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Novel Treatment of odor and VOCs Using Photolysis

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Abstract

Public concerns about offensive odor from livestock operations are on the rise, bringing up an increasing demand on odor treatment. In this work, a bench-scale standard gases generation and UV treatment system was built up, where standard gas mixtures including sulfuric compounds (H_2S , methylmercaptan, ethylmercaptan, DMS and butylmercaptan), volatile fatty acids/VFAs (acetic acid, propionic acid, butyric acid and isovaleric acid) and phenolic compounds (p-cresol, 4-ethylphenol, indole and skatole), which have been proposed to be responsible for odor nuisance, were utilized to simulate aerial emissions from swine barn. Permeation tubes that carry unique compounds were weighed around every four weeks and the results showed a stable permeation rate for each compound. Solid-phase micro-extraction (SPME) fiber was used to sample standard gases, and simultaneous chemical and olfactometry analyses of VOCs associated with odor were accomplished in a gas chromatography-mass spectrometry-olfactometry (GC-MS-O) system. Optimization of experimental conditions including the selection of SPME fiber and best extraction time was performed and thus Carboxen/polydimethylsiloxane (PDMS) 85 μ m fiber and 10 min extraction was used in subsequent experiments. Gas samples with UV light off (control) and on (treatment) were extracted, respectively, and were sent to GC-MS-O system for analysis. When the total flowrate was 400 ml/min, at 10min extraction, reduction rate for methylmercaptan, butyric acid and p-cresol was 96.2%, 48.15%, 92.16%, respectively, on chemical concentration, and 98.4%, 51.1%, 38.9%, on odor area count and 81.48%, 44.69% and 73.36% on odor intensity count. At 24hr extraction, reduction rate for methylmercaptan, butyric acid and p-cresol was 99.99%, 62.78%, 96.23%, respectively, on chemical concentration, and 74.66%, 45.06%, 93.56%, on odor area count and 69.93%, 40.01% and 88.66% on odor intensity count. To better simulate swine barn emissions and evaluate flowrate effect on UV degradation rate, gases were extracted at higher flowrate, 1150ml/min, 2150ml/min and 3150ml/min. The result showed reduction rate decreased as flowrate increased, but still a very good reduction rate of 79.07% on chemical concentration for p-cresol was obtained at flowrate 3150ml/min, which further verified the powerful treatment effect of UV light on VOCs and odor and feasibility of extending this technique to field applications. Chemical reaction mechanism was preliminarily investigated based on the new compounds identified from the treatment sample, which was accordance with previous studies.

Keywords

UV photolysis, VOCs; Odor; SPME; GC-MS-O; Livestock operations

Disciplines

Bioresource and Agricultural Engineering

Comments

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Authors

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NOVEL TREATMENT OF ODOR AND VOCs USING PHOTOLYSIS

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***Abstract:** Public concerns about offensive odor from livestock operations are on the rise, bringing up an increasing demand on odor treatment. In this work, a bench-scale standard gases generation and UV treatment system was built up, where standard gas mixtures including sulfuric compounds (H_2S , methylmercaptan, ethylmercaptan, DMS and butylmercaptan), volatile fatty acids/VFAs (acetic acid, propionic acid, butyric acid and isovaleric acid) and phenolic compounds (p-cresol, 4-ethylphenol, indole and skatole), which have been proposed to be responsible for odor nuisance, were utilized to simulate aerial emissions from swine barn. Permeation tubes that carry unique compounds were weighed around every four weeks and the results showed a stable permeation rate for each compound. Solid-phase micro-extraction (SPME) fiber was used to sample standard gases, and simultaneous chemical and olfactometry analyses of VOCs associated with odor were accomplished in a gas chromatography-mass spectrometry-olfactometry (GC-MS-O) system. Optimization of experimental conditions including the selection of SPME fiber and best extraction time was performed and thus Carboxen/polydimethylsiloxane (PDMS) 85 μ m fiber and 10 min extraction was used in subsequent experiments. Gas samples with UV light off (control) and on (treatment) were extracted, respectively, and were sent to GC-MS-O system for analysis. When the total flowrate was 400 ml/min, at 10min extraction, reduction rate for methylmercaptan, butyric acid and p-cresol was 96.2%, 48.15%, 92.16%, respectively, on chemical concentration, and 98.4%, 51.1%, 38.9%, on odor area count and 81.48%, 44.69% and 73.36% on odor intensity count. At 24hr extraction,*

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Keywords. UV photolysis, VOCs; Odor; SPME; GC-MS-O; Livestock operations

1. INTRODUCTION

Public concerns about offensive odor from livestock operations are on the rise. A lot of research studies associated with aerial emissions and odor from different livestock operations have been conducted through the whole world, involved with VOC emissions from livestock and crop sources in UK (Hobbs et al. 2002, 10), odor, ammonia and hydrogen sulfide from swine building in South Korea (Kim et al. 2005), ammonia, volatile fatty acids (VFAs) and other odorants near beef feedlots in Canada (McGinn et al. 2003), ammonia emissions from swine feeding operations (Arogo et al. 2003) and from swine houses (Harper et al. 2004), aliphatic amines from cattle feed yard (Mosier et al. 1973) and VOCs from swine manure (Zahn et al. 2001) in the United States. Odor can be defined as the perception experienced when one or more chemicals come into contact with receptors on the olfactory nerves. Odor from livestock operations has been found to be closely related to VOCs, ammonia, and hydrogen sulfide, and odor intensity and the concentration of VOCs in air emitted from swine manure management systems were strongly correlated (Zahn et al. 2001). Research studies in awareness of the relationship between VOCs and odor can track back to 1970s, when 10 compounds that were indicated as “interesting for the manure odor” were identified: indole, skatole, phenol, p-cresol and the carboxylic acids C₂-C₅ (Schaefer 1977). In the past 2 decades, more and more compounds have been found to be responsible for the offensive nuisance. A positive relationship between ammonia concentration and odor intensity was found (McGinn et al. 2003), while VFAs, phenols and indoles were reported as individual odorants from ageing pig waste (Hobbs et al. 1999). Three categories of substances (indoles, VFAs and methylthiol) were determined as key compounds of pig odor (Willig et al. 2004). A number of research studies were conducted on odor control, however, current odor control strategy falls into 3 categories, enhancing dispersion, reducing odor emissions and reducing odor generation. Enhancing dispersion included setbacks (Stowell et al. 2005), windbreak walls (Ford et al. 2003), while odor emissions were reduced using vegetable oil sprinkling

