cresol, p-ethylphenol, indole, and skatole was used. The standard mixture was injected into the gas sampling bottle and a SPME fiber was used for the sampling of VOCs in the gas phase. The masses sorbed on the SPME fiber were analyzed using GC/MS. All samples were analyzed in triplicate and three data points were averaged. The averaged data was used for the linear regression. Results showed that the masses sorbed on SPME for phenolic and indolic compounds increased in curvature as sampling time increased from 5 minutes to 30 minutes (Figure 4-9, 4-10, 4-11, 4-12, 3-14). A previous study by Pawliszyn (1997) showed that the sample concentration has no affect on the concentration time profile. When the extraction method and distribution constants between the SPME and sampling system remain constant, the equilibrium profile and time should be the same for all other concentration. Therefore, the extraction behavior should be linear for all concentration ranges. However, the results showed that the extraction behaviors for phenolic compounds on SPME fibers were not same for the gas phase concentrations at 0.4 and 4 μg/L.

These results suggest the possible systematic experimental errors. It is possible that the errors resulted from a depletion of available sorption sites on SPME fiber. In this experiment, it was assumed that the sorption abilities for the SPME fibers were the same and calibrations for individual SPME fibers were not conducted. When a small portion of the fiber coating is damaged, the sorption ability would be greatly reduced even though the damage was too minor to be detected. To avoid this problem, calibrations for all individual SPME fibers would be required. The lifetime of a new SPME fiber is 50 to 100 samplings depending on sampling conditions. As a SPME fiber ages, the sorption ability of the fiber is reduced. Therefore, usages and sampling histories for all SPME fibers should be carefully recorded. Secondly, the error may result from environmental conditions, such as temperature. Room temperatures fluctuated from 22.3°C to 24.3° during the experiment, and temperature in the sampling bottle was not controlled and the temperature changes were ignored because the difference was approximately 2 °C. A previous study showed that the increase in the sample temperature increased the analyte concentration in the headspace, thereby providing faster extraction (Wercinski and Pawliszyn, 1999). This error can be corrected by sampling SPME fibers at several different temperatures. Another error may result from the standard solution. A new working standard solution was made when the old one was older than 7 days. Experimental error may be introduced in preparing the standard. To avoid this error, the new standard must be calibrated prior to being used for the gas standard.

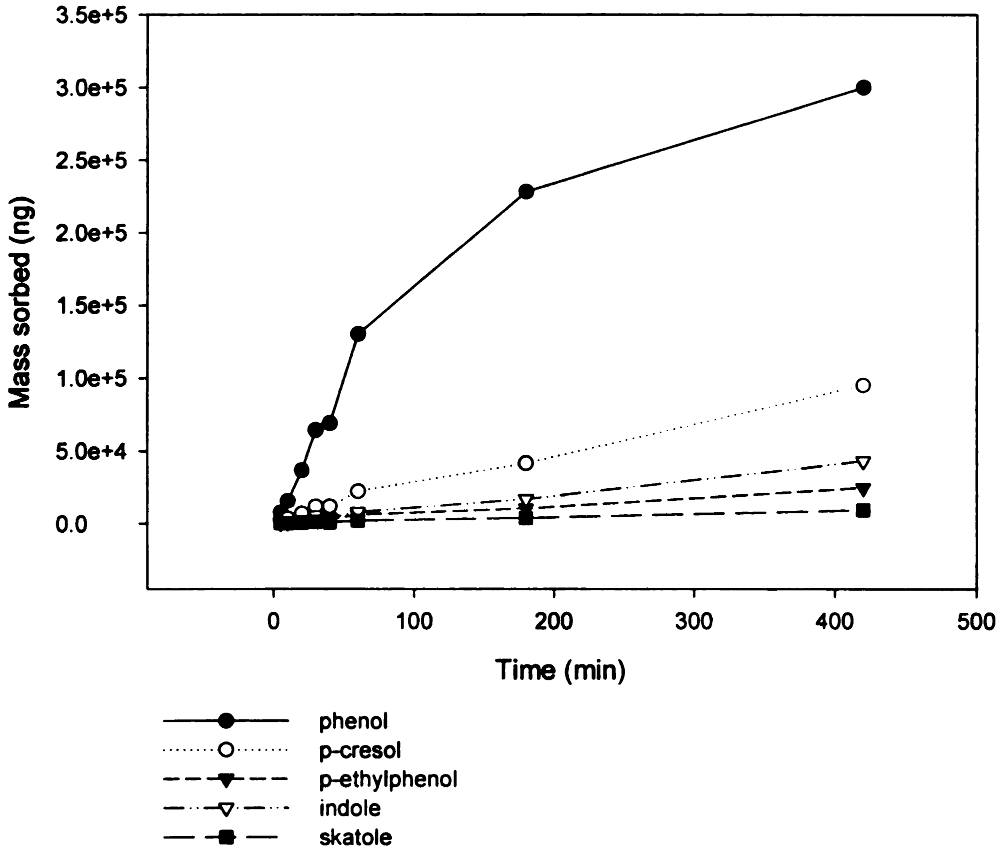


Figure 4-3. Adsorption time profile for phenolic compounds using a static adsorption conditions using SPME CAR/PDMS. (The standard contained 4.3, 4.1, 4.1, 4.1, 4.1

μg/L of phenol, p-cresol, p-ethylphenol, indole, and skatole, respectively.) The average temperature was 23°C and pressure was 1 atm.

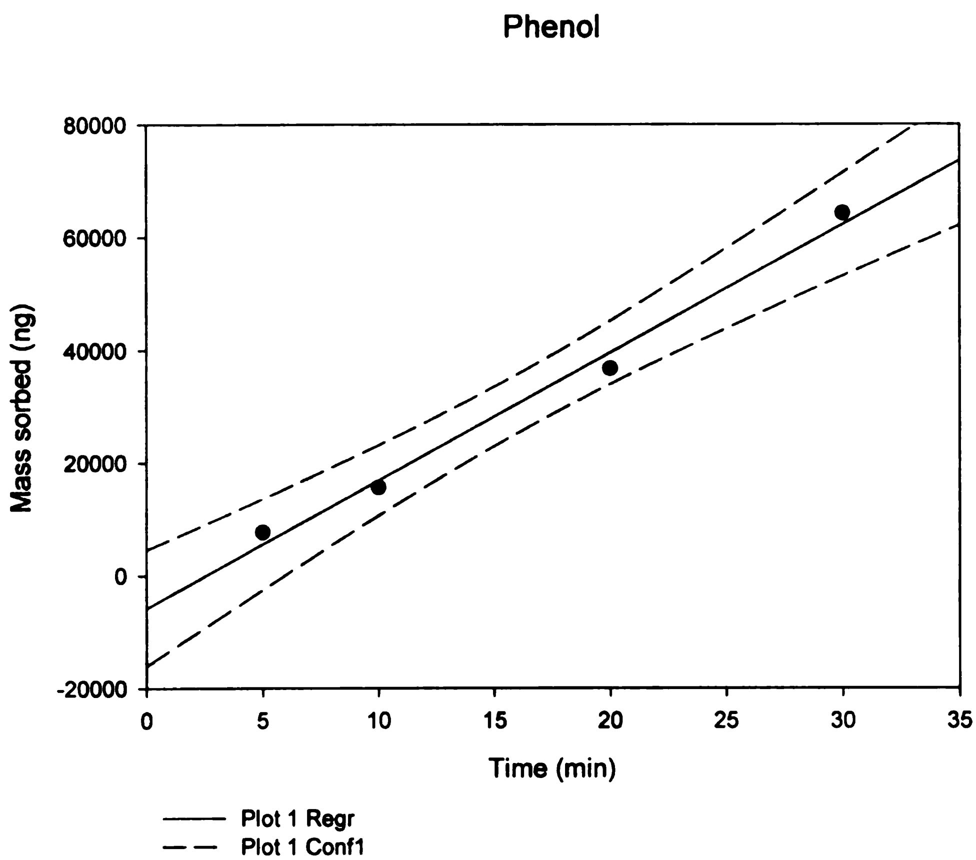


Figure 4-4. The relationship between the sorbed mass and sorption time on SPME for Phenol (4.3 μg/L). The upper and lower lines represent the 95% confidence interval. The average temperature was 24°C and pressure was 1 atm.

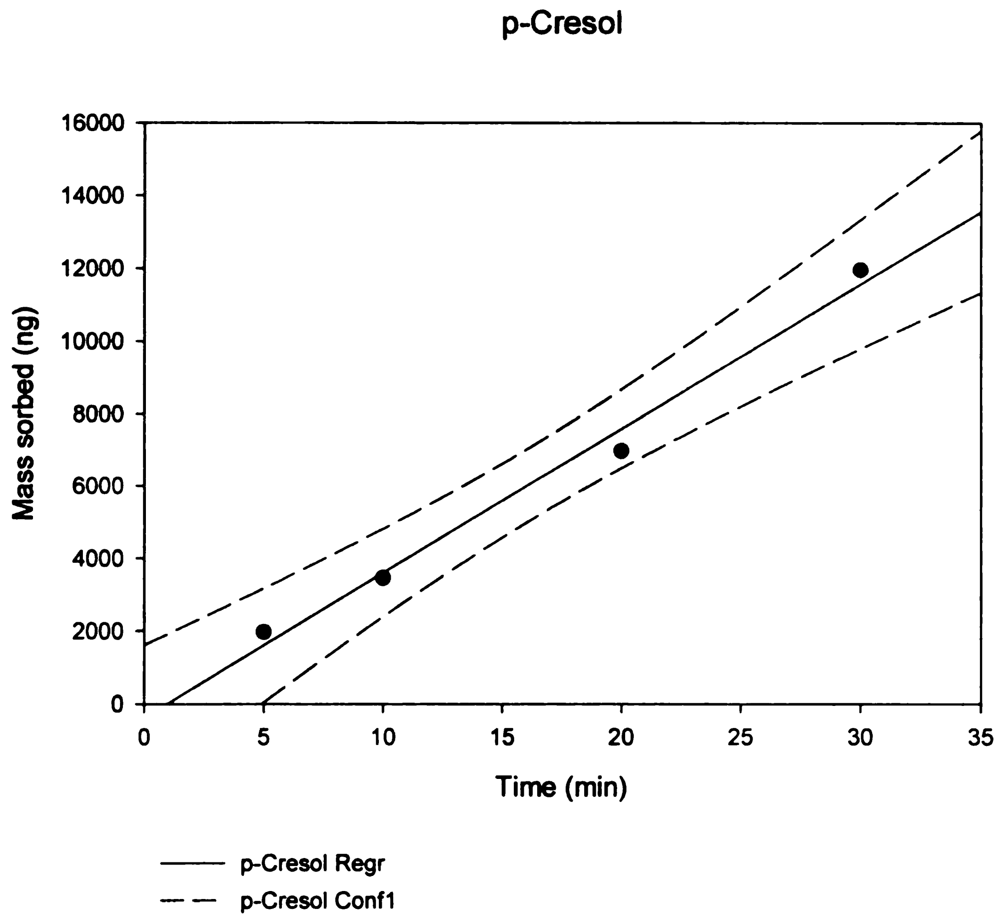


Figure 4-5. The relationship between the sorbed mass and sorption time on SPME for p-Cresol (4.1 μg/L). The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

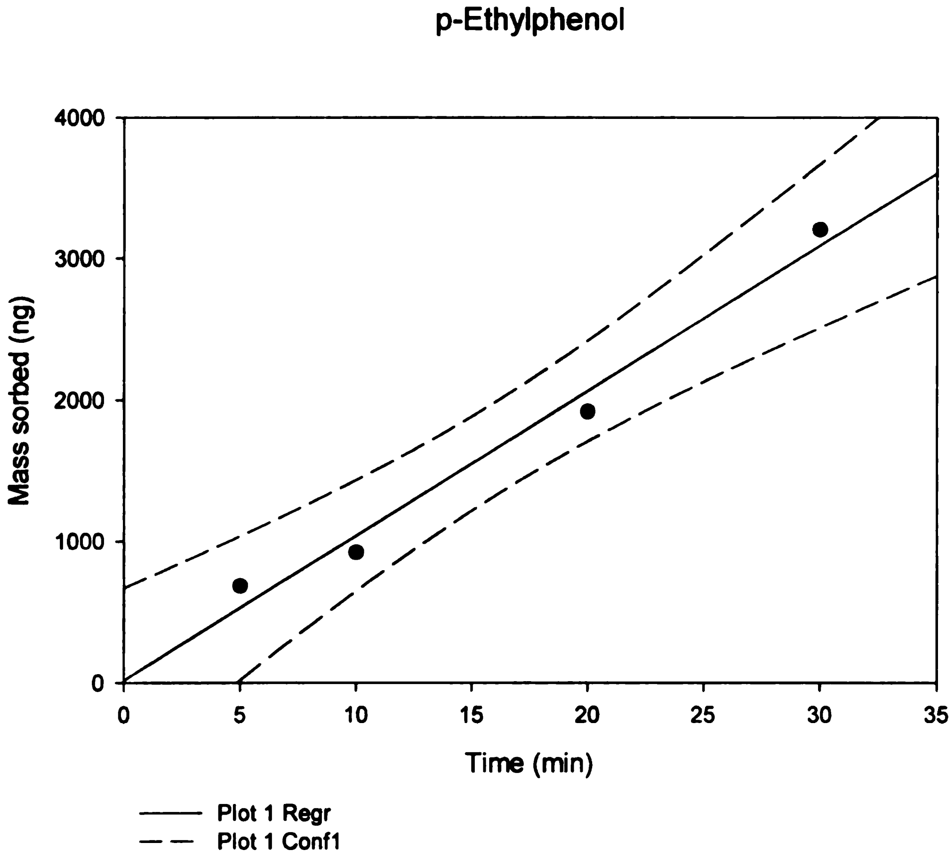


Figure 4-6. The relationship between the sorbed mass and sorption time on SPME for p-Ethylphenol (4.1 μg/L). The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

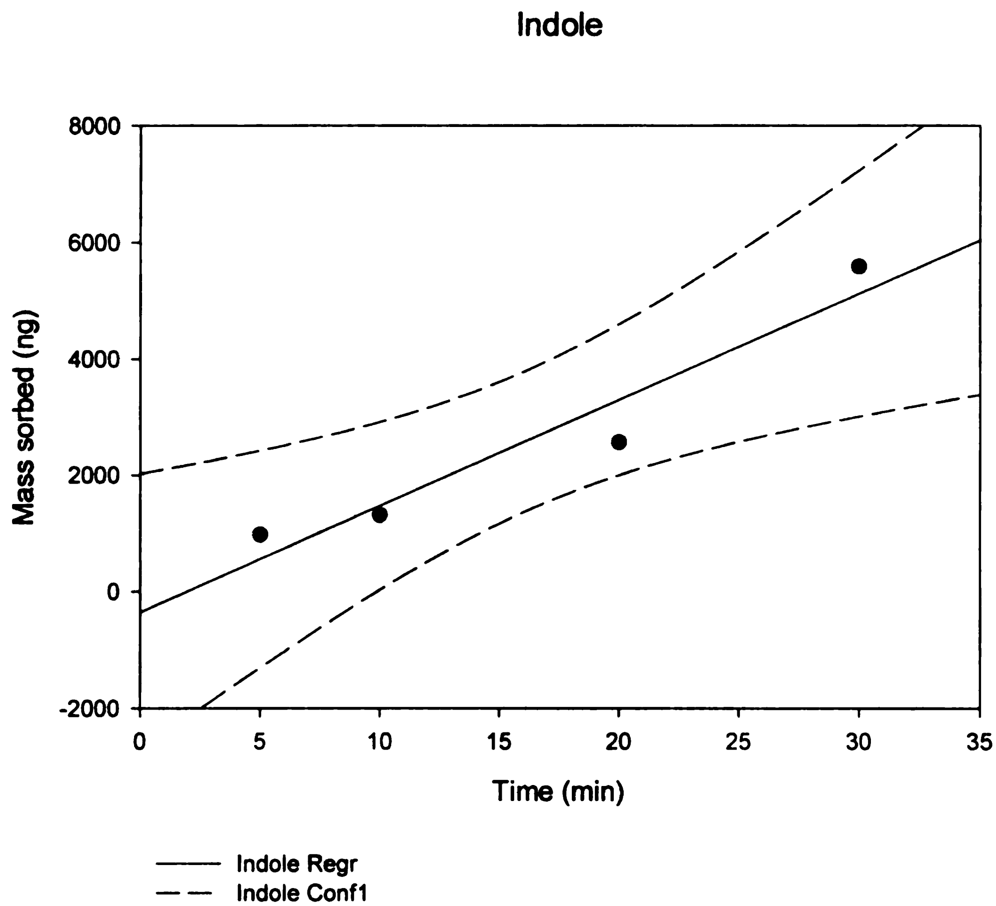


Figure 4-7. The relationship between the sorbed mass and sorption time on SPME for Indole (4.1 μg/L). The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

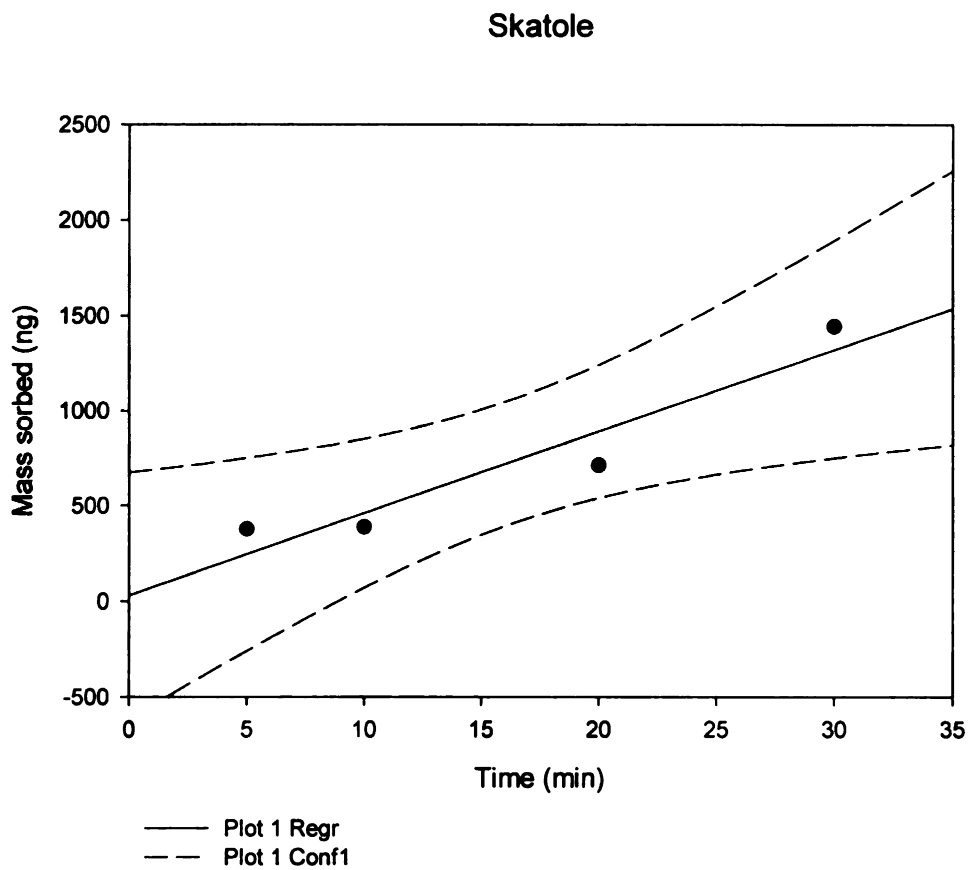


Figure 4-8. The relationship between the sorbed mass and sorption time on SPME for Skatole (4.1 μg/L). The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

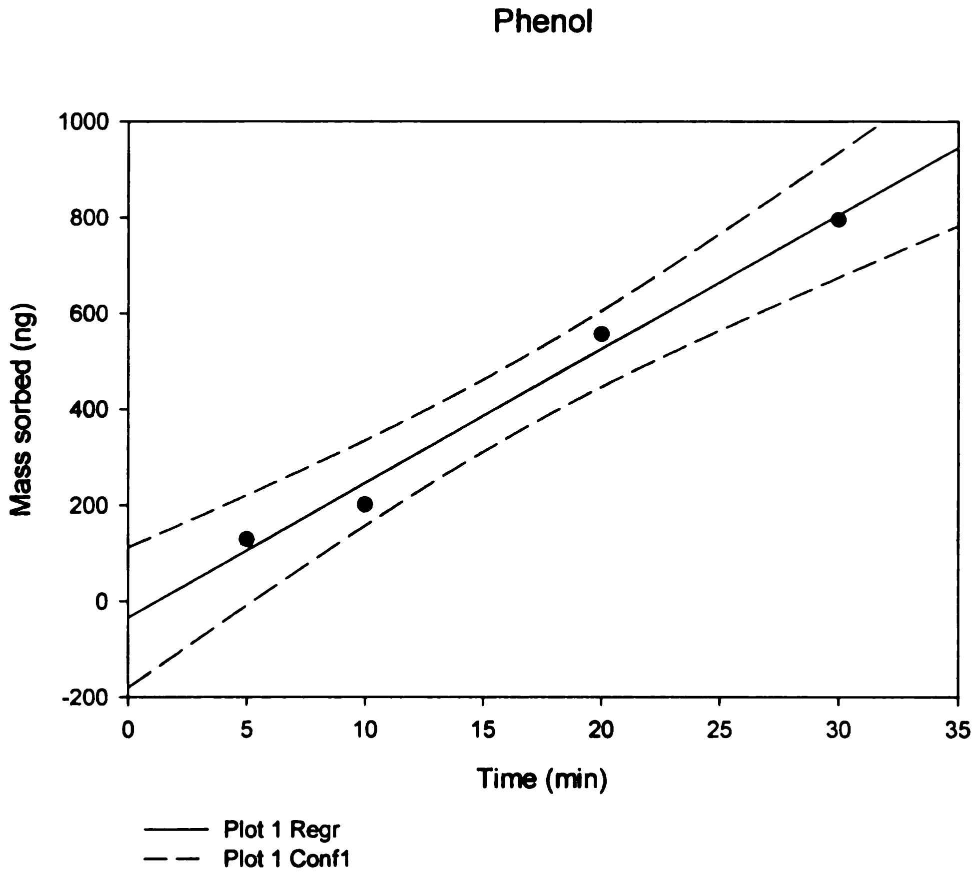


Figure 4-9. The relationship between the sorbed mass and sorption time on SPME for Phenol at lower concentration (0.43 μg/L). The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

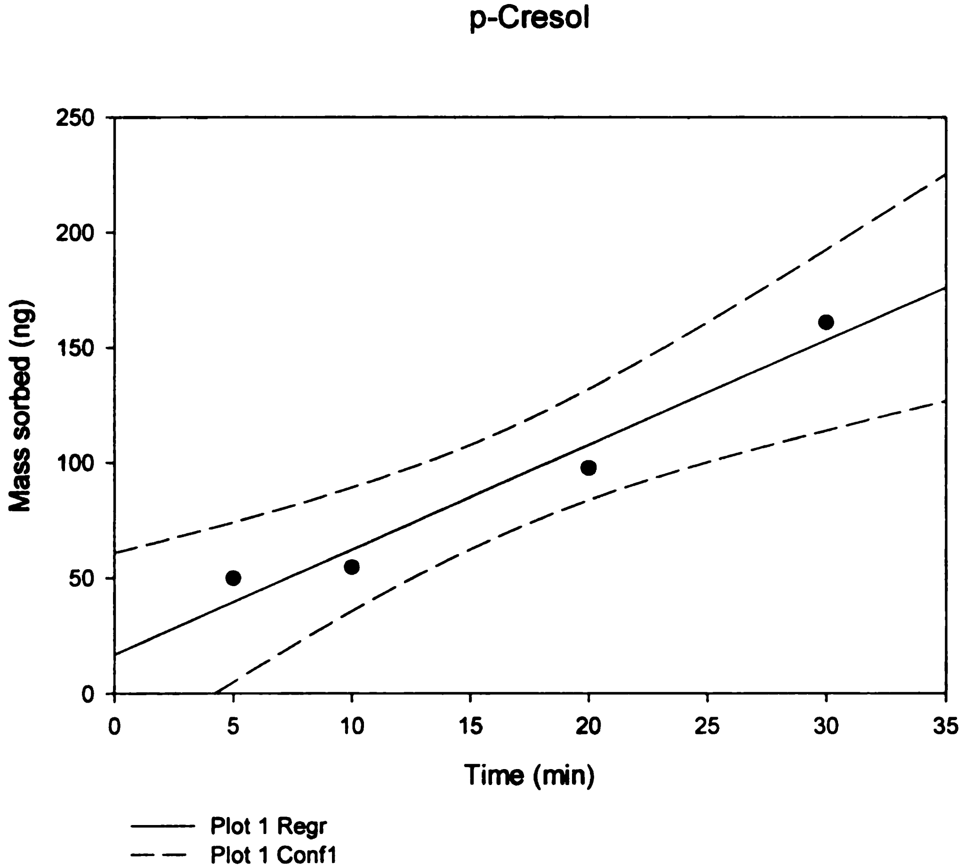


Figure 4-10. The relationship between the sorbed mass and sorption time on SPME for p-Cresol at lower concentration (0.41 μg/L). The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

p-Ethylphenol

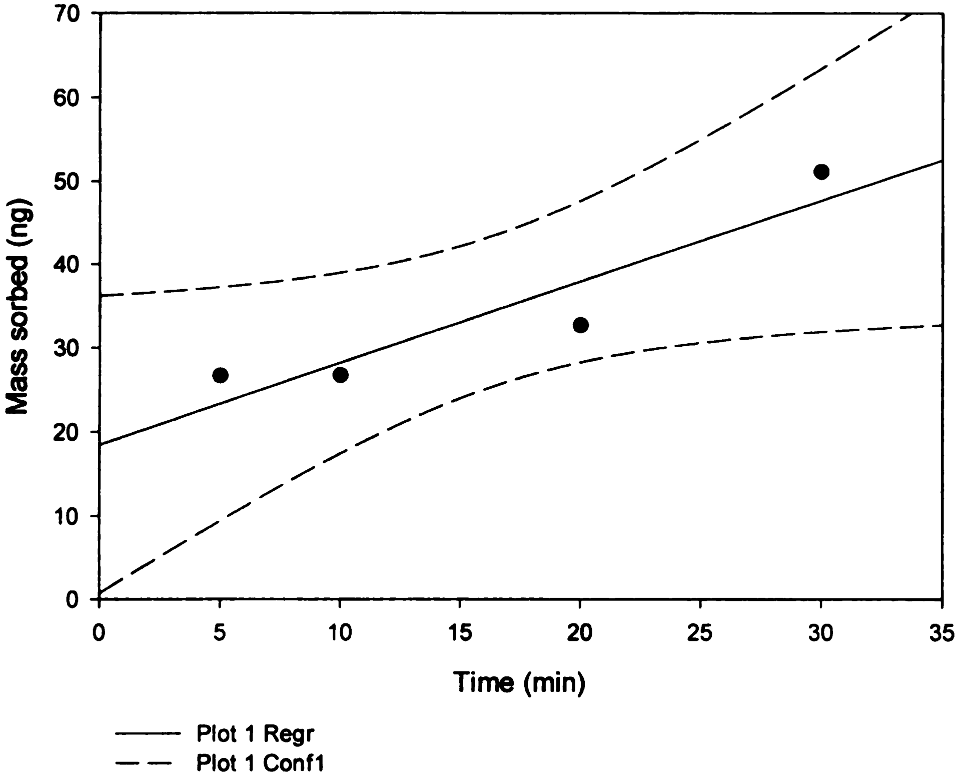


Figure 4-11. The relationship between the sorbed mass and sorption time on SPME for p-Ethylphenol at lower concentration (0.41 μg/L). The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

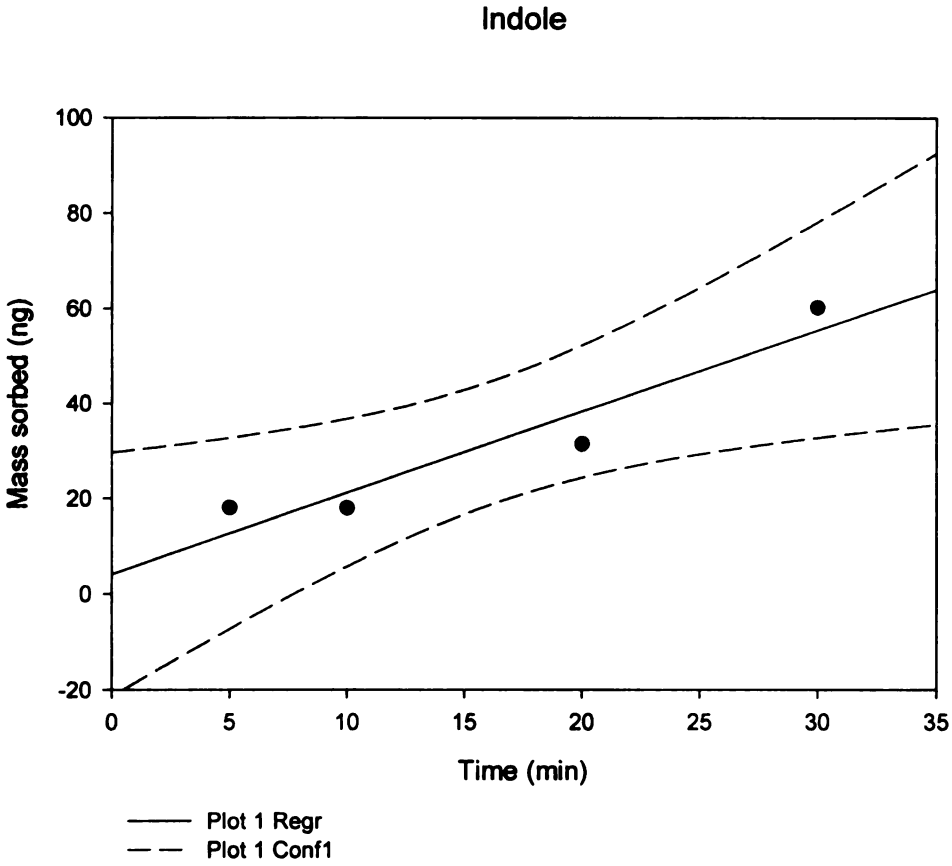


Figure 4-12. The relationship between the sorbed mass and sorption time on SPME for Indole at lower concentration (0.41 μg/L). The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

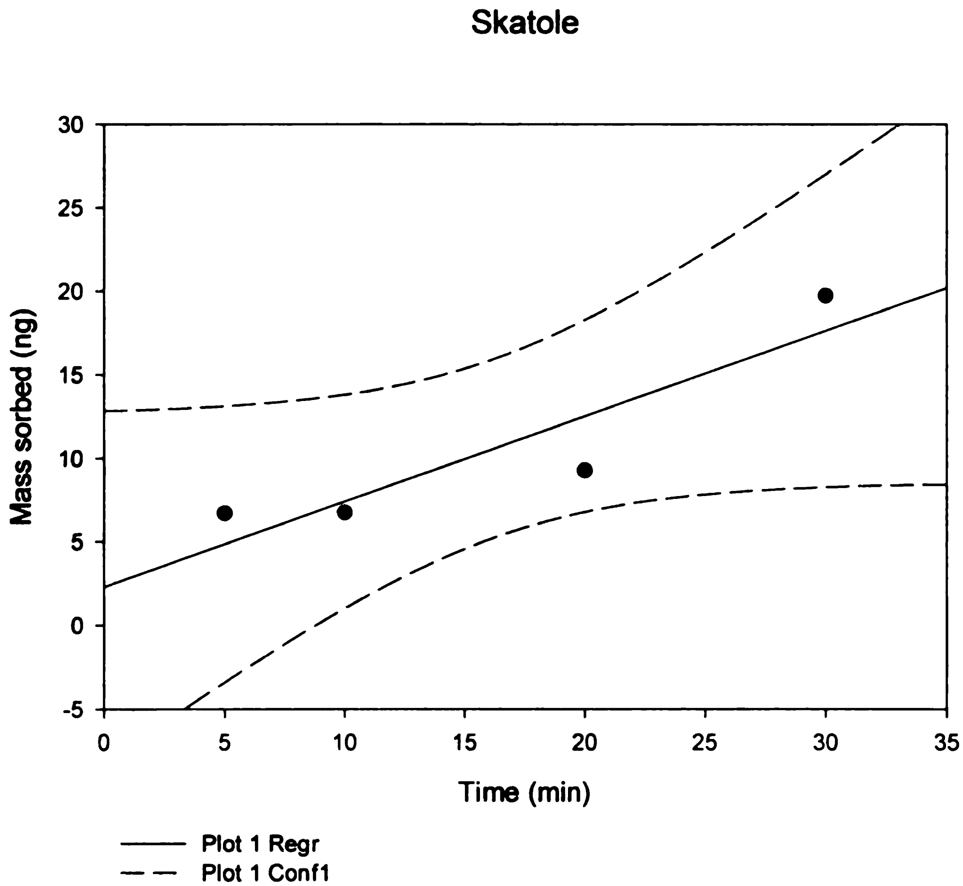


Figure 4-13. The relationship between the sorbed mass and sorption time on SPME for Skatole at lower concentration (0.41 μg/L). The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

4.5.2 Concentration Effects on SPME Adsorption

The effect of concentration on the sorbed mass of chemical onto SPME coatings was determined. Serially diluted test mixtures were used for this experiment. The diluted standard mixtures were injected into the gas sampling bottle. Two (2) μL of liquid volume was injected in all cases. SPME sampling from the gas sampling bottle was conducted when the all liquid sample was evaporated. The sampling times were 30 minutes. Room temperature varied from 22°C to 24°C and the pressure was 1 atm.

The results showed that the mass of phenolic compounds sorbed on SPME fiber increased as the concentration in the air increased (see Figures 4-14, 4-15, and 4-16). However, the mass of phenol sorbed on SPME fiber did not respond linearly at 95% confidence interval as injection mass increased when the gas phase concentrations were increased from 0.4μg/L to 4μg/L. Similar results were shown for p-cresol, p-ethylphenol, indole and skatole. Result showed that linearity was observed for certain concentration ranges for 30 minutes sampling.

The results suggest possible systematic errors. Standard solutions were made from the high concentrated stock mixture solution which contained all phenolic and indolic compounds in methanol. The standard solutions were used for SPME gas sampling. The fifth data points for all figures differed significantly from the linear regression line (see Figures 4-14, 4-15, 4-16, 4-17 and 4-18). This result suggests that there was a mistake on making the standard solution for the data. Calibration of the standard solution must be conducted to avoid this error.

For the indolic compounds, the masses sorbed on SPME coating were less than that of those of the phenolic compounds (Figures 4-17 and 4-18). This result indicates that the adsorption rates of indolic compounds on SPME CAR/PDMS coating are slower than those of phenolic compounds, resulting in less sorption of indolic compounds.

To see the effect of molecular weight on sorption, a graph for the molecular weight and sorption rate were constructed (Figure 4-19). The initial sorption rate was calculated using the mass sorbed after 5 minute sampling. The graph shows that the initial sorption rates for phenolic compounds decreased exponentially as the molecular weight increased. The molecular diffusion coefficients decrease as the molecular weights of the chemicals increase. It appears that molecular diffusivity is the driving force for the sorption on SPME fiber. Larger chemicals move slowly because the increased cross-sectional area reduces mean free path, that is, their ability to slip through a crowd of other molecule (Schwarzenbach et al., 1993). Molecular diffusion coefficients and the molecular weight of the phenolic compounds are described in Section 4.5.4.

For a given sampling time, the masses of indolic compounds sorbed on this SPME fiber coating can be increased by increasing sampling time. However, increasing sampling time may cause problems, such as competition and displacement of analytes from SPME fiber.

The masses of analyte sorbed on SPME fibers were linearly dependent on sampling time when the sampling times were less than 30 minutes. When the gas phase concentrations were reduced by factor 10, the masses of sorbed on SPME fiber did not respond linearly to the sampling times.

A major disadvantage with this method for the quantification is maintaining constant conditions. The results in this research were obtained under controlled laboratory conditions where temperature and humidity were relatively constant. However, the physical and environmental conditions for actual sampling in the livestock building would be difficult to control.

Humidity was not considered in this research, since it was shown that humidity does not affect greatly SPME adsorption (Martos and Pawliszyn, 1997). In addition, the coating materials used in this research are non-polar and hydrophobic compounds. Future research is suggested to determine temperature corrections. Temperature corrections can be made by measuring the amount adsorbed on SPME fiber at different gas phase concentrations and at different temperature.

Several systematic errors may have been introduced during experiments conducted as part of this research project. The working standard solution was a possible error source. When a new working standard is made, the standard must be properly calibrated. Another error source is SPME fiber. A SPME fiber has a certain lifetime on it's usage. As the fiber ages, the sensitivity of the fiber diminishes. When SPME fiber is used for the quantification of the analytes, the fiber must be carefully calibrated.

The gas phase concentrations were calculated using the concentration of the standard mixture injected into the gas sampling bottle in this research. When sorption of chemicals onto the gas sampling bottle occurs, the actual gas phase concentrations will be less than the calculated concentrations. To avoid this experimental error, the real gas phase concentration must be measured by injecting the standard gas directly into GC.

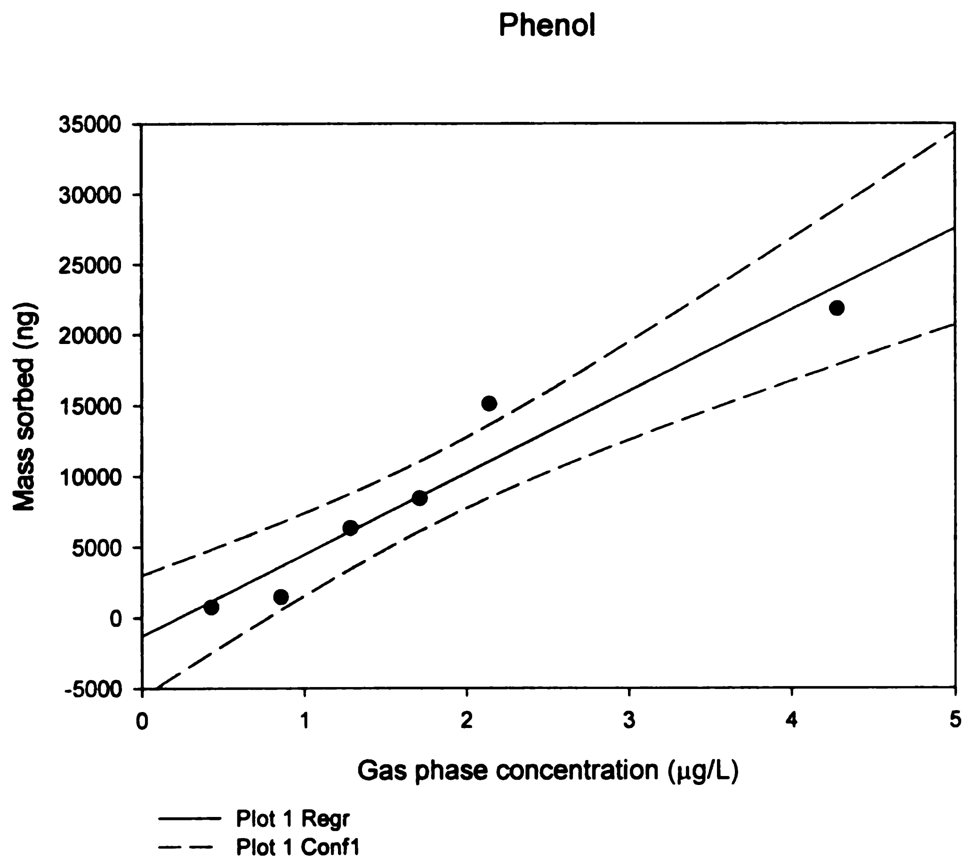


Figure 4-14. Mass injected in the gas sampling bottle vs mass recovered on SPME fiber for Phenol with sampling time of 30 minutes. The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