(Nonnenmann et al. 2003), biomass filters (Hoff et al. 1996), manure removal (Lim et al. 2004, 15), biofilters (Melse et al. 2005, 19), ozone (Kastner et al. 2005, 17; Fick et al. 2005, 9), manure additive (Heber et al. 2000, 14), decomposing malodorants in a wire-plate pulse corona reactor (Shi et al. 2005, 18), oxidation by minced horseradish roots and peroxides (Govere et al. 2005, 3). Another way is to dig into how odor generates so as to reduce generation, by dietary changes (Sutton et al. 1998, 4; Le et al. 2005, 16) or manure treatment (Westerman et al. 1997). In this work, a reaction process called photolysis using UV light is utilized to reduce odor emissions. Gas sampling process includes sampling preparation and sampling collection. Basically, sampling preparation can be realized by solvent extraction (Schiffman et al. 2001) or thermal desorption (Kai and Schafer 2004). Generally, there are three sampling methods, ambient sampling, flux chamber analysis and headspace analysis. A canister has been used for flux chamber analysis (Schiffman et al. 2001, Blunden et al. 2005). Headspace analysis method includes Tedlar bag and solid phase micro-extraction (SPME). SPME has been proven to be the most sensitive and efficient sampling methodology (Chen and Pawliszyn 2004) because SPME reduces sampling process into only one step, and shows great advantage in GC-MS or GC-Olfactory or GC-MS-Olfactory analysis (Godoi et al. 2004). More and more research studies have been conducted on livestock odor analysis using SPME (Begnaud et al. 2003, Kim et al. 2002). Basically, there are two odor measuring methods, olfactory (or sensory) and analytical (or instrumental). Analytical method shows success on odor analysis, including gas chromatography (GC) (Clanton and Schmidt, 2000) and gas chromatography mass spectrometry (GC-MS) (Schiffman et al. 2001, Zahn et al., 2001). However, many of the odorants found by the odor panelists could not be positively identified by GC-MS, which suggests that the olfactory sense of the human subjects may have been more sensitive than the applied GC-MS method (Kai and Schafer 2004). Thus, analytical and olfactory combination method has been used to better explore compounds responsible for the nuisance, mainly including GC-olfactometry (Burnett 1969, Kai and Schafer 2004) and GC-MS-Olfactory (Rabaud et al. 2002). In this work, a GC-MS-Olfactory system was used for simultaneous chemical and odor analyses.

2. METHODS AND MATERIALS

2.1 STANDARD GAS GENERATION AND TREATMENT SYSTEM

As shown in Fig. 1, compressed air supplied by one gas cylinder (with one stand by) was pretreated by dust scrubber and HC scrubber before mixing with compounds. Three mass flow controllers controlled constant gases flow to three ovens, and one bypass flow controller was installed to dilute the standard gas mixtures when necessary. Permeation tubes were placed in three ovens: phenolic compounds (p-cresol, 4-ethylphenol, indole and skatole) in an 80 °C oven, VFAs (acetic acid, propionic acid, butyric acid and isovaleric acid) and sulfuric compounds (H₂S, methylmercaptan, ethyl mercaptan, and butyl mercaptan) in two 40 °C ovens. One permeation tube carries one standard compound, and all the compounds of interest are characteristic of livestock odor. In each oven, to ensure a constant emission rate of permeation

tube, temperature was set constantly from the beginning. Gases from ovens flow into three corresponding gas collection chambers, then pool together to the control chamber added by bypass air. UV treatment takes place in the photoreactor (ACE glass, Vineland, NJ), which consists of a quartz immersion well with a circulating refrigeration structure, and a 5-watt Pen Ray UV lamp with peak wavelength at 254nm (UVP, Upland, CA). To avoid temperature effect caused by huge heat generated by UV lamp, a circulating refrigeration bath was used. The photoreactor was put into an enclosure lest its strong UV light will hurt people. Treated gases flow into the treatment chamber, and finally are dispersed by fume hood. Two holes were made on each of control and treatment chambers, for SPME fiber sampling and temperature measurement. The whole system is placed in an enclosure. Since the effect of temperature on extraction efficiency of SPME fibers is considerable (Pawliszyn. 1997), temperature control measures were taken by wrapping the chambers with tygon tubing which was connected with circulation refrigeration bath and by applying heat tapes to the gas conveying pipe between chambers and ovens to prevent condensation.