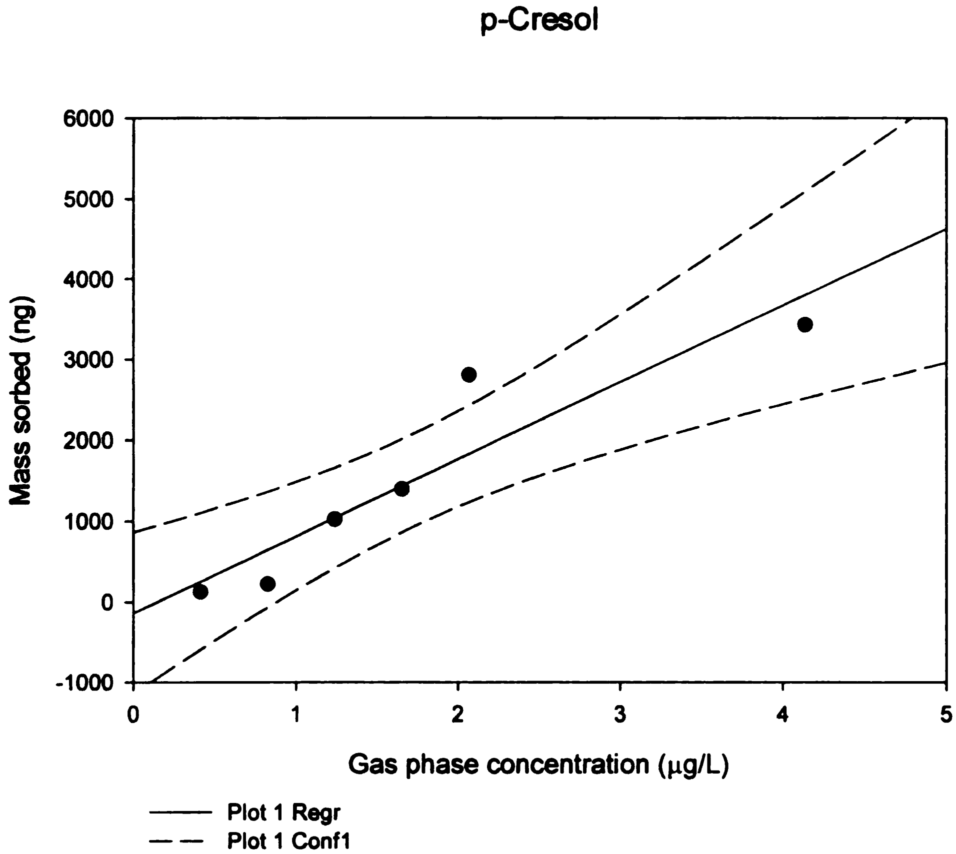


Figure 4-15. Mass injected in the gas sampling bottle vs mass recovered on SPME fiber for p-Cresol with sampling time of 30 minutes. The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

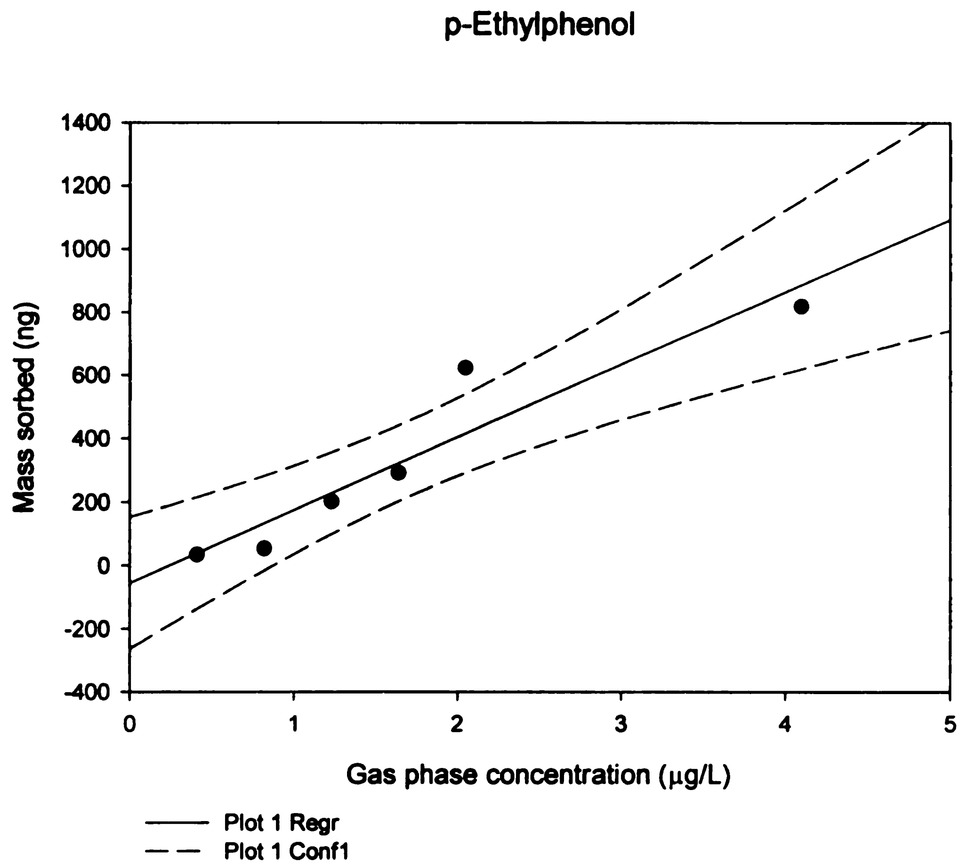


Figure 4-16. Mass injected in the gas sampling bottle vs mass recovered on SPME fiber for p-Ethylphenol with sampling time of 30 minutes. The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

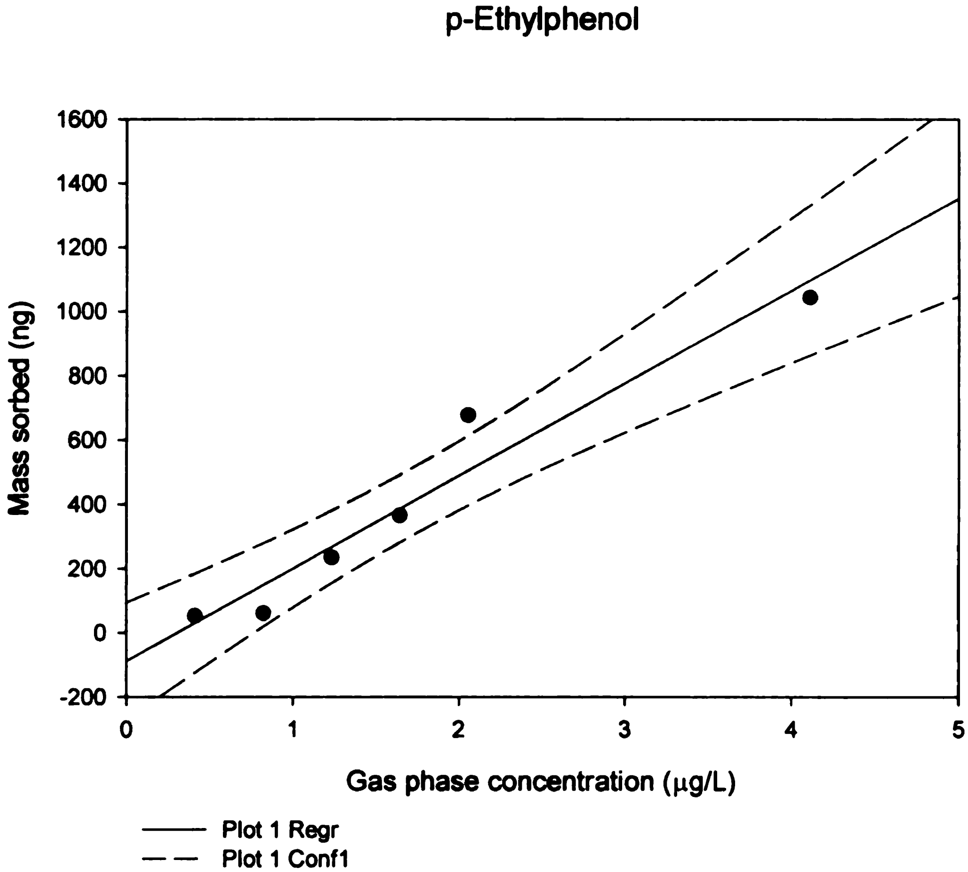


Figure 4-17. Mass injected in the gas sampling bottle vs mass recovered on SPME fiber for Indole with sampling time of 30 minutes. The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

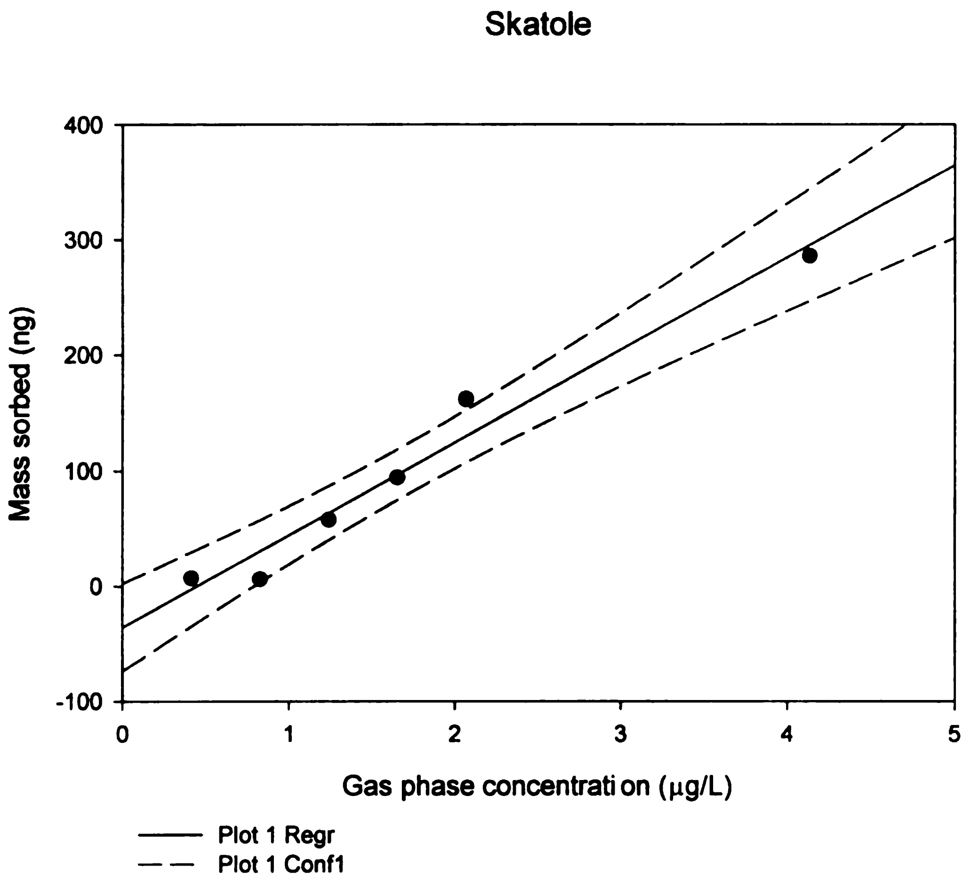


Figure 4-18. Mass injected in the gas sampling bottle vs mass recovered on SPME fiber for Skatole with sampling time of 30 minutes. The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

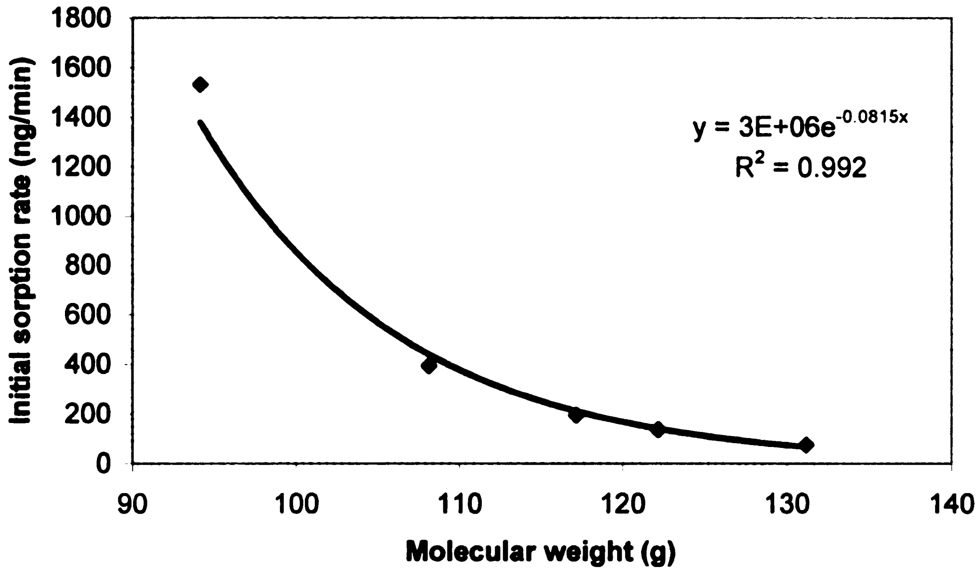


Figure 4-19. Effect of molecular weight of chemicals on SPME initial sorption rate. Initial sorption rates were calculated using 5 minute sampling data.

4.5.3 Quantification of SPME analyses using the calibration factors

As described in the introduction, the amount adsorbed on SPME fiber increases linearly as the gas phase concentrations increases when the sampling time is constant. In this section, quantification of SPME was conducted by calculating the calibration factors. Temperature and pressure during the experiment was 21±2°C and 1 atm, respectively.

Known amounts of a test mixture were injected into the GC/MS and the response factors for the compounds were calculated using equation (3). The same standard solutions were injected into the gas sampling bottle for SPME sampling. The amount adsorbed on SPME fiber was calculated using equation (4), and the calibration factors for the compounds were calculated using equation (2). Table 4-2 shows the amount recovered on SPME and K′ (calibration factors) values for phenolic and indolic compounds for a sampling time of 30 minutes. The mass sorbed on SPME fiber (n) was calculated using equation (4) for the response factor, which obtained by the liquid standard injection, and GC response for SPME. The calibration factors (K') were calculated using equation (2) using the known gas phase concentrations and the mass sorbed on SPME fiber (n).

SPME CAR/PDMS coatings were exposed to the volatile compounds for 30 minutes and the adsorbed amounts (n) on SPME coatings were analyzed. With the adsorbed amounts (n) and calibration factors (K'), the gas phase concentrations for the compounds were calculated. Table 4-3 shows the GC responses of the phenolic and indolic compounds which were adsorbed on SPME fibers, RF and K' values. The gas phase concentrations were calculated using these values in Table 4-4 and the calculated gas phase concentrations and the actual amounts injected into the gas sampling bottle are listed in Table 4-4.

The standard errors for the calculated gas phase concentrations were 6.23%, 36.6%, 28.2%, 6.27%, and 24.5% for phenol, p-cresol, p-ethylphenol, indole and skatole at 95% confidence level, respectively.

For the calculation of the calibration factors, K', it was assumed that the gas phase concentrations for the phenolic compounds were same as the amount injected into the gas sampling bottle. Table 4-4 shows that the calculated gas phase concentrations were less than the actual amounts injected into the gas sampling bottle for all compounds. This result indicates that the actual gas phase concentrations may not to be the same as the amount injected into the gas sampling bottle. This could happen when the all compounds are not evaporated in the bottle. This problem can be tested by the direct gas injection into GC. Another explanation for this is saturation of fibers. This reflects the situation in which at higher sorbate concentrations, it becomes more difficult to sorb additional molecules. This can happen when sorption sites are filled or remaining sites are less attractive to the sorbate molecules. This problem can be tested by using serial steps of standard gases for SPME sorption. When the chemical is sorbed onto the glass bottle surface, the actual gas phase concentration would be less than the injected one. This is called "wall effect". Results for the concentration effects on SPME sorption showed that there were non-linearity relationships between the gas phase concentrations and SPME sorption for phenol at the concentration ranges from 0.4 to 4 μg/L (Figure 4-14). This result suggests that wall effect may occur in the sampling bottle. This problem also can be tested by measuring the gas phase concentration using direct gas injection into the GC.

Environmental conditions, such as temperature and humidity affect on SPME sorption. When the temperature in the sampling environment is not constant, this quantification method will not give accurate gas phase concentrations. Since the humidity did not affect greatly on SPME sorption as discussed previously, humidity effect may be ignored when non-polar SPME fibers are used.

Table 4-2. The amount recovered and Calibration factors for phenolic and indolic compounds with SPME CAR/PDMS fiber for 30 minutes sampling time.

Phenol	C_g **(μg/L)**	**n (ng)**	**K′ (ng/μg/L)**	**average K′**	**95% CI**
	0.214	0.014	0.066	0.097±0.053	0.104
	0.428	0.028	0.065		
	0.856	0.041	0.048		
	1.284	0.118	0.092		
	1.712	0.204	0.119		
	2.568	0.495	0.193		
p-Cresol	0.207	0.004	0.018	0.031±0.018	0.034
	0.414	0.009	0.023		
	0.827	0.013	0.016		
	1.241	0.034	0.027		
	1.654	0.065	0.039		
	2.482	0.155	0.062		
p-Ethylphenol	0.205	0.002	0.009	0.016±0.007	0.014
	0.410	0.008	0.019		
	0.820	0.005	0.007		
	1.230	0.018	0.015		
	1.640	0.041	0.025		
	2.459	0.053	0.021		
Indole	0.206	0.006	0.031	0.025±0.010	0.019
	0.411	0.016	0.039		
	0.822	0.011	0.014		
	1.234	0.023	0.019		
	1.645	0.045	0.027		
	2.467	0.043	0.018		
Skatole	0.207	0.011	0.052	0.032±0.019	0.037
	0.413	0.025	0.059		
	0.827	0.017	0.020		
	1.240	0.028	0.023		
	1.654	0.046	0.028		
	2.480	0.027	0.011		

C_g: gas phase concentration
n: mass sorbed on SPME)ng)
K′: calibration factor (K'=n/C_g)
CI: confidence interval

Table 4-3. GC response of test mixture, RF, and K' values for the quantification of phenolic compounds with 30 minutes sampling time.

Compounds	Response	K'	RF*
Phenol	548664	0.097	5.58E-08
p-cresol	198826	0.031	9.05E-08
p-ethylphenol	171311	0.016	5.21E-08
Indole	279680	0.025	5.18E-08
Skatole	347702	0.032	4.92E-08

RF*: Response factors were obtained by dividing the amount of liquid standard injected to GC/MS by instrumental response (area).
K': calibration factor

Table 4-4. Comparison of actual gas phase concentration to the calculated concentration using RF and K' values for 30 min adsoprtion.

Compounds	Amount on SPME (μg)	Calculated gas conc. (μg/L)	95% CI Calc.	Actual gas conc. (μg/L)	Calc./Act.
Phenol	0.031±0.004	0.32±0.044	0.109	0.856	0.369
p-Cresol	0.018±0.008	0.58±0.259	0.642	0.827	0.704
p-Ethylphenol	0.009±0.003	0.56±0.199	0.494	0.820	0.681
Indole	0.014±0.001	0.59±0.047	0.117	0.822	0.717
Skatole	0.017±0.006	0.53±0.173	0.429	0.827	0.644

4.5.4 SPME quantification method with diffusion theory

The quantification of phenolic and indolic compounds sorbed on SPME fiber was conducted using the diffusion theory. Molecular diffusivities for phenolic and indolic compounds were calculated using Fuller's method (1966) as shown in Equation 6.

There are several ways to estimate the molar volume of the organics. One of the methods is to estimate V_{voc} by dividing the chemical molecular mass by its liquid density. Since liquid phenol and p-cresol were used in the test mixture, their molar volumes were simply calculated by dividing their molecular mass by their liquid densities.

Another way to estimate the chemical molar volume is to calculate the "size" of the atoms making up the chemical's structure (Schwarzenbach et al., 1993). Table 4-5 shows molar volumes of various atoms deduced by regression of available diffusion data.

Table 4-5. Estimation of Diffusion Volumes of the constituents of organic molecules

Element	Volume Contribution (cm^3/mol)
C	16.5
H	2.0
O	5.5
N	5.7
Cl	19.5
S	17
Rings	–20.2

Source: "Environmental Organic Chemistry" (Schwarzenbach et al., 1993).

Molar volumes of the p-ethylphenol, indole and skatole were estimated using the values in Table 4-5. For example, the estimation of the molar volume of p-ethylphenol is shown below. The molecular structure of p-ethylphenol is $C_8H_{10}O$ and it has a ring.

$$\overline{V}_{p\text{-ethylphenol}} = 8(\mathrm{C}) + 10(\mathrm{H}) + 1(\mathrm{O}) + \text{ring}$$
$$= 8(16.5) + 10(2.0) + 5.5 - 20.0$$
$$= 137.3 \text{ cm}^3/\text{mol}$$

Diffusion coefficients were calculated using equation 6. A sample calculation for the diffusion coefficient of phenol is shown in Appendix F. Table 4-6 shows the molar volumes and diffusion coefficients for phenolic and indolic compounds.

Table 4-6. Molecular diffusivity and molar volume for phenolic and indolic compounds

Compound	Molecular structure	Molecular weight	$\overline{V}$ (cm^3/mol)	D_g (cm^2/s)
Phenol	C_6H_6O	94	87.96	0.086
p-Cresol	C_7H_8O	108	104.58	0.079
p-Ethylphenol	$C_8H_{10}O$	122	137.3	0.069
Indole	C_8H_7N	117	129.5	0.071
Skatole	C_9H_9N	131	131.8	0.070

Gas phase concentrations for phenolic compounds using the amount sorbed on SPME fibers and sampling time were calculated using equation (5). Physical characteristics of the SPME fiber coatings are: film thickness of 75 μm, length of 1 cm and core rod thickness of 0.011 cm. Since commercial SPME fibers have constant fiber length and film thickness, equation (5) can be simplified to equation (8).

$$C_g = n\alpha/t \quad \text{............} \quad (8)$$

Then α can be written as equation (9) from equations (5) and (8),

$$\alpha = \frac{\ln\left(\frac{b+\delta}{b}\right)}{2\pi D_g L} \quad \text{............} \quad (9)$$

Since thickness (b), length (L) are constant, α depends on the effective stationary boundary δ and molecular diffusivity (D_g). Molecular diffusivity is constant when the sampling temperature and atmospheric pressure are the same. Then α depends only on effective stationary boundary, δ.

The α values for phenolic and indolic compounds were calculated using the known C_g and n at various time t. The dimensionless k values in equation (8) have been calculated using α values. For the calculation of the effective boundary layer δ, equation (5) has been rearranged as shown below:

When $k = \ln\{(b + \delta)/b\}$, equation 5 becomes $C_g = \dfrac{nk}{2\pi D_g Lt}$ .... (10)

Since $C_g = n\alpha/t$ (eqn.10), $\alpha = (2\pi D_g L)k$. The k values for the phenolic and indolic compounds are listed in Table 4-7. A sample calculation for the dimensionless k value and α value is shown in Appendix G.

Table 4-7. Dimensionless average k values for phenolic and indolic compounds for SPME CAR/PDMS fiber coating.

Compound	D_g (cm^2/s)	Average log α	Average k	Coefficient of variance (CV)	95% confidence interval
Phenol	0.086	5.11±0.027	70.36±4.54	0.0645	5.63
p-Cresol	0.079	5.59±0.052	193.95±22.7	0.1172	28.2
p-Ethylphenol	0.069	6.04±0.061	482.19±62.8	0.1301	62.8
Indole	0.071	5.97±0.075	420.16±70.1	0.1669	87.1
Skatole	0.070	6.42±0.088	1182.53±223	0.1887	277

Sampling times for the k values were 30 sec to 150 sec. D_g values were calculated at 20 °C and 1 atm.

SPME fiber coatings are very fragile. When the tip of the fiber is worn by accident, the mass sorbed on the fiber coating will be reduced resulting in reporting less C_g than actual gas concentration in the air. Therefore, k value has to be corrected with the adjusted fiber length to avoid the error.

The response of SPME fiber sorption for rapid sampling was tested, and results are shown in Figures 4-20, 4-21, 4-22, 4-23, and 4-24. The linear regression line for phenolic and indolic compounds at sampling time from 30 sec to 2.5 minutes are also shown. The mass sorbed on SPME fiber increased linearly as the sampling times increased from 30 seconds to 2.5 minutes for phenolic and indolic compounds at 95% confidence interval. The masses of indolic compounds sorbed on SPME fiber were less than those of phenolic compounds. This result indicates that the sorption rates for indolic compounds are less than phenolic compounds resulting in less sorption of indolic compounds. The mass uptake rates decreased as sampling times increased for indolic compound, suggesting that the competition with phenolic compounds for sorption sites on SPME fibers. The effect of molecular weight on sorption rates were observed in Figure 4-25. Graph shows that the sorption rates decreased exponentially as the molecular weight of the chemical increased. As the masses of the chemical increase, the molecular diffusivities decrease due to the slower movement to the sorbate. This result is similar to that previously shown in Figure 4-19.

Using calculated k values (Table 4-7), diffusion coefficient and gas phase concentrations, the quantification of SPME CAR/PDMS fiber coatings was conducted. Five 1 min SPME air samples were taken using SPME CAR/PDMS coatings. Table 4-8 shows the calculated and measured C_g values. The calculated gas phase concentration for phenol was 20% less than the actual gas phase concentration. The calculated gas phase concentrations for p-cresol and p-ethylphenol were 6% and 5% higher than the actual gas phase concentrations. The calculated gas phase concentration for indole was 17% higher than the actual gas phase concentration and the calculated gas phase concentration for the skatole was 40% higher than the actual concentration. This error may be induced from the k value. The result suggests that k values for the indolic compounds are not constant for the time range of 30 seconds to 2.5 minutes. Gas phase concentrations also affect on the k values. In this experiment, relatively high gas phase concentrations were used for the calculation of k values (see Table 4-8). To adapt this quantification method for the field samples, k values for the phenolic and indolic compounds must be re-evaluated using the environmental data (temperature, atmospheric pressure) and lower concentrations of standard gases.

Table 4-8. Comparison of actual gas concentration and the calculated gas concentration.

Compound	**Average C_g (calc.) µg/L**	**CV**	**C_g (act.) µg/L**	**C_g(act)/C_g(cal)**	**Standard error**
Phenol	10.31±0.732	0.071	12.84	1.245	0.85
p-Cresol	13.12±0.572	0.044	12.408	0.946	0.66
p-Ethylphenol	12.97±1.043	0.080	12.296	0.948	1.20
Indole	14.40±0.666	0.046	12.34	0.856	0.77
Skatole	17.30±0.928	0.054	12.40	0.717	1.07

C_g: gas phase concentration (µg/L)

CV: coefficient of variance

The quantification method with rapid diffusion based SPME sampling is useful since the effect of temperature and pressure can be accounted using equations 5 and 6 without making the gas standard calibrations for different sampling environment.

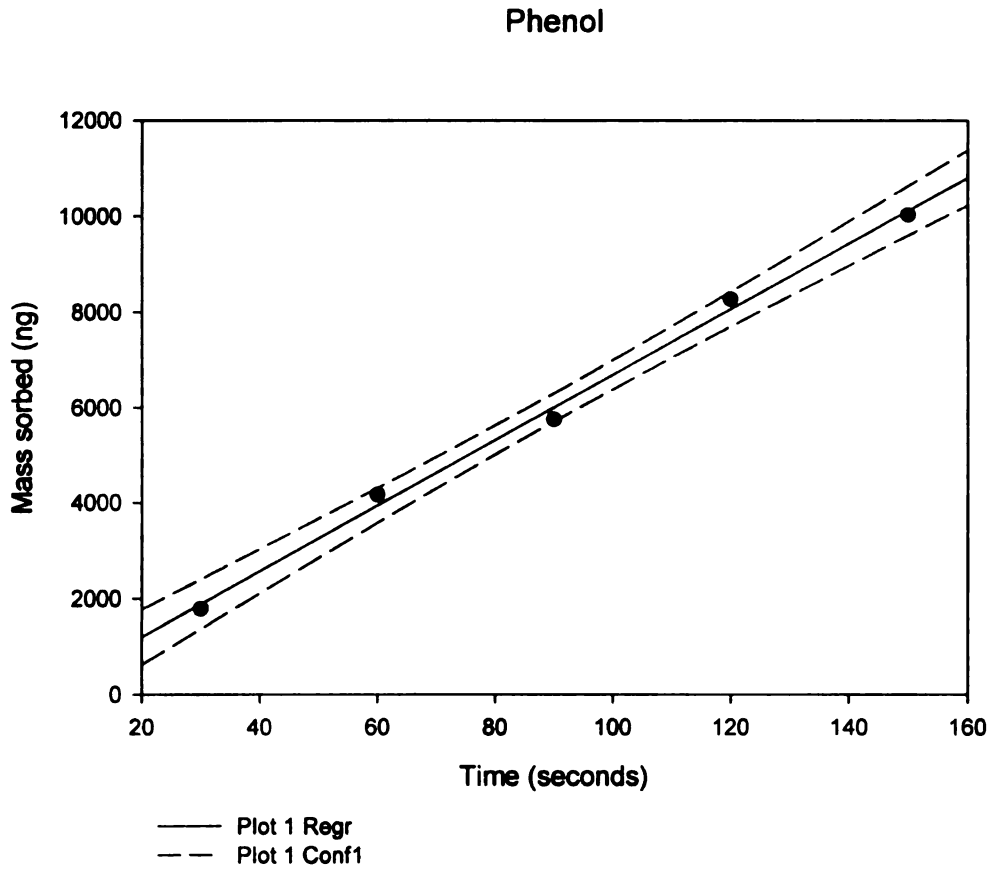


Figure 4-20. The relationship between the sorbed mass and sorption time on SPME for rapid diffusion based sampling for Phenol. The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

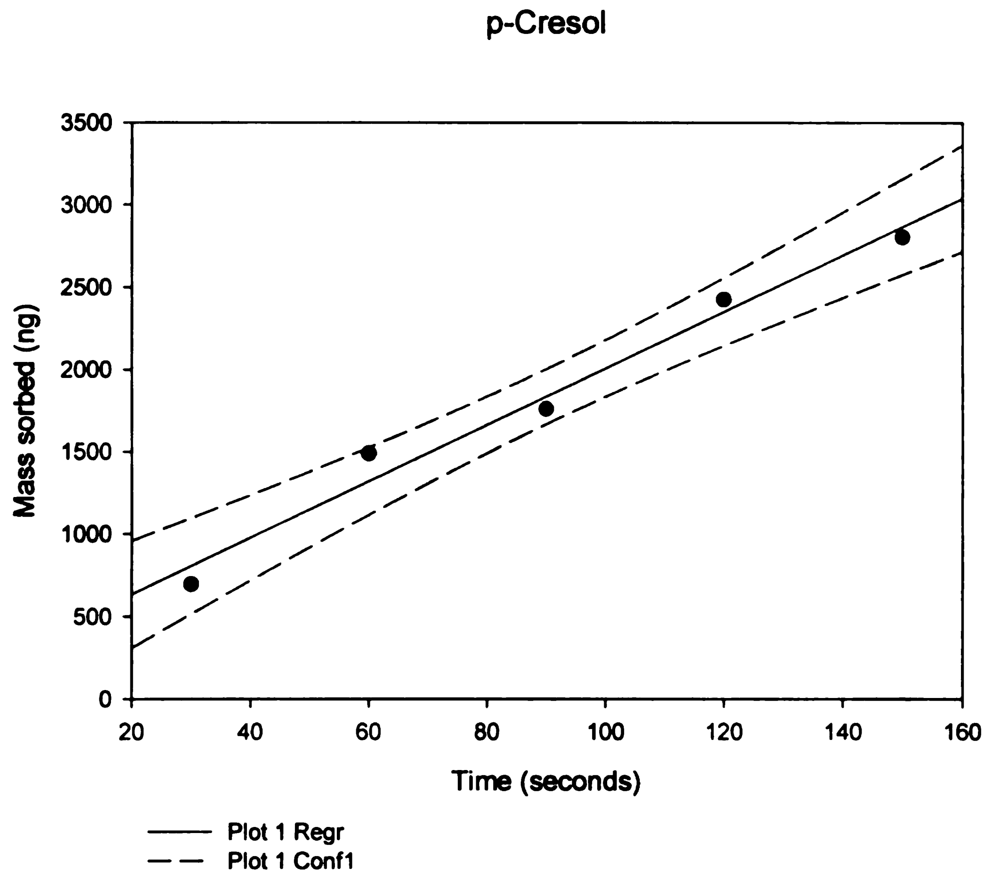


Figure 4-21. The relationship between the sorbed mass and sorption time on SPME for rapid diffusion based sampling for p-Cresol. The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

p-Ethylphenol

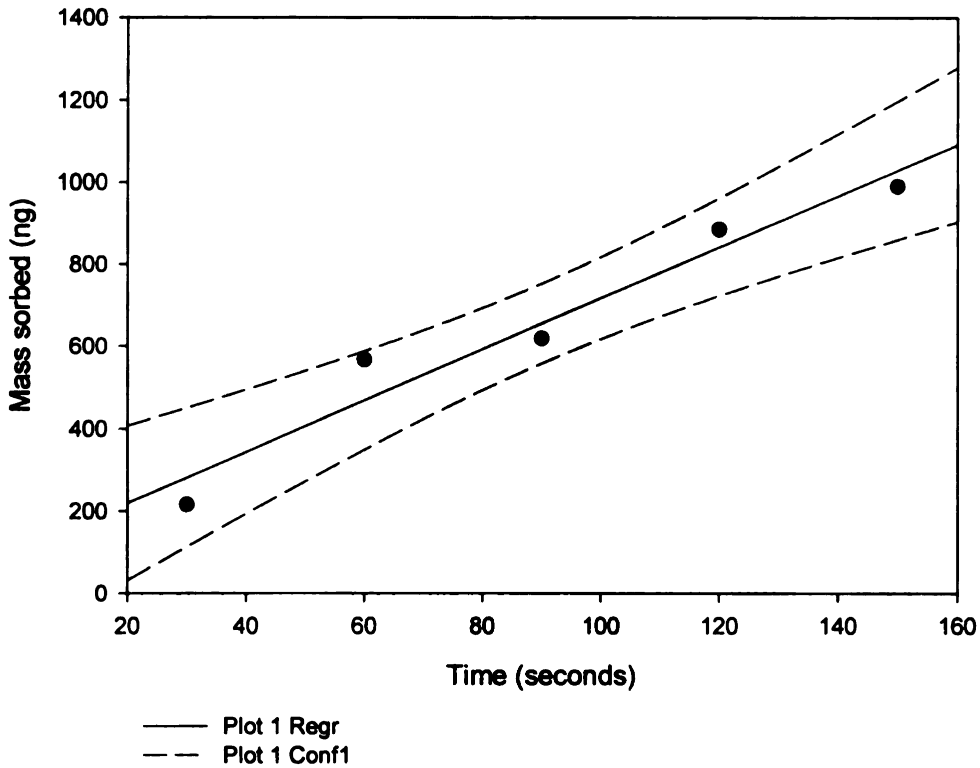


Figure 4-22. The relationship between the sorbed mass and sorption time on SPME for rapid diffusion based sampling for p-Ethylphenol. The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

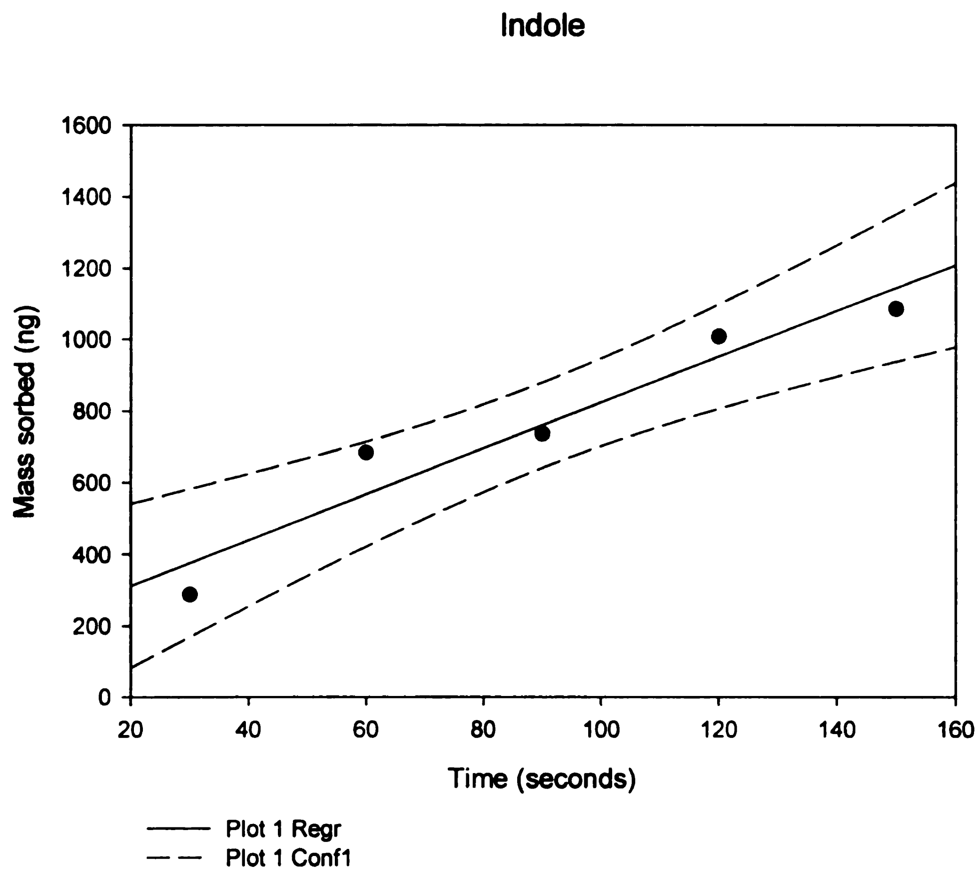


Figure 4-23. The relationship between the sorbed mass and sorption time on SPME for rapid diffusion based sampling for Indole. The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

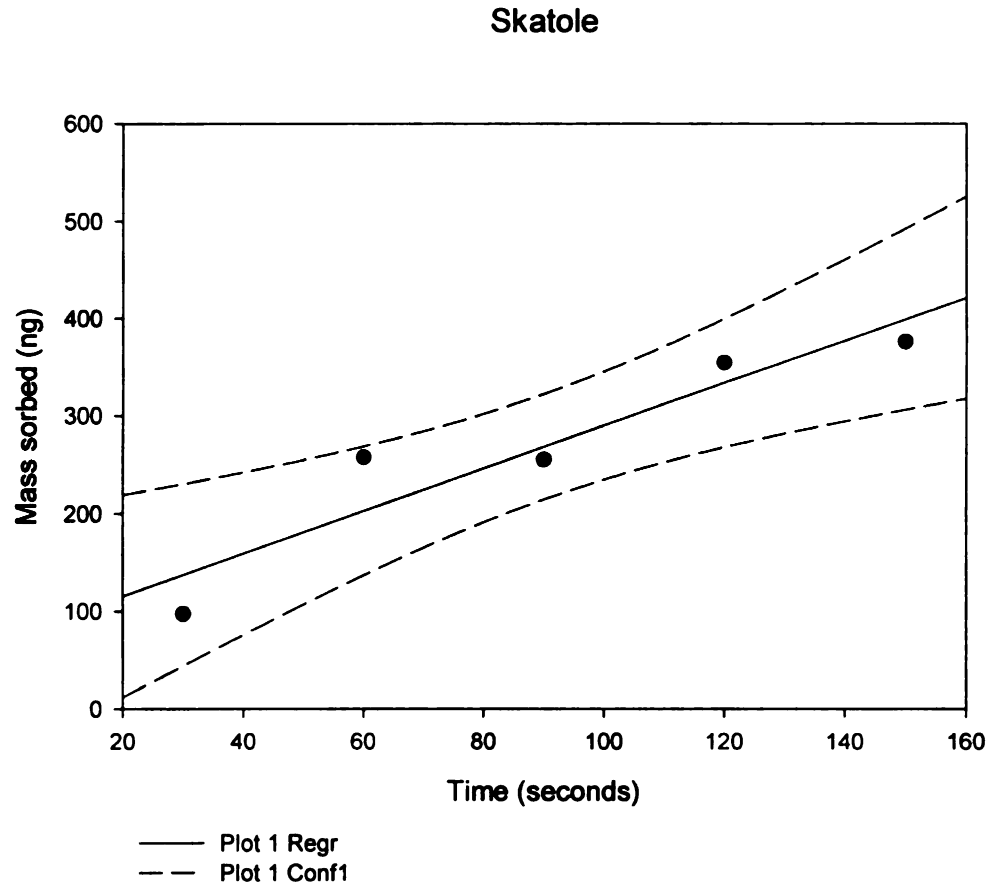


Figure 4-24. The relationship between the sorbed mass and sorption time on SPME for rapid diffusion based sampling for Skatole. The upper and lower lines represent the 95% confidence interval. The average temperature was 23°C and pressure was 1 atm.