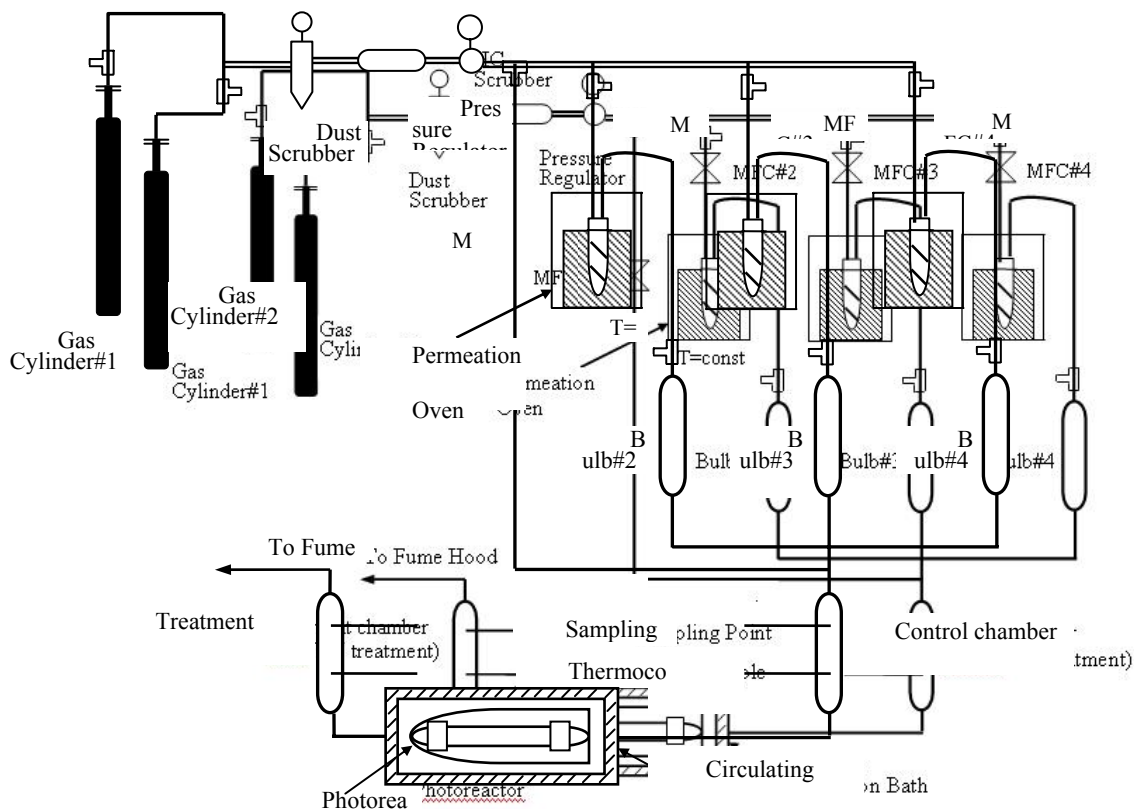


Fig. 1. Standard gas generation and treatment system utilizing permeation tubes and flow through. Permeation tubes that carry unique compounds categorized into three chemical function groups were placed in three ovens at different temperatures, 80 °C for phenolic compounds, 40 °C for VFAs and sulfuric compounds.

2.2 STANDARD GAS CONCENTRATIONS

Standard gas mixtures generation by permeation tubes can be a continuous and reliable technique to generate VFAs (Spinhire and Koziel. 1997). Among 13 compounds, isovaleric acid, skatole, and indole were made on our own, while the left 10 compounds were purchased from VICI Metronics and KIN-TEK laboratory. Under constant conditions, the gravimetric loss of compounds in each tube was measured in triplicates around every four weeks. As shown in Fig. 2. curving mass over time showed a linear relationship between mass and time for 11 compounds with $R^2 > 0.99$ except that the mass of skatole and indole varied widely from time to time, in accordance with previous study (Koziel et al. 2004).

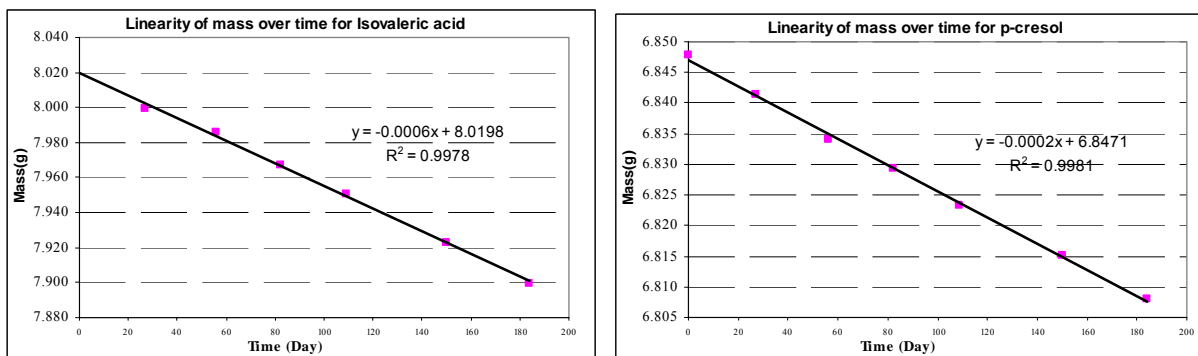


Fig. 2. Weight loss of permeation tube over time for two key compounds responsible for livestock odor, isovaleric acid and p-cresol

The emission rate of each tube was determined by the following equation:

$$E = \frac{\Delta m}{t}$$

Where E is the emission rate of each compound (ng/min), Δm is the average mass loss between two weighing times (ng), and t is the weighing period. Based on the emission rate, the concentration of the gases then can be estimated by the equation:

$$C_{gas} = \frac{E}{Q}$$

Where C_{gas} is the concentration of compound of interest (ng/L), E is the emission rate of each compound (ng/min), Δm is the average mass loss between two weighing times (ng), and t is the weighing period. Based on the emission rate, the concentration of the gases then can be converted to volumn concentration by the equation:

$$C_{ppm} = C_{gas} \frac{RT}{MW \times P \times 1000}$$

Where C_{ppm} is concentration in parts per million (ppmv), R is ideal gas law constant equal to 0.08208 atm.m³/kg.mol.K, P and T are atmospheric pressure (atm) and temperature (K), and MW is molecular weight of each compound (g/mol).

The theoretical concentration based on the emission rate is calculated, with a maximum concentration at 100ml/min flow and a minimum concentration at 5000 ml/min, listed in Table 1. This system can very well simulate the real gas emissions from the livestock operations where VOCs are in very low concentration.

Table 1 the maximum and minimum concentration of compounds generated by the standard gas system

Compounds	E(ng/min)	MW	Max(flow 100ml/min)			Min(flow 5000 ml/min)		
			Cng/ml	Cppm	Cppb	Cng/ml	Cppm	Cppb
Hydrogen sulfide	83.06	34	0.83	0.63	628.65	0.017	0.013	12.57
Methyl mercaptan	68.08	48	0.68	0.36	364.99	0.014	0.007	7.30
ethyl mercaptan	177.70	62	1.78	0.74	737.52	0.036	0.015	14.75
Dimethyl Sulfide	176.33	62	1.76	0.73	731.87	0.035	0.015	14.64
Butyl Mercaptan	86.47	90	0.86	0.25	247.22	0.017	0.005	4.94
acetic acid	309.10	60	3.09	1.33	1325.66	0.062	0.027	26.51
Propionic acid	161.36	74	1.61	0.56	561.11	0.032	0.011	11.22
butyric acid	49.70	88	0.50	0.15	145.33	0.010	0.003	2.91
Isovaleric acid	471.81	102	4.72	1.19	1190.31	0.094	0.024	23.81
p-cresol	144.34	108	1.44	0.34	343.91	0.029	0.007	6.88

The stability of the standard gases in the control chamber was checked daily, and the gas stability was confirmed by the very small variation in MS peak area over time, as shown in Fig. 3 and Table 2. HS-SPME extraction was performed at 10 min, 29°C, based on a 44 day period (from 02-06-07 to 03-11-07).

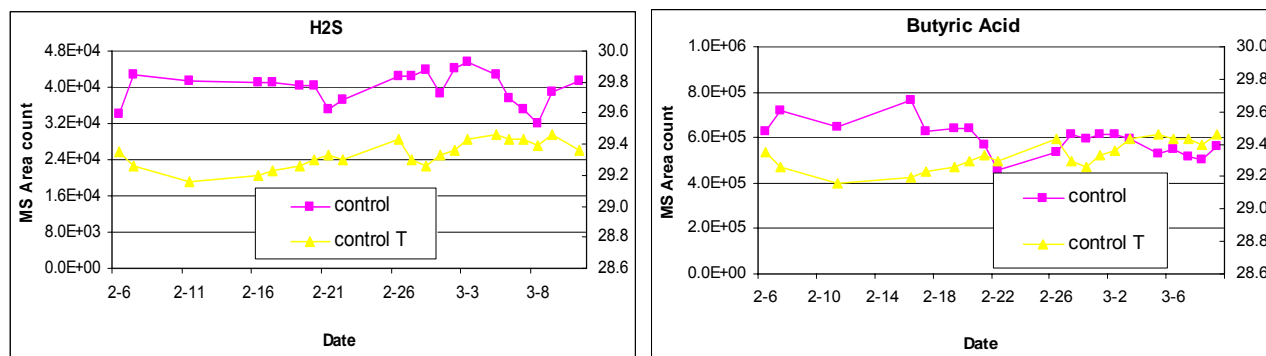


Fig. 3 The stability of selected compounds H₂S and butyric acid over a 44 day period. Gas samples were taken from the control chamber and the inner temperature was recorded daily.

RSDs of MS peak area from GC response based on a 44 day period were shown in table 2. The ethylmercaptan permeation tube was about to run out during this period and thus excluded from this list. A new permeation tube was replaced later. Most of the compounds have a RSD < 10%, while p-cresol showed 16.69% variation within 44 days, probably because the permeation tube was replaced recently and thus has not reached to its equilibrium yet.

Table 2 RSDs of MS area count from GC response of standard compounds within 44 days

Compounds	H ₂ S	MeMercaptan	DMS	BuMercaptan	Acetic	Propionic	Butyric	Isovaleric	p-cresol
RSD%	10.08	10.88	8.53	8.96	5.88	5.06	6.74	3.68	16.69

Thus, the standard gases mixtures generated by the system have consistent concentration as far as the flow rate is kept constantly.