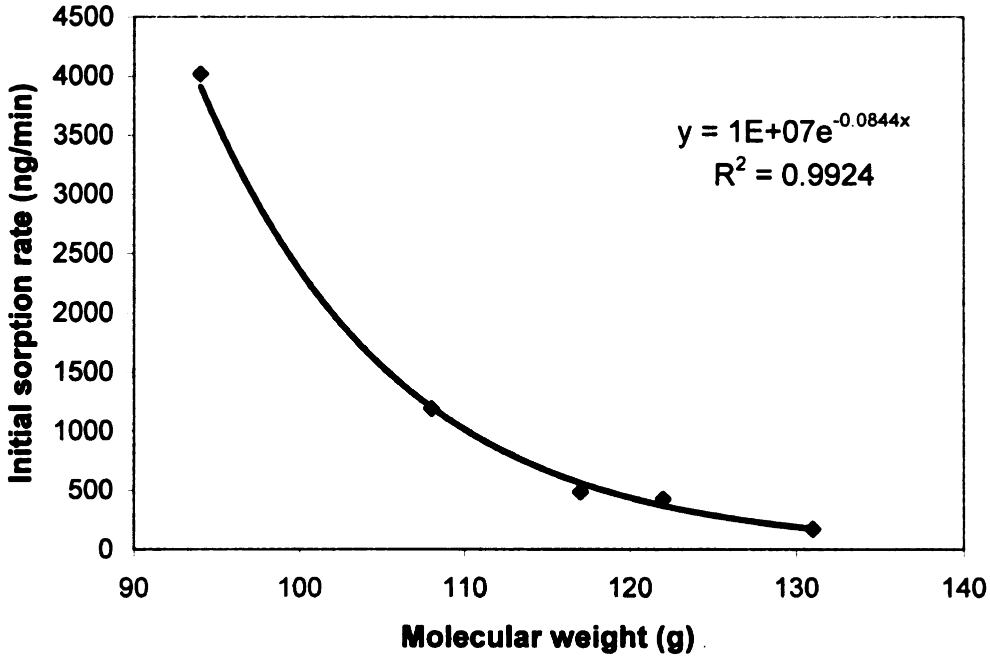


Figure 4-25. Effect of molecular weight of chemicals on SPME sorption rate. Sampling times were 5 seconds to 2.5 minutes. The average temperature was 23°C and pressure was 1 atm.

4.5.5 Analysis of phenolic and indolic compounds in swine building air with SPME

Two types of SPME fiber coatings were used for the sampling of phenolic and indolic compounds in swine house. Samples were taken in the MSU Swine Teaching and Research Farm. Two sampling times, 1 min and 10 min were used for this experiment. Initial results for the quantification of SPME samples with a 30 minute sampling time showed that the adsorption amounts and gas phase concentrations for phenolic and indolic compounds did not show the linear relationships. Therefore, a shorter sampling time, 10 minutes, was used for the sampling of the phenolic and indolic compounds with CAR/PDMS.

Figure 4-26 shows the chromatogram of air samples which were taken in the swine building using SPME CAR/PDMS fibers for 1 and 10 min. The chromatogram shows that the analytes adsorbed on SPME coatings were same but the amount adsorbed on the fiber was greater for 10 minute sample. Results showed that the recoveries of phenolic and indolic compounds from swine building air were small with SPME CAR/PDMS coatings for both 1 min and 10 min samplings. The majority of compounds adsorbed on SPME CAR/PDMS coatings in swine building were volatile fatty acids (VFAs).

Table 4-9 shows the amount of VFAs adsorbed on SPME fibers when it was sampled for 1 minute and 10 minutes. The amounts adsorbed on SPME fibers for 10 minute sample were about 10 times greater than 1 minute sample.

Table 4-9. Amount of VFAs adsorbed on SPME fibers for 1 minute and 10 minute sampling using PDMS/CAR fiber coating.

Compound	10 min	1 min	Ratio (1min/10min)
Acetic acid	171.23	24.39	0.14
Propionic Acid	120.77	13.58	0.11
Butyric acid	80.64	9.06	0.11
Valeric acid	27.35	4.47	0.16

4.5.5.1 Rapid air sampling with SPME CAR/PDMS

Quantification of the phenolic and indolic compounds in the swine building air was conducted using SPME CAR/PDMS fibers. The dimensionless values, k, for the phenolic and indolic compounds were used for the calculation of the gas phase concentrations. Calculated concentrations for phenolic and indolic compounds are listed in Table 4-10. The calculated concentrations for phenolic and indolic compounds fell within the concentration ranges found in previous research (O'Neill and Phillip, 1992).

Table 4-10. Quantification of the phenolic and indolic compounds in swine building air with rapid SPME air sampling method

Compounds	Avg. k	t (sec)	D_g (cm^2/s)	C_g (mg/m^3)
phenol	70.4±4.54	60	0.086	0.164±0.011
p-cresol	194±22.73	60	0.079	0.397±0.047
p-ethylphenol	482±62.75	60	0.069	0.489±0.064
Indole	420±70.13	60	0.071	0.237±0.040
Skatole	1180±223	60	0.070	0.219±0.041

4.5.5.2 Comparison of SPME fiber coatings.

To observe sorptive abilities of these compounds on different types of fiber coatings, two types of SPME fiber coatings, carboxene/PDMS (CAR/DPMS) and PDMS/divinylbenzene (PDMS/DVB), were used for the adsorption of phenolic and indolic compounds in swine building air. Figure 4-27 shows the chromatograms for air samples that were taken on SPME CAR/PDMS and PDMS/DVB coatings. Chromatogram shows that VFAs favored CAR/PDMS fibers and phenolic and indolic compounds favored PDMS/DVB fibers. Table 4-11 shows the amount of phenolic and indolic compounds which were adsorbed on two SPME fibers. The amounts of VFAs adsorbed on two types of fibers are listed in Table 4-12.

This result suggests that using these two types of SPME fibers would be useful for the sampling of VFAs and phenolic compounds in the livestock building air since PDMS/CAR favors VFAs and PDMS/DVB favors phenolic compounds. As part of this research, the quantification of gas phase concentration using PDMS/DVB fibers was not determined.

Table 4-11. Comparison of the adsorbed amounts of phenolic and indolic compounds on two different SPME fibers. (Sampling time for both was 10 min. Unit for the amount adsorbed is ng.)

Compound	CAR/PDMS	PDMS/DVB	Ratio (CAR/DVB)
Phenol	165	231	0.72
p-Cresol	219	993	0.22
p-Ethylphenol	35.3	122	0.29
Indole	24.9	51.4	0.49
Skatole	6.75	43.2	0.16

Table 4-12. Concentration of VFAs in swine building air sampled on SPME fibers. (VFA concentrations are in μg as carbon)

Compound	CAR/PDMS	PDMS/DVB	Ratio (CAR/DVB)
Acetic acid	68.5	6.30	10.9
Propionic acid	58.8	16.5	3.56
Butyric acid	2.70	1.88	1.43
Iso butyric acid	41.3	26.4	1.56
Valeric acid	2.87	3.05	0.94
Iso valeric acid	13.2	16.5	0.80
Total VFAs (μg as C)	187	70.6	2.65

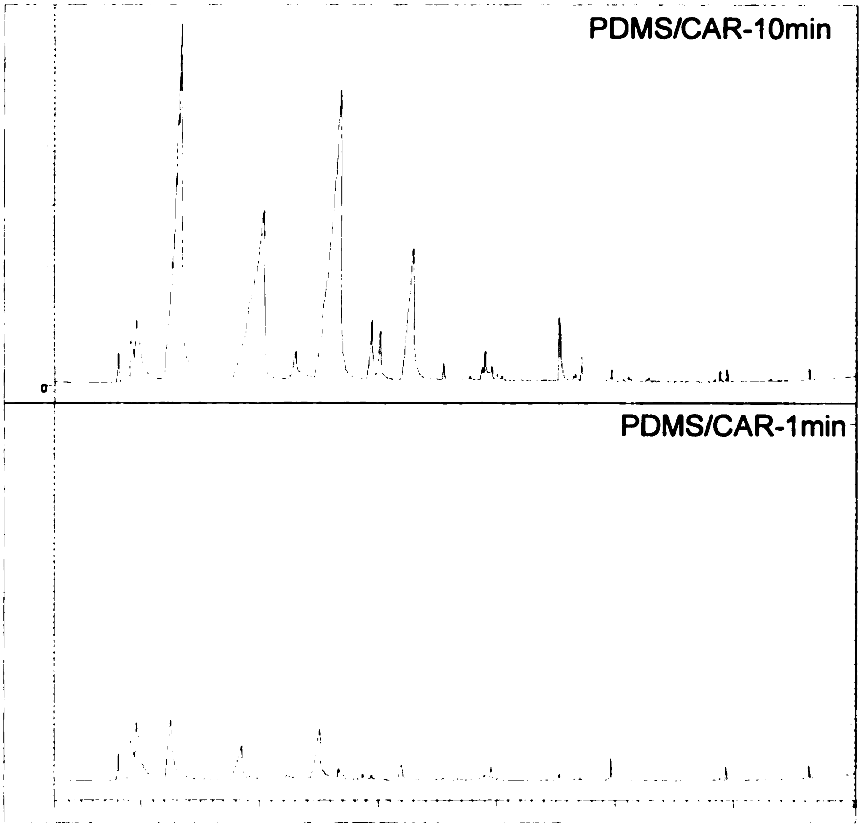


Figure 4-26. Chromatograms of air samples sampled on CAR/PDMS fiber coatings for 1 and 10 minutes in swine building.

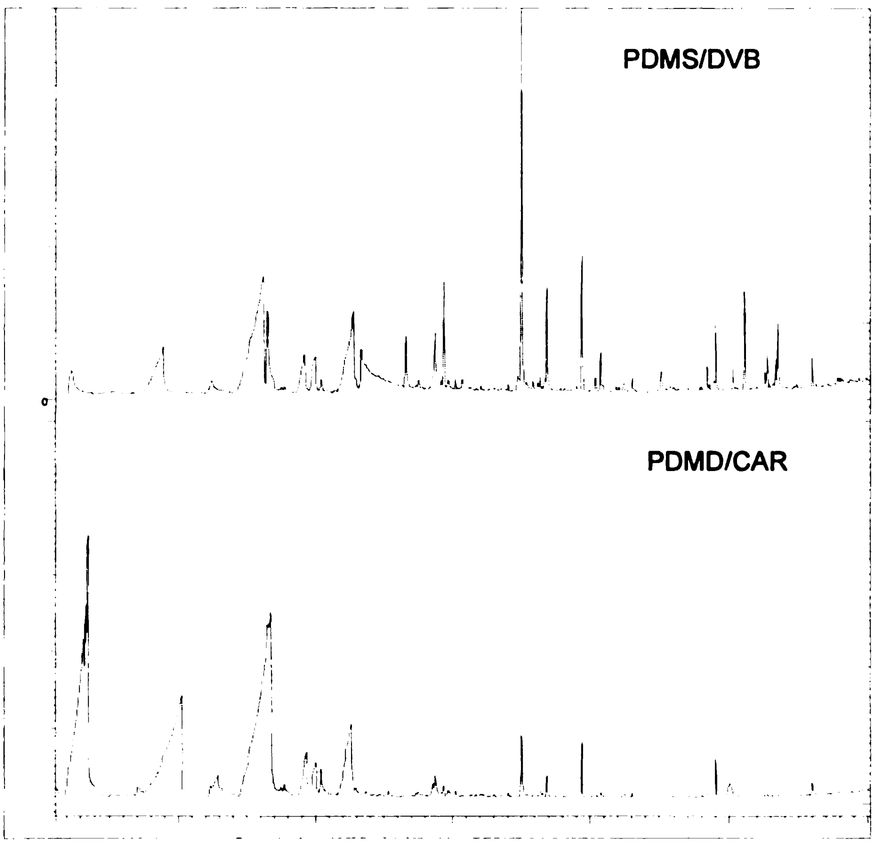


Figure 4-26. Chromatograms of air samples sampled on two different SPME fiber coatings. (Sampling time was 10 min for both fibers and sampling was done at the same location.)

4.6 Conclusions

Major odorous compounds in swine building air were sampled with SPME CAR/PDMS coatings in a laboratory experimental system. The results showed that the masses of phenolic and indolic compounds sorbed on SPME fiber coatings increased as sorption times were increased, but the sorbed amounts did not reach equilibrium even when the sampling time was 420 minutes. The amounts of phenolic and indolic compounds adsorbed on SPME CAR/PDMS coatings are linearly increased as the sampling time increased up to 30 minutes. When the gas phase concentrations were reduced by a factor of 10, the masses of sorbed on SPME fiber could be described by a linear relationship as the sampling time increased up to 30 minutes, but the SPME extraction profile was different from the extraction profile for higher concentration. Pawliszyn (1997) showed that the sample concentration has no affect on the concentration time profile. When the extraction method and distribution constants between the SPME and sampling system remain constant, the equilibrium profile and time should be the same for all other concentration. Therefore, the extraction behavior should be linear for all concentration ranges. However, the results showed that the extraction behaviors for phenolic compounds on SPME fibers were not same for the gas phase concentrations at 0.4 and 4 μg/L.

These results suggest the possible systematic experimental errors. It is possible that the errors resulted from a depletion of available sorption sites on SPME fiber. To avoid this problem, calibrations for all individual SPME fibers would be required. As a SPME fiber ages, the sorption ability of the fiber is reduced. Therefore, usages and sampling histories for all SPME fibers should be carefully recorded.

Room temperatures fluctuated from 22.3°C to 24.3° during the experiment, and temperature in the sampling bottle was not controlled and the temperature changes were ignored because the difference was approximately 2 °C. A previous study showed that the increase in the sample temperature increased the analyte concentration in the headspace, thereby providing faster extraction (Wercinski and Pawliszyn, 1999). This error can be corrected by sampling SPME fibers at several different temperatures.

Experimental error may be introduced in preparing the standard. To avoid this error, the new standard must be calibrated prior to being used for the gas standard.

Previous studies have shown that humidity effect on SPME sampling was minor. The mass loading on SPME fiber was reduced about 10% when the relative humidity was greater than 95% (Martos and Pawliszyn, 1997). Therefore, humidity effect on sorption on SPME CAR/PDMS coating was not considered in this research.

Diffusion based rapid air sampling with SPME CAR/PDMS coating was conducted using the phenolic and indolic compounds. The results showed that the mass sorbed on SPME fiber coatings was linearly dependent on sampling time when the sampling time was less than 150 seconds. With the data obtained, quantification of the phenolic and indolic compounds in swine building air was conducted. The calculated concentrations for the phenolic and indolic compounds were 0.042, 0.089, 0.096, 0.49 and 0.040 ppm for phenol, p-cresol, p-ethylphenol, indole and skatole, respectively. These concentrations fell within the concentration ranges found in previous research (O'Neill and Phillip, 1992).

Field samplings with two different SPME fibers showed that CAR/PDMS coatings favored VFAs and PDMS/DVB coatings favored phenolic and indolic compounds in swine building air. This result suggests that these two fibers can be useful for analysis of odorous compounds in livestock building air. For the quantification of VFAs in livestock building air, further investigation is needed.

As shown in previous chapters, SPME was the most promising air sampling method for the detection of odorous VOCs from the livestock building air. In spite of the difficulty on quantification of VOCs on SPME, still it has more advantages on air sampling than other techniques. Experiment with SPME PDMS/CAR fiber for air samplings showed that the mass sorbed on SPME fiber can be relatively easily quantified using the two theories: equilibrium and non-equilibirum theory. Some systematic errors were observed during the experiment. This study suggested that some modifications are required for the accurate quantification of VOCs on SPME fiber. The modification includes the standard gas generator, temperature controlled air sampling systems and individual re-calibration of SPME fibers whenever it is used for the sampling. This study also showed that the SPME fibers can be used for the sampling of phenolic compounds in livestock building air using the rapid sampling method. Once the diffusion coefficient, environmental conditions (temperature and atmospheric pressure), and the dimensionless calibration factor (k), the analysis of the chemical sorbed on SPME fiber can be calculated using the data without further calibration steps.

CHAPTER 5. OZONATION EFFECT ON ODOR AND VOLATILE ORGANIC COMPOUNDS IN SWINE PRODUCTION FACILITY.

5.1 Introduction

Ozone is a powerful oxidizer. It has been widely used for disinfection and oxidation for domestic wastewater, water and industrial wastewater e.g., (Kruithof and Masschelein, 1999; Lezcano et al., 1999; Carini et al., 2001; Finch et al., 2001; Turan-Ertas, 2001). Ozone is able to oxidize odorous volatile compounds such as; phenol, p-cresol, p-ethylphenol, indole and skatole, in swine slurry and reduce malodors in stored swine slurry by oxidation of odorants (Wu, 1999).

In a recent review paper, "Century 21 - Pregnant with Ozone", Rice (2002) stated that

"Many odors can be destroyed by ozone – e.g., hydrogen sulfide, odors caused by cigars and cigarettes, and volatile organic comounds (VOCs), perspiration odors, odors in animal rearing facilities, etc." This paper summarized the previous research on the use of ozone for odor control and included four conclusions. First, the oxidation of odorants can occur when ozone is allowed to the odorants for sufficient contact time. Second, the gas phase oxidations are relatively slow compared to the oxidation in aqueous phase. Third, residual ozone must be destroyed before it is discharged in to the atmosphere. And finally, ozonation must be done when human beings are not in the facilities.

Ozone has been used widely for the indoor air control in recreational areas, such as casinos, offices and hotel. A study by Kilham and Dodd (1999) showed that ozone could be used to remove offensive odors and to destroy volatile organic compounds and smoke. Ozone was introduced in the air conditioning system of the building. The effect of ozone on a subset of volatile organic compounds (VOCs) found in tabacco smoke has been examined (Shaughnessy et al., 2001). Shaugnessy et al. showed that the ozonation was not effective at reducing the concentrations of the saturated VOCs, however ozone greatly reduced the concentrations of the compounds with unsaturated carbon bonds. The effect of ozonation on sub-micron particles in office building have been studied (Weschler and Shields, 1999). Terpenes (limonene, alpha-terpene, or a terpene-based cleaner whose major constituent is alpha-pinene) were introduced into the office and the subsequent particle formation and redistribution were monitored. This study showed that ozone/terpene reactions were the significant source of sub-micron particles in the office building.

Ozone has been used to remove hydrogen sulfide in the presence of concurrent substances, such as toluene, ethanol, and n-butanol (Masuda et al., 2001) with a combination of an activated carbon system. Masuda et al. (2001) showed that the ozone was effective to increase the removal efficiency for hydrogen sulfide.

Ozonation in livestock production units has been studied by several commercial farms and University researchers (Edie, 2001; Vansickle 2002; Ozone Solutions Inc.; 2002). A report from Picket Fence Farms Inc., ozone decreased the number of *Ecoli* by 75%, reduced by 50% in number of pigs laid on, and increased pigs weaning weight by the 15% (Ozone Solutions Inc. 2002). According to this report, the sows consumed up to 20% more feed because of better air quality. A recent study showed that that ozone reduced the concentration of low molecular weight volatile fatty acids on the dust samples taken in a swine house (Oehrl et al., 2000).

5.2 Hypotheses

1) Ozone will reduce the concentrations of major odorous compounds in the swine building air.
2) Ozone will improve the odor in swine building air.

5.3 Objectives

This research was conducted to observe the air quality changes that resulted from the ozonation of air in livestock buildings. The most widely reported malodorous volatile organic compounds associated with livesotock operations i.e., VFAs and phenolics, were monitored. The experiment was conducted in rooms where the air was ozonated and in a control room where the air was not ozonated.

5.4 Materials and Methods

5.4.1 Swine Housing

Four environmental rooms, located at Michigan State University Dairy Teaching and Research Farm, were used for this research. The layout of the facilities is shown in Figure 5-1. Each room contained one 12' by 16' pen. Each pen contained 24 pigs. Mortalities were 0% for control, low, and medium ozone injection. The mortality in the pen with high ozone injection rate was 8.2%. The mortalities in this pen were not related to ozone treatment but it was related to a hip injury, inflicted by another pig. A manure handling and storage pan was located directly beneath the flooring of each pen. The air samples were taken 1m above the flooring.

Temperature was measured using a digital thermometer (copper constant thermocouple) and a data-logger (CSI 23-X). Ventilation airflow rates were determined based on air velocity traverses across exhaust fan outlet cones. The air velocity measurements were made using a vane anemometer. Two heating/ventilation/air conditioning (HVAC) systems were installed in the facility and each HVAC controls air exchange for two chambers. The east HVAC controlled rooms 1 and 2, and west HVAC controled rooms 3 and 4.

5.4.2 Ozone Distribution

Figure 5-2 shows the ozone distribution in the rooms. Ozone was injected at the rates of 0, 2, 4, and 6 ft^3/hr to provide the ozone dose of approximately 0 (control), 0.01 (low), 0.05 (medium), and 0.1 (high) ppm, respectively. Ozone was distributed through PVC tubing to the rooms. Every group of 24 pigs was subjected to a fixed level of ozonation, each group of pigs was moved every two weeks to another randomly selected pen. The ozone concentration in the ozonated rooms was measured every day.