2.3 HS-SPME

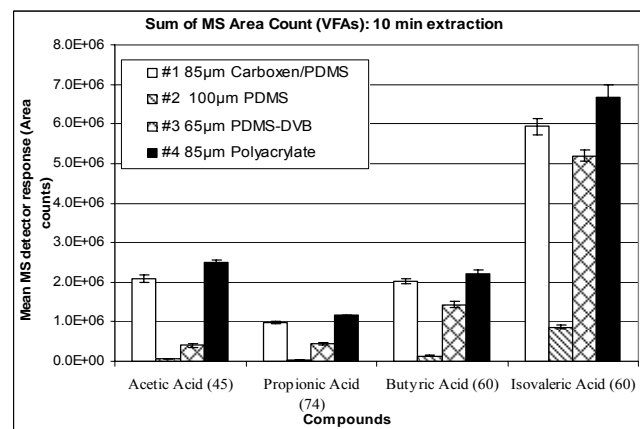
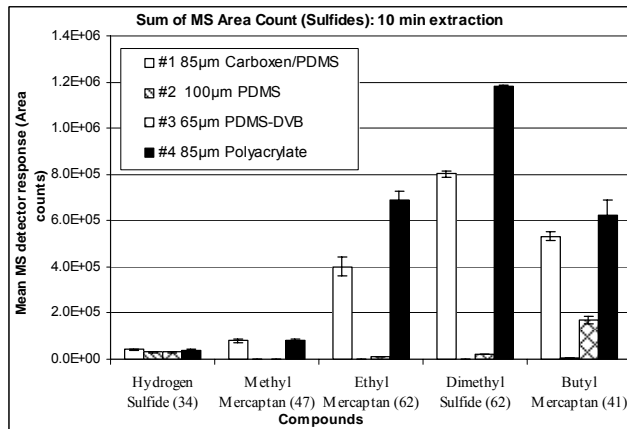
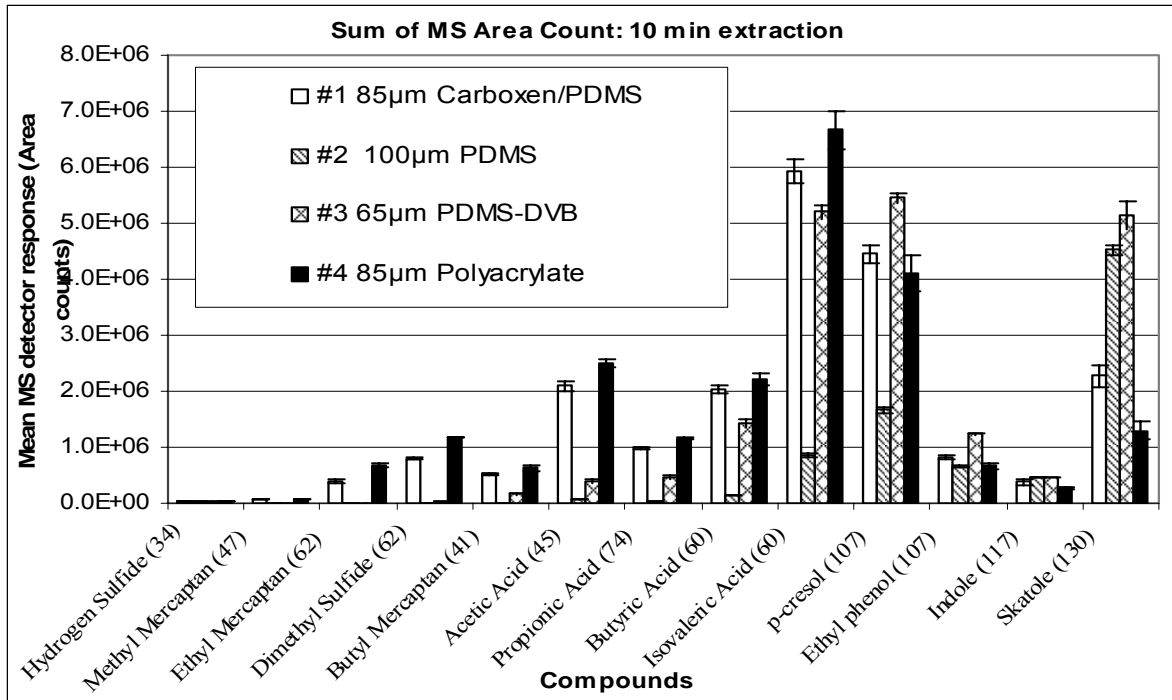
HS-SPME extractions were performed with a SPME fiber coupled with a manual fiber holder from Supelco (Bellefonte, PA, USA). To evaluate the efficiency of SPME coating in trapping VOCs associated with swine odor, four commercial fibers were used. Before use, each fiber was conditioned in a heated GC splitless injection port under Helium flow. After conditioning, SPME fiber was then quickly moved to the sampling port of the chamber of interest in the standard gas system and performed extractions at desired time. Once extraction was done, the SPME fiber was removed from the chamber and immediately inserted into the injection port of GC for analysis. The desorption time of SPME fiber was 40 min at 260 °C.

2.4 OPTIMIZATION OF HS-SPME EXTRACTION

2.4.1. Selection of SPME coating

In this study four different SPME fiber coatings, 85µm Carboxen/PDMS, 65µm PDMS/DVB, 85µm Polyacrylate (PA) and 100µm PDMS, were evaluated for best trapping capacity of swine barn characteristic VOCs by SPME

extraction. Standard gas mixtures from the standard gas generation system were extracted at 29.5°. Extraction time was 10 min, and the extractions were performed continuously within one day to rule out the error due to gas variability between days. Comparison of extraction efficiency by the four SPME coatings was shown in Fig. 4. For both sulfides and VFAs, 85µm PA has the best extraction capacity based on 10 min extraction, and 85µm Car/PDMS followed next. PDMS/DVB fiber was the best extraction fiber for phenolic compounds, and Car/PDMS also showed a very good extraction. PDMS/DVB fiber, however, was really poor in trapping sulfides and had much lower extraction capacity for VFAs than Car/PDMS, and was not considered for extracting all compounds. The method development for groups of analytes requires the primary consideration be given to the most difficult analytes and should be based on overall extraction efficiency ((Pawliszyn. 1997), therefore, because of its overall performance on extracting all the compounds, 85µm Carboxen/PDMS was selected to do all the following extractions in this study.