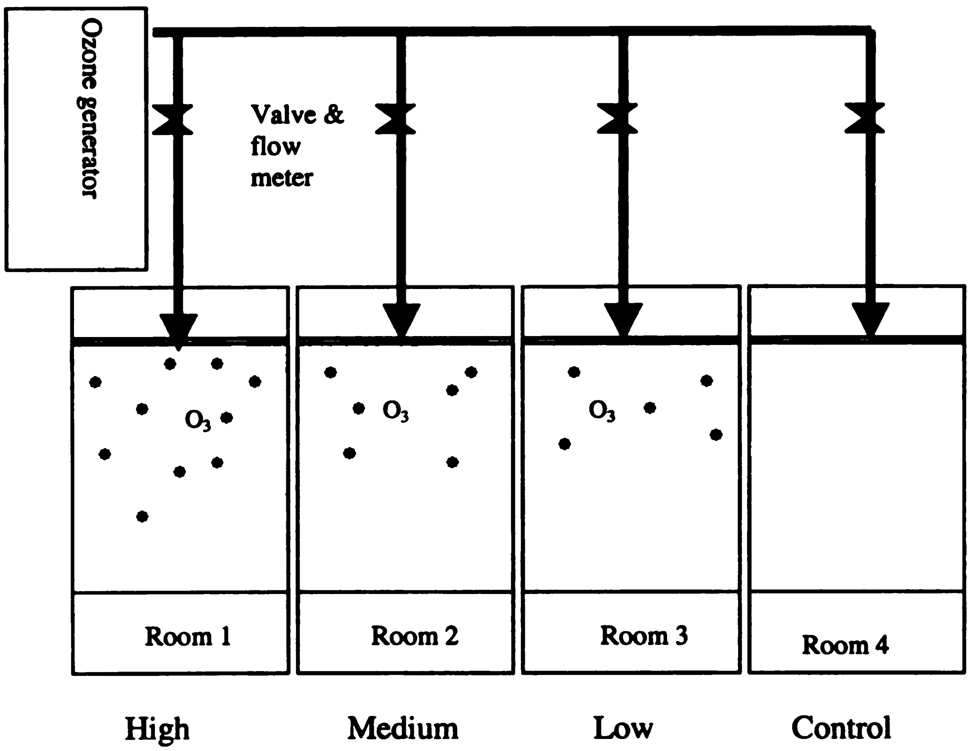
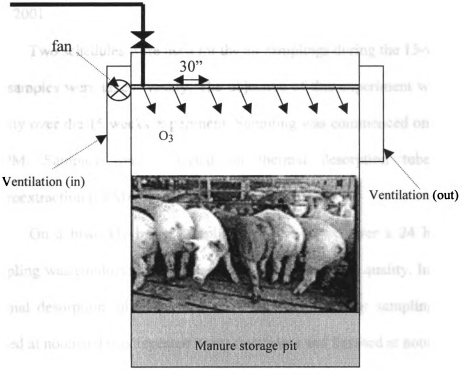


Figure 5-1. Environmental chambers at Michigan State University.



Pen size: 12' x 16'

Figure 5-2. Diagram of one pen in the environmental chamber at MSU.

5.4.3 Air Sampling

The experiment began on July 15th, 2001 and was terminated on September 30th, 2001.

Two schedules were used for the air samplings during the 15-week experiment. Air samples were taken weekly. The objective of this experiment was to monitor air quality over the 15 weeks experiment. Sampling was commenced on every Sunday at 4 PM. Samples were collected on thermal desorption tubes, Solid Phase Microextraction (SPME) fibers, and glass fiber filters.

On a biweekly basis, sampling was conducted over a 24 hour period. This sampling was conducted to monitor diurnal changes in air quality. In this experiment, thermal desorption tubes and SPME fibers were used for sampling. Sampling was started at noon and was repeated every four hours and finished at noon of the next day.

Custom designed thermal desorption tubes were purchased from Supleco Co. (Bellefonte, PA). Tubes contained Tenax TA plus Carboxen and Tenax TA plus Carbosieve SIII. The air flow rate was regulated between 150 to 200 mL/min and the total sample volume did not exceed 5 L. The tubes were conditioned as described in section 2.1.1.

SPME PDMS/CAR fibers were used to sample the air. Sampling times were varied according to the research objectives. Fiber conditionings and sampling methods are described in section 2.1.3.

For the sampling of dust, a 37mm cassette filter holder (225-3, SKC, Inc.) with a membrane filter (pore size of 1.0 μm, SKC Inc. 226-7) and a support pad (Metricel, Gelman Lab.) were used. The sampling method is described in section 2.1.4.

5.4.4 Test mixture

Phenol, p-cresol, p-ethylphenol, indole, and skatole and VFAs (acetic, propionic, butyric, is-butyric, valeric, and iso-valeric acids) were studied in this research. A stock solution for phenolic compounds was prepared in methanol. Analytical grade phenol, p-cresol, p-ethylphenol, indole and skatole were purchased from Sigma-Aldrich Co. (St. Louis, MO). The standard VFA mixture was purchased from Supelco Co. This standard mixture contained 10 mM of acetic acid, butyric acid, formic acid, heptanoic acid, hexanoic acid (n-Caproic acid), isobutyric acid, isocaproic acid (4-Methyl-n-valeric acid), isovaleric acid, propionic acid, n-valeric acid, in 100 mL deionized water.

5.4.5 Quantification of the compounds.

The column used in the research was DB-5MS (J&W Scientific) which is non-polar column. The dimensions of the column are given in Section 2.2.2. The separation of phenolic compounds with this column was good. However, for the VFA compounds, some isomers, such as valeric and iso-valeric acids were not well separated using this column. Therefore, the amount collected on SPME and TD tubes for VFAs was converted to carbon, and added all VFAs and finally reported as total carbon for VFAs.

5.4.6 Desorption methods

Thermal desorption was used for the removal of VOCs from the sorbent tubes. The conditions used are described in section 2.2.1.

Dust particles on filters were analyzed using thermal desorption. Since the conventional solvent desorption method dilutes VOCs during the desorption processes from filters, it lowers the sensitivity of the analysis. Therefore, thermal desroption method was used for desorption of VOCs from the filters.

For the analysis of VOCs on a filter, the filter was placed on an empty ¼" stainless steel TD tube. The desorption processes and conditions were same as described in section 2.2.1.1.

5.4.7 Gas chromatography and mass spectrometry

GC/MS was used for the separation and identification of the compounds in the air samples. The analytical conditions for TD/GC/MS and SPME/GC/MS are described in the section 2.2.2.

5.4.8 Odor measurement: Olfactometry

The olfactometric measurements were conducted at Agricultural Air Quality Laboratory at Purdue University. Air samples for the odor tests were collected in a 1L-Tedlar bag. Tedlar bags were purchased from SKC Inc. (Eighty Four, PA). All new bags were purged with high purity air three times prior to the sampling. An air sampling pump (SKC Inc.) was used for the air sampling in ozonated rooms and control rooms. Inlet air samples were taken at the outside of the environmental chambers at the inlets of the two heating/ventilation/air conditioning systems.

The air samples were shipped overnight to Purdue University for analysis by a trained odor panel. The odor analysis was conducted the day following sampling.

Odor intensity and offensiveness measurements were made at recognition in which the odor was first detected, and at full strength in wich the air samples were delivered to the olfactometer without mixing with dilution air. Data in the results section shows the offensiveness and intensities at full strength. Intensity is numerically recorded. A larger number means the odor is more intense. Odor offensiveness was recorded as negative numbers. Larger negative values mean that sample was more offensive. Dilution to threshold is the ratio of the dilution air volume to sample volume when odor is first detected by the panelists. A large dilution threshold (DT) means that odor was detected when large volume of dilution air was used. This means that the sample has low odor threshold.

5.5 Results

5.5.1 Air ventilation data

Air velocity traveling across exhaust fan outlet was measured using a vane anemometer. The air ventilation rate was calculated using the cross sectional area and the air velocity. The calculation is shown in the Appendix A. Figure 5-3 shows the air ventilation rate which were averaged every four hours.

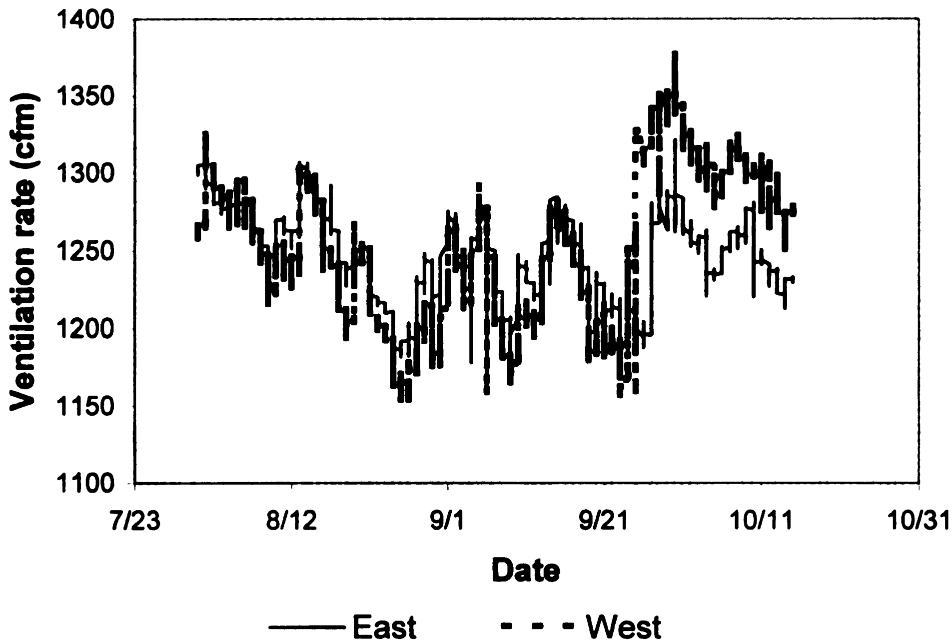


Figure 5-3. Air ventilation rate in the swine building. The data is shown for the east and west fans. East fan controls the air exchange in rooms 1 and 2 and west fan controls air exchange in rooms 3 and 4.

5.5.2 Temperature

Figure 5-4 shows the temperature in the four rooms. Temperature was measured in two locations in each room and the figure shows the average temperature in each room. Temperature readings were recorded every 5 minutes. In this figure, one hour average temperature values were used.

Figure 5-5 shows the temperature changes and ventilation rates in room 1and 2 from July 31st to September 28th. The graph shows that the ventilation rates were increased as the room temperature increased.

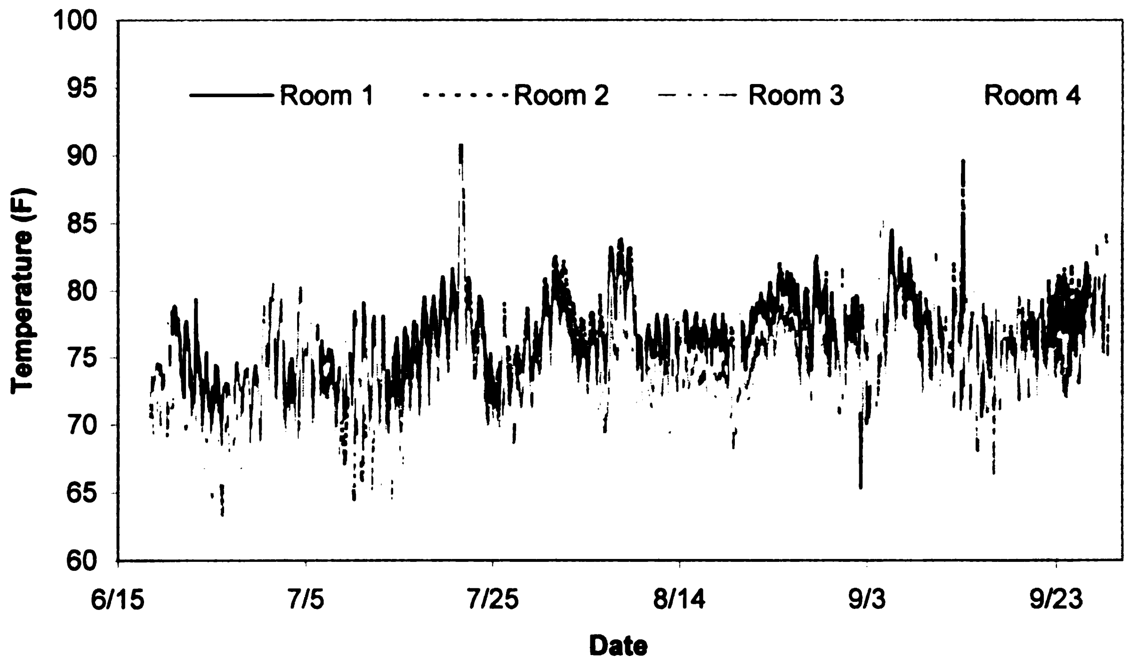


Figure 5-4. Temperature changes in the environmental chambers.

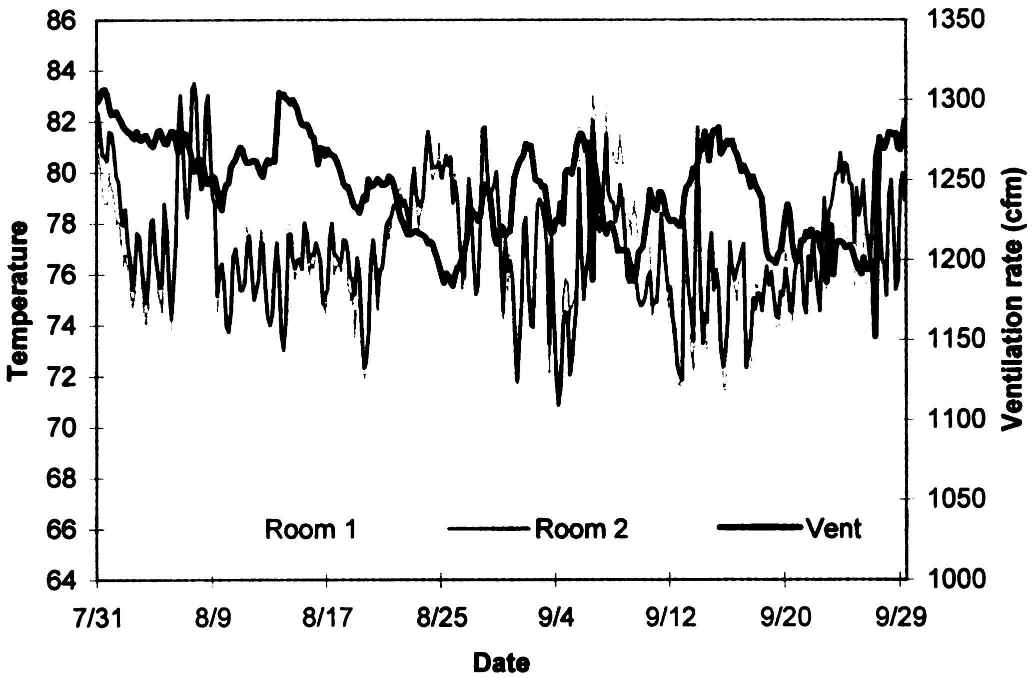


Figure 5-5. Temperature and ventilation rate in swine building (Room 1&2).

5.5.3 Olfactometry data

Four measurements were made for the olfactometry tests: dilution threshold, offecsiveness, intensity, and characteristics.

5.5.3.1 Dilution threshold (DT)

The data in table 5-1 show that the detection threshold was higher for the control room and that the DTs decreased as ozone level increased. The effect of ozone on odor dilution threshold was highly significant at $p<0.01$ for all ozonated rooms. Odor dilution threshold in the highly ozonated room was significantly different from those in low ozonated room at 0.02 while there were no differences in odor DTs between the medium dosage and low dosage ozonated room (o.53), and between highly and medium ozonated rooms (0.15). These results indicate that no significant additional benefit as to the reduction of odor DTs in highly ozone dosage room as compared to the medium dosage.

Table 5-1. Detection Threshold for air samples in swine building.

Date	Inlet	High Ozone	Medium Ozone	Low Ozone	Control	NB*
7/6/01	46	327	386	621	1090	1510
8/3/01	48	382	683	683	808	1580
8/31/01	63	676	866	799	1110	1430
9/28/01	39	317	622	734	944	1030

*NB: normal butanol

5.5.3.2 Odor offensiveness and intensity

Figure 5-6 shows the odor offensiveness for the air samples. Ozone did not significantly reduce the odor offensiveness in swine building air at $P>0.5$ for all treatments. A study by Hargesheimer (1996) supports this finding. Hargesheimer (1996) showed that ozone did not remove bad odors in drinking water while it altered the fish odor to an undesirable "plastic-like" odor.

The result suggests that the VOCs that affect offensiveness are still present after ozone treatment or the by-products by the ozonation have an offensive odor.

Figure 5-7 shows the odor intensity in swine building air in the control and ozonated rooms. Again, ozonation had no significant effect on odor intensity.

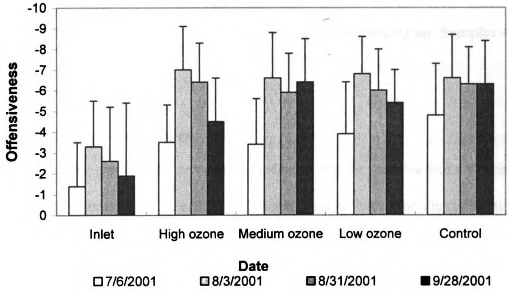


Figure 5-6. Effect of ozonation on odor offensiveness in swine building air. Samples were taken at noon.

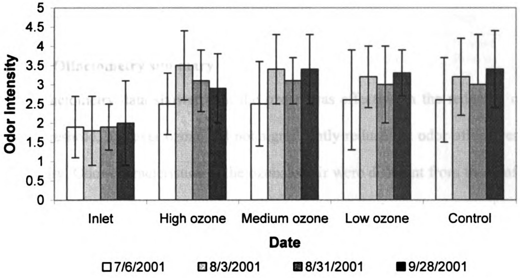


Figure 5-7. Effect of ozonation on odor intensity in swine building air. Samples were taken at noon.

5.5.3.3 Odor characteristics

Table 5-2 shows the odor characteristics of the air samples from the control and ozonated rooms. Both ozonated and control room had odor characteristics of manure and urine. The highlighted data indicates the unique smells in ozonated rooms which are different from the odor characteristics in control room. The data indicate that the ozonated rooms had slightly different odor characteristics from those for the control room. Air in the ozonated room was reported to have a greasy, soapy, sour, mossy or musky odor, whereas the control room did not show such odor characteristics. Soapy smell was reported in all ozonated rooms. Acidified smells, such as sour, sauerkraut, vomit smells were reported in low, medium, and high ozone level room, respectively. As ozone level increased the intensity of the acidified smell increased. This finding suggests that ozone may produce the acidified smells in swine building air.

5.5.3.4 Olfactometry summary

Olfactometry data showed that the ozone was effective in the reducing odor dilution threshold, however ozone did not significantly reduce the odor offensiveness and intensity. Odor characteristics of the ozonated air were different from those of the air in the control room. These results suggest that some odorous compounds were destroyed by ozone but the residual compounds still exhibited a strong and offensiveness odor. Another possibility is that the by-products formed during ozonation had an offensive odor. A previous study for ozonation on odor and taste in drinking water has shown that ozone altered odor characteristics in drinking water but it did not reduce odor intensity (Hargesheimer and Watson, 1996). A study by Esswein and Boeniger (1994) showed that ozone was not effective in reducing formaldehyde where formaldehyde is the main odor producer. A publication from US EPA also showed that the ozone was not effective in reducing odor causing chemicals at concentrations below the public health concern (IOA Publications, 2002).

Table 5-2. Odor characteristics for air samples in swine housing air.