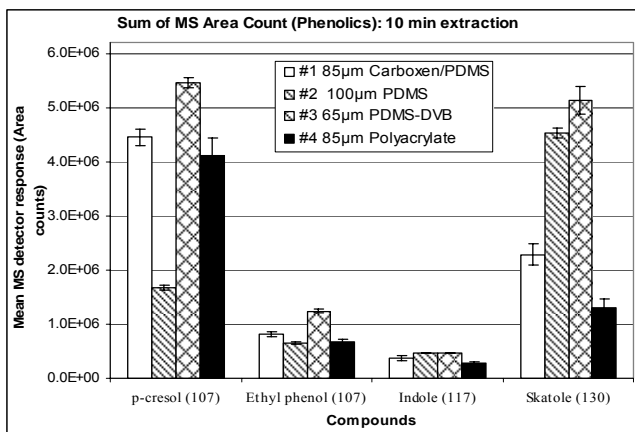
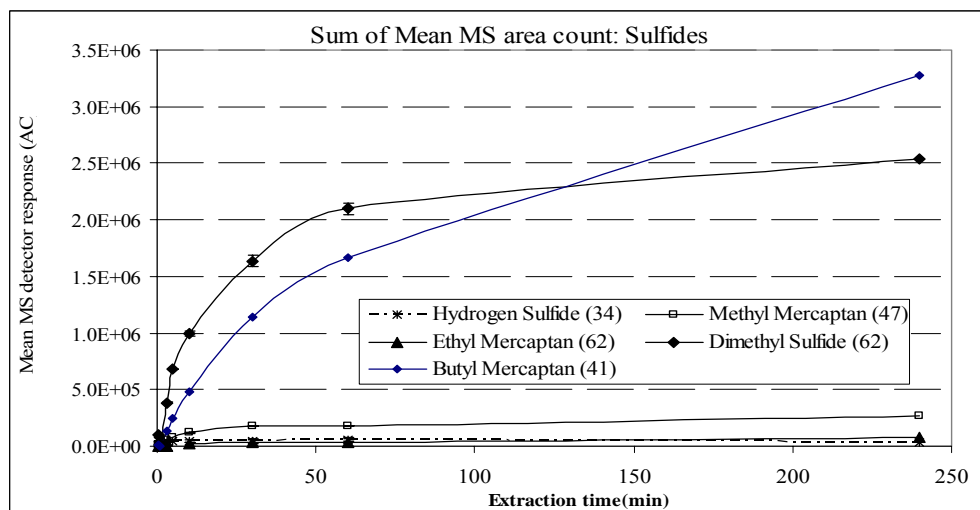


Fig. 4. Comparison of extraction efficiency of four different fibers (Carboxen/PDMS, PDMS/DVB, PA and PDMS) for standard gas mixtures characteristic of swine barn odor. Extractions were conducted at 29.5 for 10 minutes.

2.4.2 Effect of extraction time

Experiment was performed in triplicates at an 8-point time series basis ranging from 30s to 4h to evaluate the effect of extraction time, and the mean GC response was curved over extraction time, as shown in Fig. 5, VFAs and p-cresol showed very good linearity in the time period 30s~4h, with $R^2 > 0.9062$ (acetic, 0.9469; propionic, 0.9686; butyric acid, 0.9843; isovaleric, 0.9026; p-cresol, 0.9939). Sulfuric compounds also showed linearly increasing extraction efficiency over a shorter period of time, when using 0.90 as R^2 cutoff, 30s~10min for methyl mercaptan ($R^2=0.9238$) and DMS ($R^2=0.938$), 30s~4h for butyl mercaptan ($R^2=0.9108$), however, the linear range for H_2S was much shorter ($R^2=0.9108$ for 30s~3min and $R^2 < 0.5$ for any longer period of time). Very small increase was found for methyl mercaptan and hydrogen sulfide at longer extraction time, which was due to their low affinity for fiber and they would eventually lose their place in competition with compounds with higher affinity. Hence 10 min extraction was chosen for most of the analyses in this work.