Date	Inlet	6cft	4cft	2cft	0cft
7/6/01	Musty Fresh air Salty Plastic Corn Dust Musty Fetid Smoke	Mildew Mold Foul Earthy Greasy Swamp Urea Manure Smoke Soap Vomit	Mildew Mold Foul ari Greasy Fecal Sauerkraut Corn Dust Smoke Soap Pig feces	Sewage Lightly bitter Salty Fecal Burnt oil Corn Dust Cadaverous Soap Urine Fermented	Manure Rancid Foul Fecal Salty Blood Urea Manure Septic Spicy
8/03/01	Chemical Septic Spicy Foul Rotten Solvent Dust Phenol Cork Hay Smoked leaves	Sewer Pungent Decayed Dirt Spicy Foul Rotten meat Urine H2S Fecal Smoke Cigars	Cat urine Fecal Dirt Foul Spicy Fecal Decayed Rotten egg Decayed Leaves Musty Peat moss	Cat urine Fecal Foul Earthy Pungent Fecal Rotten egg Salty Garbage Sewer Raw meat Rotten egg	Cat urine Dirt Foul Blood Fecal Salty Rotten egg Sewer Swamp Ammonia Rotten leaves
8/31/01	Grass Dirt Grain Mold Chemical New plastic H2S Feces Smoke Hay wood Animal Farmhouse	Mold Rotten Urine Moldy Pungent Rotten egg Feces Salty Garbage Rotten meat	Grass Dirt Grain Moldy Dust Spicy Pungent Urine Ashes Spicy Acidic Feces Animal vomit	Grass Dirt Grain Sour Ferment Foul Pungent Spicy Ashes Feces Foul Smoke Animal vomit	Sewer Moldy Sour Grain Rotten egg Foul Ammonia Salty Feces Smoke Rotten leaves Garlic Rotten meat
9/28/01	Fresh Plastic Foul Septic Wood H2S Earthy Garbage	Foul Pungent Musty Stale Septic Sauerkraut Cat urine Fresh cow manure Musk Fecal	Rancid Fecal Pungent Urine Stale Cat urine Fresh cow manure	Foul Fecal Pungent Urine Septic Grassy Musty Cat urine Fresh cow manure Strong fecal	Rancid Bitter Fecal Urine Foul Pungent Sewer Anesthetic Cat urine Fresh cow manure

5.5.4 Ozonation effect on Volatile Organic Compounds in Swine Production Unit.

As described in the method section, three air sampling methods (SPME, TD, and filter) were used. For each sampling method, two groups of compounds were analyzed; phenolic compounds and VFAs.

5.5.4.1 SPME air sampling

5.5.4.1.1 Volatile Fatty Acids

Short chain VFAs (C2, C3, iso-C4, C4, iso-C5, and C5) were determined. VFAs adsorbed on SPME fiber coatings were analyzed and the individual VFA concentrations were converted to a carbon basis, added and reported as total carbon. The data shown in the Figure 5-8 shows the total VFAs recovered from SPME fiber. Ozone appeared to have no effect on total VFA concentrations in the swine building air. T tests for control and ozonated rooms showed the ozonation effect was not significant at the 95% level. Figure 5-8 and 5-9 show the ozonation effect on VFAs for the weekly and bi-weekly air samples, respectively. The VFA concentrations appeared to decrease over time. This result suggests that generation of VFAs decreases, as pigs get older. However, the effect of pig ages on VFAs generation has not been well documented.

There was no co-relationship between VFAs and room temperature.

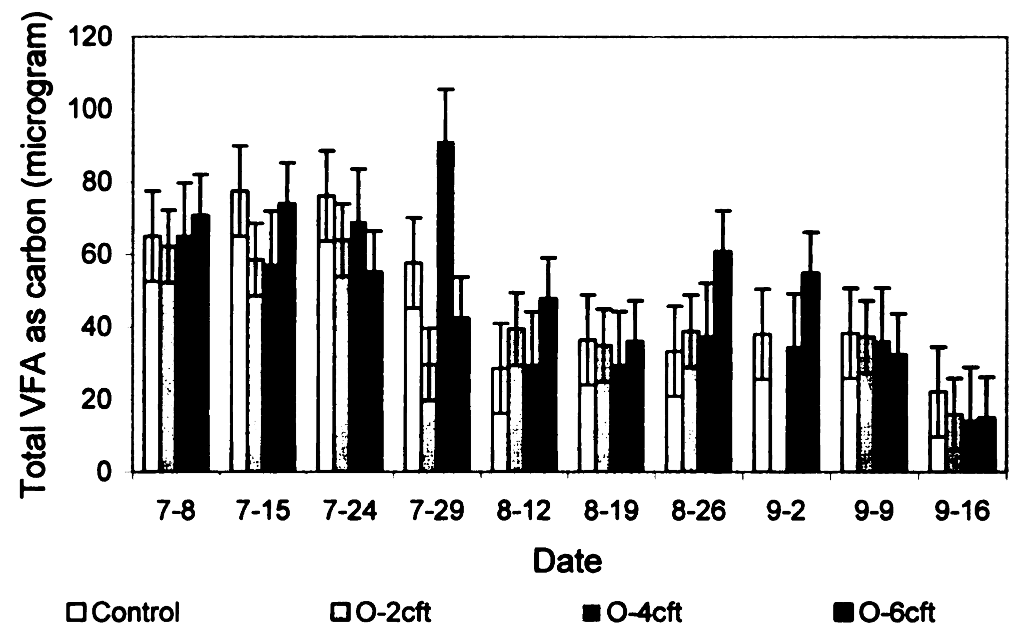


Figure 5-8. The total VFA concentrations adsorbed on SPME fibers for weekly samples.

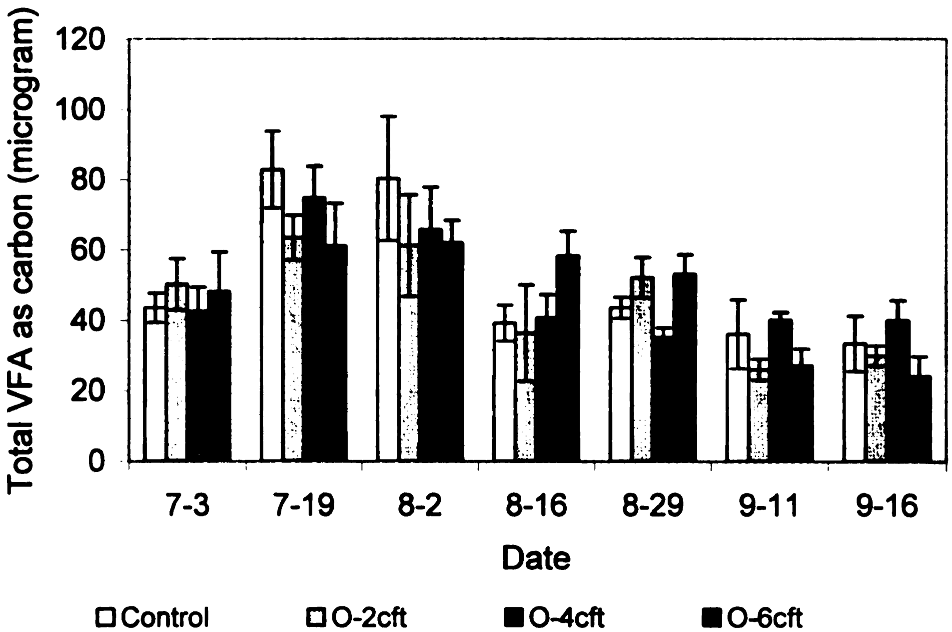


Figure 5-9. The average VFA concentration adsorbed on SPME fibers for bi-weekly samples.

5.5.4.1.2 Phenolic compounds in swine building air.

Figure 5-10 shows the average phenol levels for the bi-weekly air samples. Seven phenol levels for a day samples were averaged. Results showed that ozonation significantly reduced the phenol level in bi-weekly samples at 95% confidence level (<0.001). Phenol level was lower in the highest ozone treatmed room than in the other rooms (<0.02) but there were no difference in phenol level between the low and medium ozone treated rooms at 0.53. Figure 5-11 shows the GC response for phenol for weekly samples. This result was obtained from the weekly samples that were taken at the same time (4:00 PM) on every Sunday. Result showed that ozonation did not change the phenol level in weekly samples (>0.4). Ozone was effective at reducing overall phenol levels in ozone treated rooms but it did not reduce the phenol level in the weekly samples. This result implies that there were diurnal effects on phenol level in bi-weekly samples.

Figure 5-12 and 5-13 show the diurnal variations in phenol level in swine building air in July 19th and August 2nd 2001. Figures show the phenol level changes over time, however there were no significant ozonation effect on phenol levels.

The average mass of phenol adsorbed on SPME fiber for the whole test period were 125±15, 109±21, 107±10, and 98±8 μg for control room, ozonated rooms with low, medium, and high ozone dose respectively. The average percent reduction of phenol in ozonated rooms were 12, 14, and 21% for the rooms with ozone treatment of low, medium and high ozone dose, respectively.

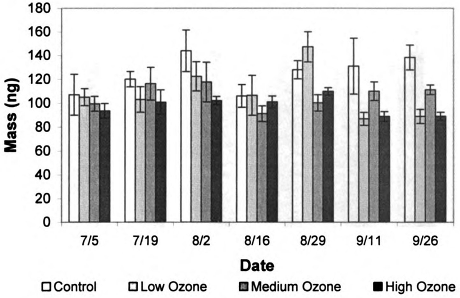


Figure 5-10. Average Phenol level in bi-weekly air samples. (Sampling method was SPME)

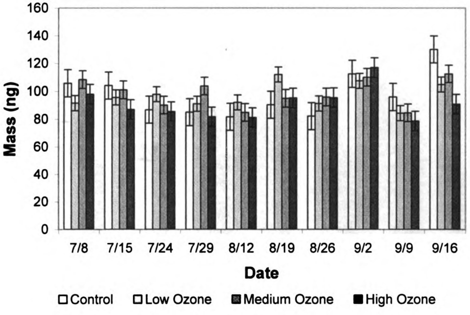


Figure 5-11. Phenol level in weekly air samples. (Sampling method was SPME)

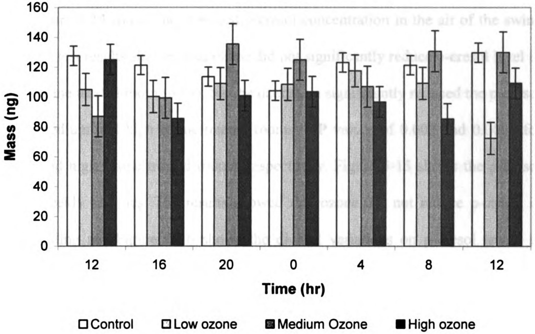


Figure 5-12. Diurnal variations in phenol level. (Sampling was done in July 19th 2001.)

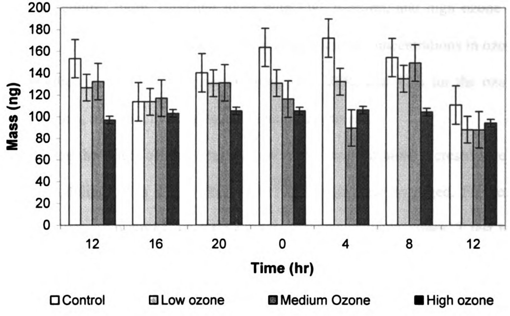


Figure 5-13. Diurnal variations in phenol level. (Sampling was done in August 2nd 2001.)

Figure 5-14 shows the averaged p-cresol concentration in the air of the swine building. T test results showed that ozone did not significantly reduce p-cresol level in the low ozone treated room (0.14), but the ozonation significantly reduced the p-cresol level in medium and high ozone treated rooms at P values of 0.002 and 0.0002 for medium and high ozone treated rooms, respectively. Figure 5-15 shows the p-cresol level in weekly samples. The results showed that ozone did not reduce p-cresol in swine building air. Figure 5-16 shows the diurnal variations on p-cresol levels in swine building air sampled on July 19th 2001 for 24 hour sampling period. Ozone reduced the p-cresol level in the highest ozone treated room (0.002) but there no ozonation effects on low and medium ozone treated rooms. The averaged data showed that p-cresol concentrations for the whole experiment period were decreased in ozonated rooms. The averaged mass of p-cresols were 287±98, 247±103, 217±72, and 198±91 for control room, ozonated room with low, medium, and high ozone dose, respectively. The percent reductions in the average p-cresol concentrations in ozonated rooms for the whole experiment period were 14%, 28%, and 41% for the ozonated rooms with low, medium, and high ozone dose, respectively.

To see the effect of sampling time on VOC concentration, p-cresol levels for the same sampling times during the whole experiment were averaged. Figure 5-17 shows the averaged p-cresol concentrations at different sampling times. T test results (at 95% CI) showed that sampling time of the day did not significantly affect on p-cresol levels in both ozonated rooms and control room. Similar results were shown in Figure 5-12 and 5-13. Ozone was effective at reducing the average phenolic concentrations in ozonated rooms, however the sampling time of the day did not affect on phenolic concentration.

All lighting in the swine rooms was from artificial lights. They were either on or off. Pig activity is higher when the lights are on, and pig activity causes gases that can react with ozone to be released. Figure 5-18 shows relationship between lights being on and p-cresol concentration in the air. Lighting did not significantly affect on p-cresol level in swine building air.

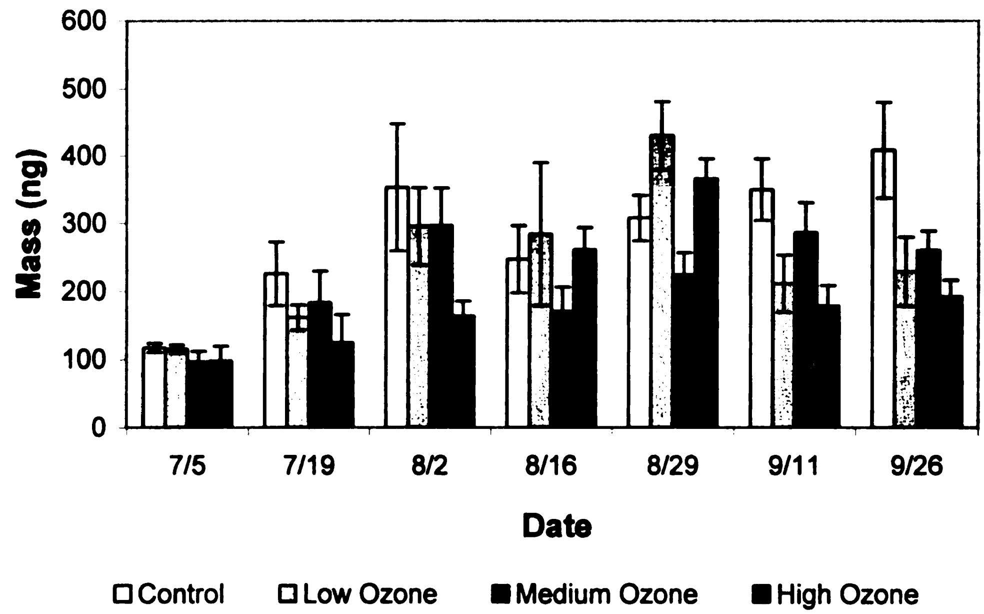


Figure 5-14. Average p-Cresol level in bi-weekly samples. (sampling method was SPME)

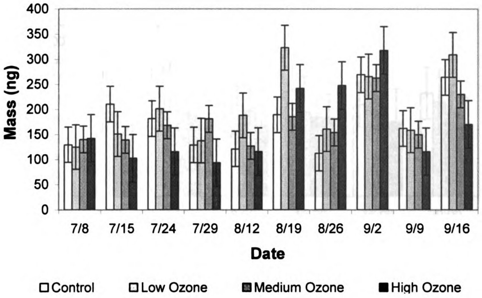


Figure 5-15. p-Cresol level in weekly samples. (Sampling method was SPME)

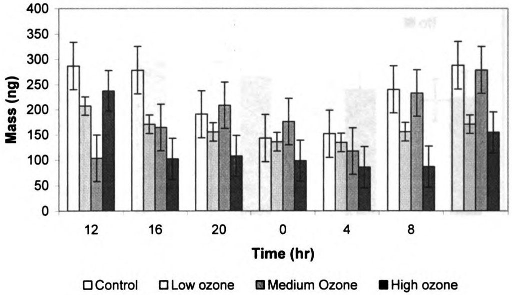


Figure 5-16. Diurnal variations in p-Cresol level. (Sampling was done in July 19th 2001)

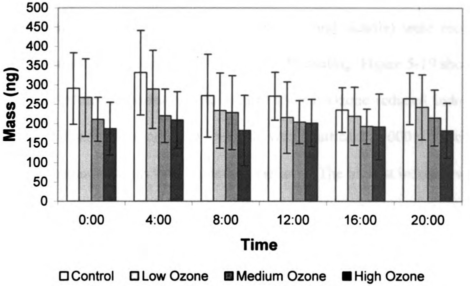


Figure 5-17. Effect of samplings times on p-Cresol level. (Sampling method was SPME and the a bar represents the averaged p-cresol concentration at the certain sampling time)

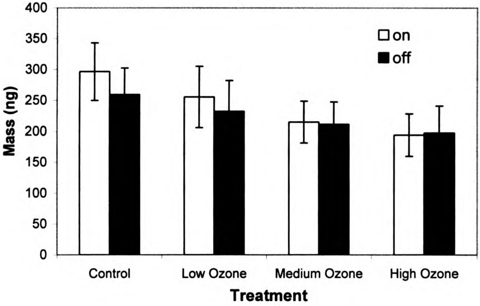


Figure 5-18. Effect of light on the average p-Cresol concentration. (Sampling method was SPME. Concentrations of p-cresol that were measured when the light was on and off were averaged.)

5.5.4.1.3 Ozonation effect on indolic compounds

Small quantities of indolic compounds (indole and skatole) were recovered from the swine building air using a SPME CAR/PDMS coating. Figure 5-19 shows the GC response of indole for ozonated and control rooms. Ozone reduced indole and skatole level in the ozonated rooms at a level that was significant (0.0001). Indole was not found in the ozonated room with highest ozone level. The highest indole level was found in the control room. Figure 5-20 shows the average skatole adsorbed on SPME fiber coatings from bi-weekly samples. The amount of skatole adsorbed on SPME fiber coatings was reduced as ozone level in the room as increased. No skatole was found in ozonated room with highest ozone dose. This suggests that ozone may reduce the level of indolic compounds in the swine building air. Previous research (Wu et al., 1999) has shown that ozone reduced indolic compounds in swine slurry.

Weekly air samples also showed similar results. Figure 5-21 shows the indolic compounds collected in swine building air in weekly samples. Skatole level was highest in the control room and no skatole was found in the ozonated room with medium and high ozone dose. Small quantities of indole were detected in the control room and there were no detectable indole in the ozone treated rooms.

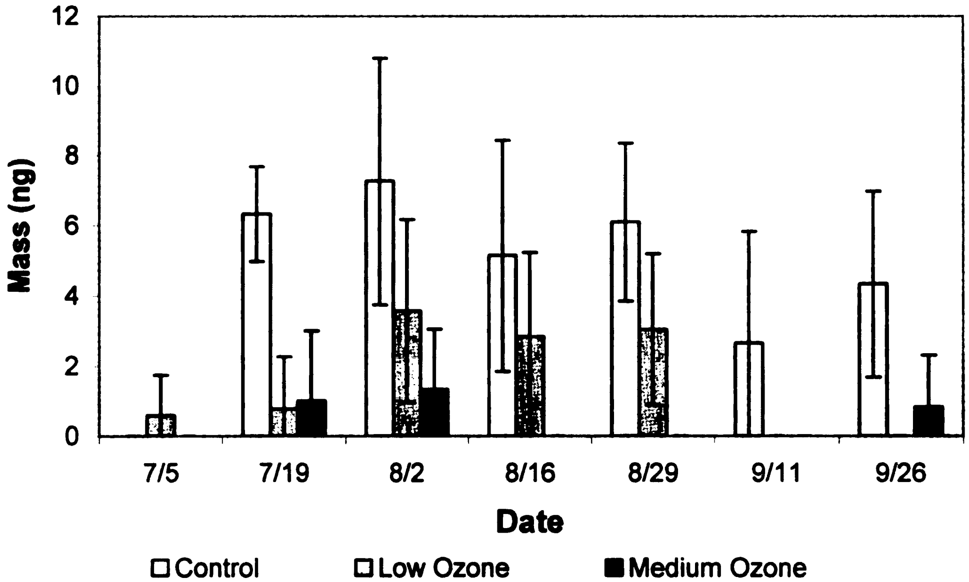


Figure 5-19. Average Indole levels in bi-weekly air samples. (Sampling method was SPME).

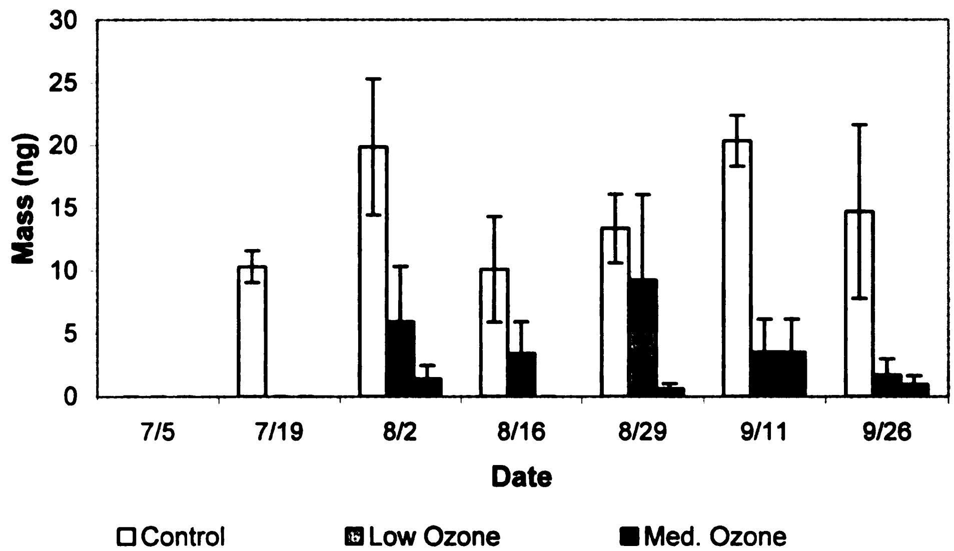


Figure 5-20. Average skatole level in bi-weekly air samples. (Sampling method was SPME).

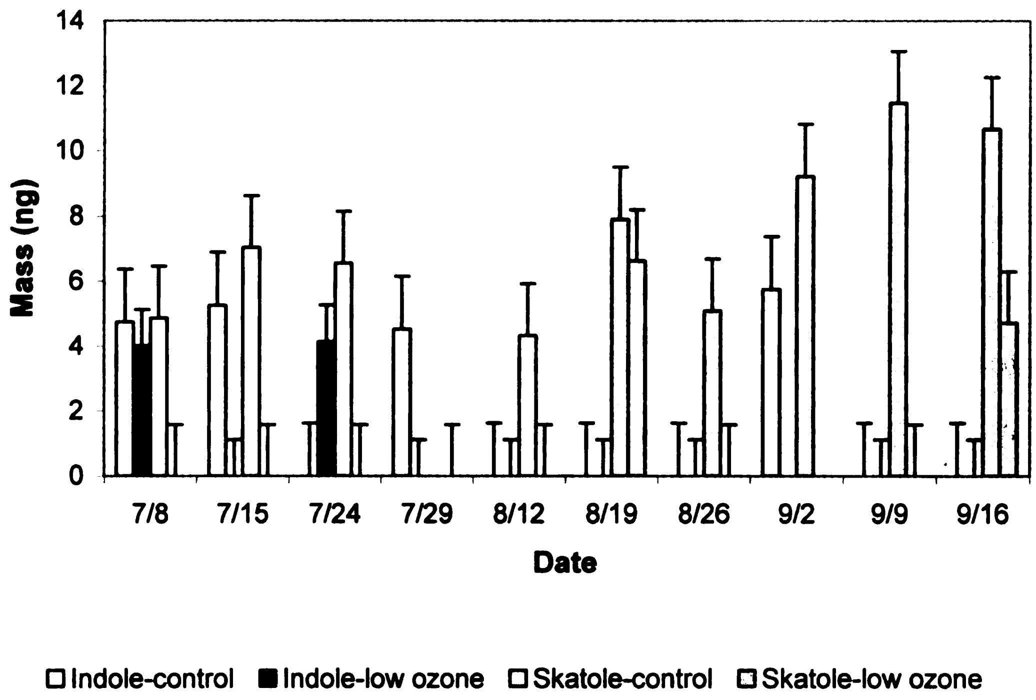


Figure 5-21. Level of Indolic compounds in weekly SPME samples. (Sampling method was SPME).

5.5.4.2 VOCs in Thermal Desorption Tubes

Figure 5-22 shows a typical GC chromatogram for air sample taken with a TD tubes. As shown in Table 5-3 and 5-4, the major volatile organic compounds detected were hydrocarbons and substituted benzenes (benzene, toluene, and xylene).

Quantification analysis for VOCs in TD samples was not conducted in this research. Most of the compounds found in both ozonated and control room were aromatic hydrocarbons. A few notable differences in air samples between the control and ozonated rooms were detected. First, benzyl alcohol and methylphenol were found in the control room and ozonated room with the low ozone dose but these were not found in the medium and high ozone treated rooms.

A few VFAs compounds were found with this method, but recoveries of VFAs compounds were poor for the following reasons; firstly most of VFAs compounds had same retention times with other alcohols and substituted benzene compounds, resulting in poor separation in GC, and secondly the amount of VFAs adsorbed on sorbent tubes were very small. This method was not sensitive for the analysis of phenolic compounds in the swine building air with the total air volume of 5L. Only small quantity of p-cresol was detected with this method.

The difficulties in collection of VFAs compounds in swine building air with this air sampling method are likely due to the polarity of the sorbent materials in TD tubes. The first bedding sorbent, Tenax TA, is made of non-polar compounds which favor non-polar compounds such as benzene and xylene. Due to the high uptake of these non-polar compounds on the sorbent materials, other polar odorous compounds were not able to adsorb onto the sorbent materials resulting in poor recoveries. Results suggest that more polar sorbent materials in the TD tubes are required to collect semi to high boiling polar odorous compounds in the livestock building air.

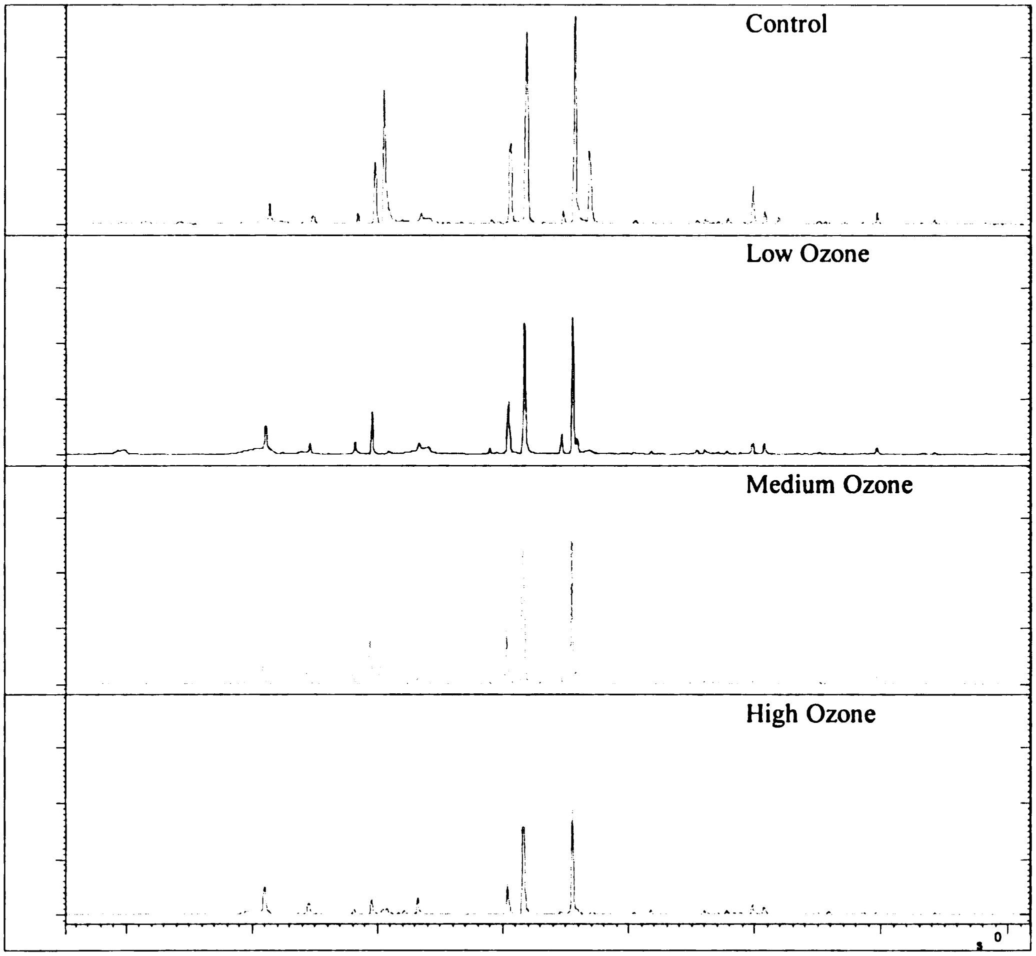


Figure 5-22. GC/MS chromatogram for TD air samples.

Table 5-3. Volatile organic compounds found in the control room using TD tubes.

RT	Compound Name	Match
6.994	Benzene	885
8.337	Methyl isobutyl ketone (MIBK)	729
10.148	Bromomethane	834
11.022	Toluene	903
14.937	4-Chlorotoluene	746
16.236	Toluene	887
16.418	p-Xylene	798
17.459	Isopropylbenzene	918
17.797	m-Xylene	722
18.594	n-Propylbenzene	931
18.88	1,2,4, trimethylbenzene	943
19.475	4-Chlorotoluene	714
20.673	sec-Butylbenzene	850
21.059	4-Isopropyltoluene	821
22.66	Benzyl alcohol	874
23.729	4-Methylphenol	785

RT: GC retention time (min), Match: MS spectrum library match (threshold: 700)

NIST MS library (provided by Varian) was used for the identification of the compounds. The search method used was "reverse search". The program looked same spectrum with the reference spectrum from the sample chromatogram and when the matching value exceeded 700, the compound was identified. When the sample spectrum matches perfectly with the reference spectrum, then match value become 1000.

Table 5-4. Volatile organic compounds found in ozonated room ($6ft^3$) using TD tube.

RT	Compound Name	Match
8.27	Methyl isobutyl ketone (MIBK)	753
10.11	Bromomethane	735
11	Toluene	939
12.812	Tetrachloroethene	890
15.008	Ethylbenzene	941
15.325	p-Xylene	944
17.539	Isopropylbenzene	928
18.672	n-Propylbenzene	937
19.642	1,2,4-Trimethylbenzene	941
20.129	1,3,5-Trimethylbenzene	958
20.74	sec-Butylbenzene	949
21.108	4-Isopropyltoluene	948

5.5.4.3 Volatile Organic Compounds in Dust Samples

Due to the relatively clean air in the environmental chambers, dust levels in the chambers were very low, so the level of VOC mass on the filters was a below the GC detection limits. Concentrations of the dust in swine building air were not measured in this research.

5.5.5 Comparison of sampling methods for detection of VOCs in swine building air.

The results showed that SPME air sampling method was more selective than sorbent tube method for both phenolic compounds and VFAs. No phenolic compounds and few VFAs were found using the sorbent tubes. For VFA compounds, peak broading was observed in GC chromatogram, however, this is not related to the sampling process but it is related to the polarity of the column material.

One disadvantage of using SPME fiber with a CAR/PDMS coating was the poor recovery of phenolic compounds. The recovery of phenolic compounds can be improved by using different types of SPME fibers. Another difficulty for SPME air sampling is quantification. A recent study by Koziel et al. (2001) showed the possibilities of quantification of SPME with rapid air sampling methods. This method is also useful for the quantification of SPME samples at different temperatures and atmospheric pressure. Koziel showed a rapid diffusive sampling method that will make quantification relatively simple. The sue of this methods for quantifying SPME results is discussed in Chapter 4.

Overall, SPME air sampling was the most effective method for the collection of phenolic and VFA compounds in swine building air. The sorbent tube method was more effective for collecting substituted benzenes.

5.5.6 Temperature effect on odor and VOCs

Table 5-5 shows the temperature, odor detection threshold, and average GC responses of phenolic compounds. Phenolic and indolic levels in control and ozonated rooms were compared with temperature and odor DT. Since four olfactometry measurements were made, only four sets of data were used. T tests for temperature effect on VOCs and odor DT found that temperature did not affect significantly on odor DT and VOC emissions in swine air.

Table 5-5. Temperature, DT, and VOCs in swine building air.

Date	Ozone dose	Temp. (°F)	DT	Phenolic and indolic compounds sorbed on SPME fiber (ng)				
				Phenol	p-Cresol	p-Ethylphenol	Indole	Skatole
7/6/01	0	70.38	1086	107	117	2.07	0	0
	2	71.94	621	105	115	2.15	0.59	0
	4	71.98	386	99.5	96.8	1.94	0	0
	6	73.55	327	93.6	98.4	1.98	0	0
8/3/01	0	74.44	808	144	353	2.93	7.26	19.85
	2	77.02	683	122	296	2.99	3.36	5.92
	4	75.80	683	118	297	2.76	1.34	1.40
	6	73.39	382	102	164	2.08	0	0
8/31/01	0	80.19	1113	128	308	2.28	6.10	13.33
	2	79.74	799	147	430	2.69	3.04	9.22
	4	76.92	866	100	224	1.92	0	5.9
	6	75.87	676	110	366	2.33	0	0
9/28/01	0	78.47	944	138	408	2.28	4.33	14.69
	2	75.47	734	89	229	1.17	0	1.71
	4	77.23	622	111	260	1.90	0.82	0.95
	6	78.82	317	89	192	1.71	0	0

Units for the phenolic and indolic compounds: ng

5.6 Conclusions

This research showed that ozonation reduced the odor detection threshold, but it did not reduce odor offensiveness or odor intensity. Odor characteristics of the ozonated air were different from those of the air in the control room. These results suggest that some odorous compounds were destroyed by ozone but the residual compounds still exhibited a strong and offensiveness odor. Another possibility is that the by-products formed during ozonation had an offensive odor. A previous study for ozonation on odor and taste in drinking water has shown that ozone altered odor characteristics in drinking water but it did not reduce odor intensity (Hargesheimer and Watson, 1996). According to US EPA publications, ozone is not effective at removing many odor-causing chemicals at concentrations that do not exceed public health standards (IAQ Publications, 2002).

Ozone was not effective in reducing VFAs but ozone reduced phenolic and indolic compounds in the swine building air. Previous research (Wu et al., 1999) has shown that ozone reduced phenolic and indolic compounds in swine slurry.

The study showed that SPME air sampling methods were suitable to collect both VFAs and phenolic compounds in the swine building air. Analysis for VFAs and phenolic compounds on thermal desorption tubes with Tenax TA plus Carbosieve was difficult because the high mass loading of non-polar hydrocarbon compounds on the tubes.

SPME air sampling appears to be an effective method of sampling for odorous compounds in livestock building air. It is an easy and solvent free method and also does not require sample pretreatment steps. However, quantification of SPME air samplings is difficult because the recovery is sensitive to environmental conditions.

CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

The main purposes of the research were to find suitable air sampling methods for the odorous VOCs, to develop a new sampling technique for VOCs in air based upon SPME, and to use the methods developed to study the effect of ozonation on levels of odorants and other VOCs in the livestock building air.

The major odorants found in the livestock building air were volatile fatty acids (VFAs) and phenolic (phenol, p-cresol, p-ethylphenol) and indolic (indole and skatole) compounds. These compounds are formed by bacteria under anaerobic conditions.

Without any further sample concentration, the solvent desorption sorbent tube methods studied were not able to detect any volatile organic compounds in the swine nursery housing air, using a sample volume of up to 36 L. This method also required handling of hazardous organic solvents for sample preparation. As sample concentration is time consuming and there is a risk that the analytes may be lost during this step, this method was deemed to be less suitable than the thermal desorption or SPME methods. Using the impinger trap method the presence volatile organic compounds in the swine nursery housing air, was not detect, using a sample volume as large as 72L, so it was also unsuitable.

Thermal desorption has been widely used for the desorption of sorbent tubes. The major advantage of the thermal desorption method over solvent desorption is that the entire sample can be introduced into the analytical instrument. Also, as no solvent is used to desorb the analytes, there is no interference due to the solvent. This research showed that multi-bed thermal desorption tubes can be used for the sampling of odorous compounds from livestock buildings. However the recovery of high boiling point compounds was not good using thermal desorption.

The SPME air sampling method developed showed good recovery of the high boiling point compounds, however this method was not good for the recovery of the low boiling point compounds. The SPME air sampling method has advantages over other sampling techniques: the major advantages of SPME are; good sensitivity, ease of sampling, and minimal sample preparation is required.

It is apparent from research that no single method for air sampling appears to be satisfactory for sampling of VOCs in swine building air. For the determination of high boiling point compounds, such as phenolics and indolics, the SPME air sampling method offered the best results. Sampling using both SPME and a Tenax TA – Carboxen sorbent tube followed by thermal desorption seems to offer the best results. For the low to mid boiling point compounds, recoveries were good using the thermal desorption sorbent tubes. For the high boiling point compounds, such as phenolics and indolics, SPME seems to be the most effective method.

A major drawback of the SPME air sampling technique is that quantification of the results is difficult. SPME fibers are not uniformly sensitive to all compounds and therefore, the relative GC peak area for an SPME sample does not reflect the true proportions of the components in the sample. Furthermore, other environmental/physical factors can affect the uptake of the contaminant on the fiber. Two methods can be used for the quantification of SPME samples; these are based on equilibrium theory and diffusion theory. This research compared the quantification of phenolic compounds using these two methods. The results showed that for phenolic compounds the mass sorbed on PDMS/CAR fiber coating, at a gas phase concentration of approximately 4 μg/L increased linearly with sampling times of up to 30 minutes. However, the mass sorbed on the SPME fiber did not increase linearly with time if the gas phase concentrations decreased by a factor of 10. Rapid sampling with SPME showed that at the higher concentration the mass sorbed on SPME fiber increased linearly with time with sampling time of up to 150 seconds.

Several systematic experimental errors were observed in the SPME experiments. For the quantification of VOCs sorbed on a SPME fiber, gas standards were prepared by injecting a known amount of the analyte dissolved in methanol into the gas sampling bottle. It was assumed that all VOCs injected in the gas sampling bottle were evaporated, and that the sorption of the analyte to the walls at the container was minimal. When sorption occurs onto the surface of the gas sampling bottle (termed a wall effect), the actual gas concentration is less than that calculated. Wall effects may not be negligible, and where this is the case the concentration of the analyte in the gas phase should be determined by direct gas injection in GC or other suitable means. Temperature is also another possible source of error. Temperature was not controlled during the sampling. Rate of uptake of the analyte on the SPME fiber increases as the room temperature increases due to the increases in molecular diffusivity. In this work temperature changes in the laboratory during the experiment were ±2°C. Calibration of the SPME fibers should be conducted under temperature controlled conditions.

The studies conducted showed that VFAs were preferentially sorbed onto CAR/PDMS fibers and that extent of sorption of phenolic and indolic compounds was greater using PDMS/DVB fibers. This result suggests that using two types of fibers may be desirable for the sampling of FVAs and phenolic compounds in the livestock building air.

The experiments conducted on the ozonation of swine building air showed that ozonation reduced the odor detection threshold in the swine building air, but it did not reduce odor offensiveness or odor intensity. The odor characteristics in ozonated room were different from those in the control room. These results suggest that some odorous compounds were destroyed by ozone, but the residual compounds still exhibited a strong and offensiveness odor. Another possibility is that the by-products formed during ozonation had an offensive odor. Studies on the composition of the air in the swine building air showed that ozonation did not significantly reduce the levels of VFAs in the building. However, the concentration of phenolic and indolic compounds in swine building air was reduced in pens where the air was ozonated. Previous research has shown that ozone is very reactive with these compounds and that ozonation of a swine slurry reduced the level of phenolic and indolic compounds (Wu et al., 1999). Research recently published by the US EPA support the conclusions made here. It was found that at concentrations that did not exceed public health standard ozone was not effective in removing odor-causing chemicals in indoor air (IAQ Publications, 2002).

6.2 Recommendations for future research

This study has compared several air sampling methods for the odorous compounds in the livestock building air and also studied the efficiency of ozone to control odor. The followings recommendations are made for future research:

1. SPME air sampling was the best method for the detection of VFAs and phenolics in swine building air. Two types of SPME fibers are recommended: PDMS/CAR for VFAs and PDMS/DVB for phenolics. When SPME air sampling methods are chosen, accurate gas standards are required for the quantification of the analytes on SPME. This study showed that the technique of preparing gas standards by dilution in a gas sampling bottle could not be used to produce accurate gas standards. Temperature control during the SPME calibration is also recommended. The sorptive abilities of commercial SPME fibers decrease with the usage, so frequent recalibration of SPME fibers is recommended.

2. Ozonation reduces the level of phenolic compounds in swine building air, however, it was not effective for the control of odor offensiveness, odor intensity or VFAs in these buildings. Given the cost of the systems, ozone seems not to be a very cost effective method for the reduction of odors in swine buildings. Other technologies for odor reduction should be considered in further research.

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