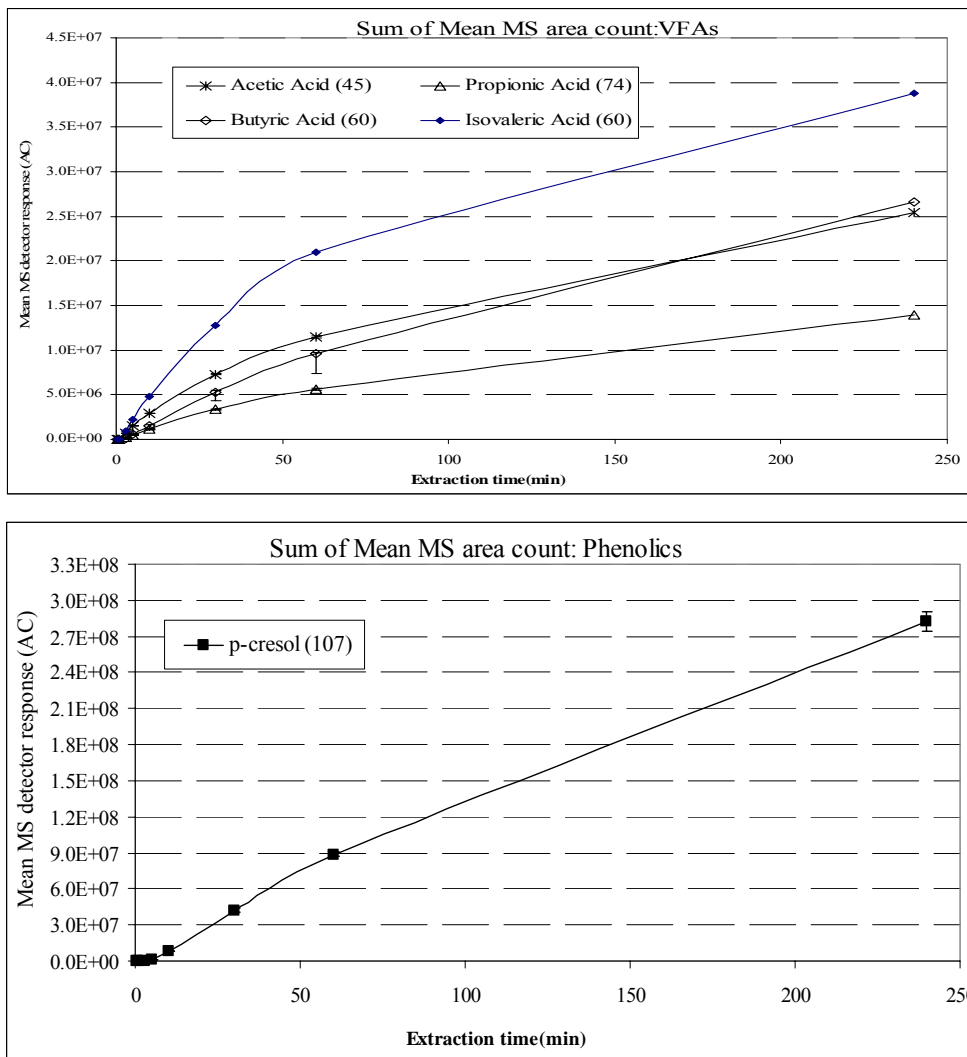


Fig. 5. Effect of extraction time on mean MS detector response using 85 μ m Carboxen/PDMS fiber at 29.5 $^{\circ}$ C at 8-point time series, 30s, 1m, 3m, 5m, 10m, 30m, 1h and 4h, respectively.

Aroma event detected by the panelist showed most of the compounds reached to its odor detection upper limit by the human nose and the odor intensity did not change much with extraction time longer than 30 min, because these compounds have a very low odor detection threshold, and gases containing a trace level of these compounds could be very odorous.

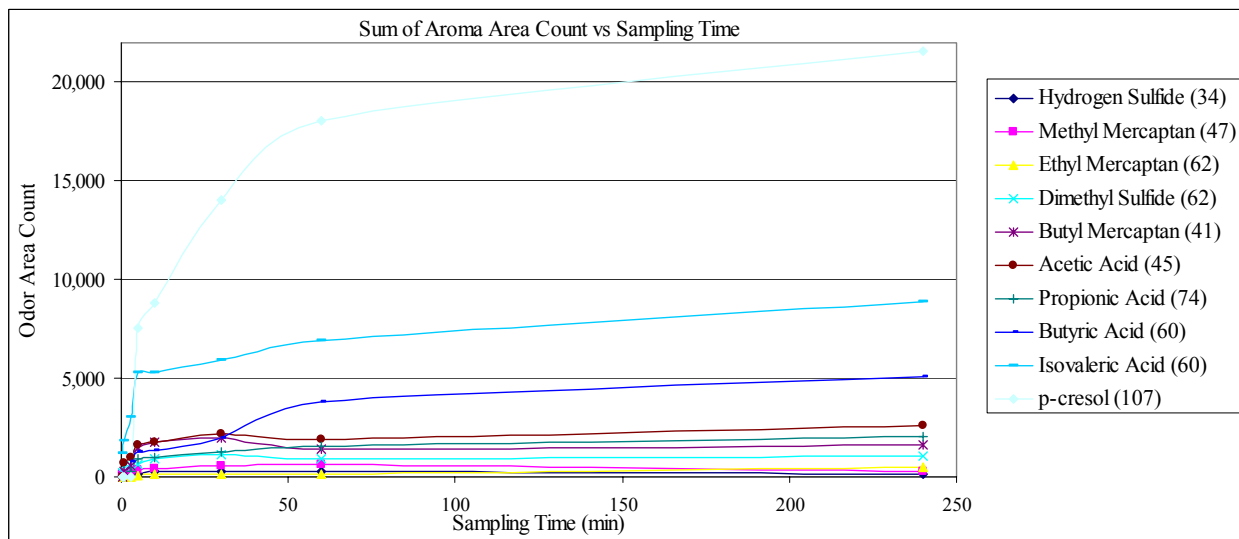
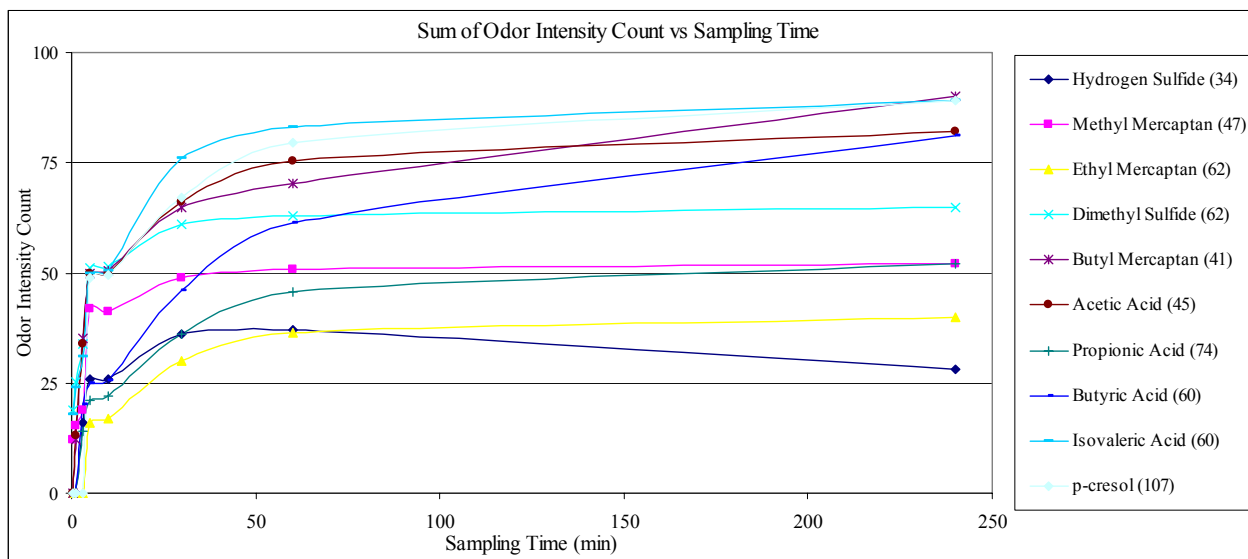


Fig.6. Effect of extraction time on odor intensity and odor area count using 85 μm Carboxen/PDMS fiber at 29.5 at 8-point time series, 30s, 1m, 3m, 5m, 10m, 30m, 1h and 4h, respectively.

2.5 GAS CHROMATOGRAPHY-MASS SPECTROMETRY-OLFACTOMETRY (GC-MS-O) SYSTEM

Multidimensional GC-MS-O (Microanalytics, Round Rock, TX, USA) was used for all analyses. The system integrates GC-O with conventional GC-MS (Agilent 6890N GC/5973 MS from Agilent, Wilmington, DE, USA) as the platform with the addition of an olfactory port and flameionization detector (FID). The system was equipped with a non-polar pre-column and polar column in series as well as system automation and data acquisition software. Full HC mode was used for all analyses in this research. The oven temperature begins from 40 ° C and holds for 3 min then increases at 7 ° C/min to 220 ° C, and finally holds for 10 min at 220 ° C. Helium is used as the carrier gas. Mass/molecular weight-to-charge ratio (m/z) range was set between 33 and 280. Spectra were collected at 6 s and electron multiplier voltage was

set to 1000V. The MS detector was auto-tuned weekly.

Since in our SGG system, all standard compounds have known retention time and known odor. To improve the accuracy, SIM (Single Ion Mode) was used if identification of compounds was not required. Identification was only needed for UV treatment experiment, when compounds were positively identified when all of the three criteria were met: (1) the retention time on the MDGC capillary column, (2) mass spectra by MS library from Bench-Top/PBM (from Palisade Mass Spectrometry, Ithaca, NY, USA), and (3) odor character. VOC abundance was measured as area counts under the MS peak, and odor was accessed by sniffing with human nose, with detection of odor character, odor intensity and odor area by multiplying odor intensity and odor lasting time for separated VOCs.

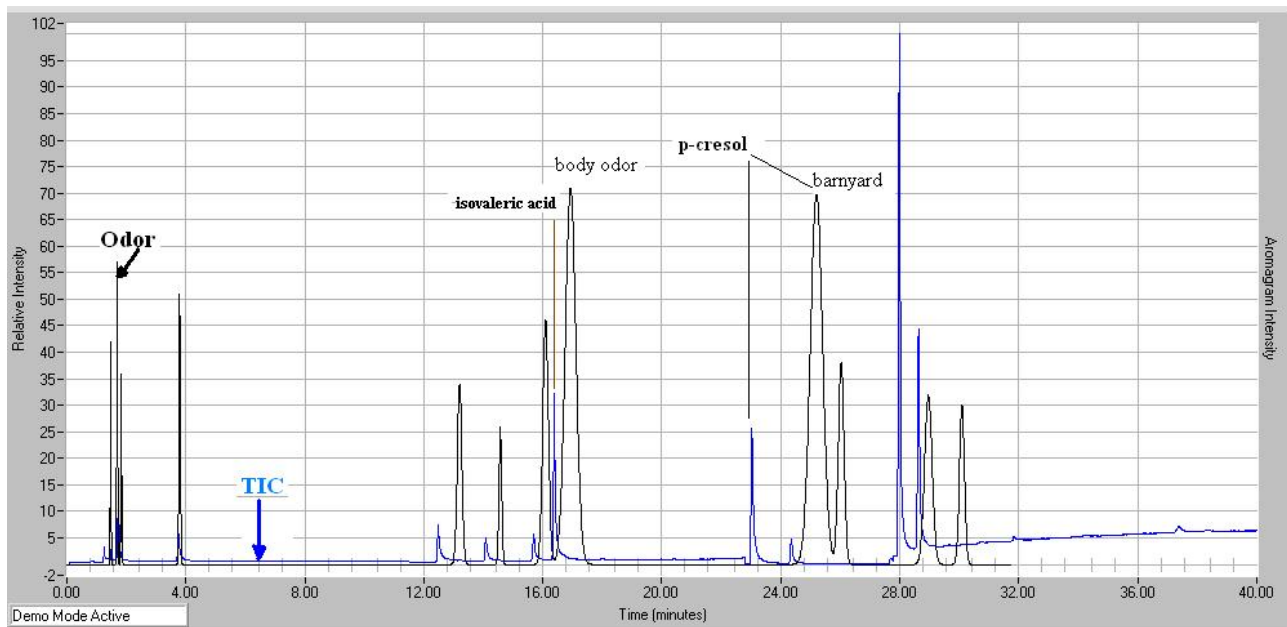


Fig. 7. Simultaneous chemical (TIC) and odor (aroma event) analysis of standard gases using GC-MS-O: linking VOCs and odor

3. RESULTS AND DISCUSSIONS

3.1 UV EFFECT ON CHEMICAL REDUCTION

3.1.1 UV effect on typical TIC/aromagram

Using our GC-MS-O system, TIC and aromagram was obtained for the gas samples from control chamber and treatment chamber with three compounds, methylmercaptan, butyric acid and p-cresol to evaluate the degradation rate of UV light, shown in Fig. 8. Obvious reduction in MS peak area was found for all of three compounds, especially for p-cresol, which smells like barnyard. Reduction in aroma peak area and odor intensity indicates UV is an effective way for odor reduction in livestock operations. It is very desirable to eventually break down VOCs into non-odorous gases such as

CO₂, however, some new odorous compounds were generated at the same time, such as acetic acid and propionic acid in the photolysis process. The reaction mechanism will be discussed a little further later.

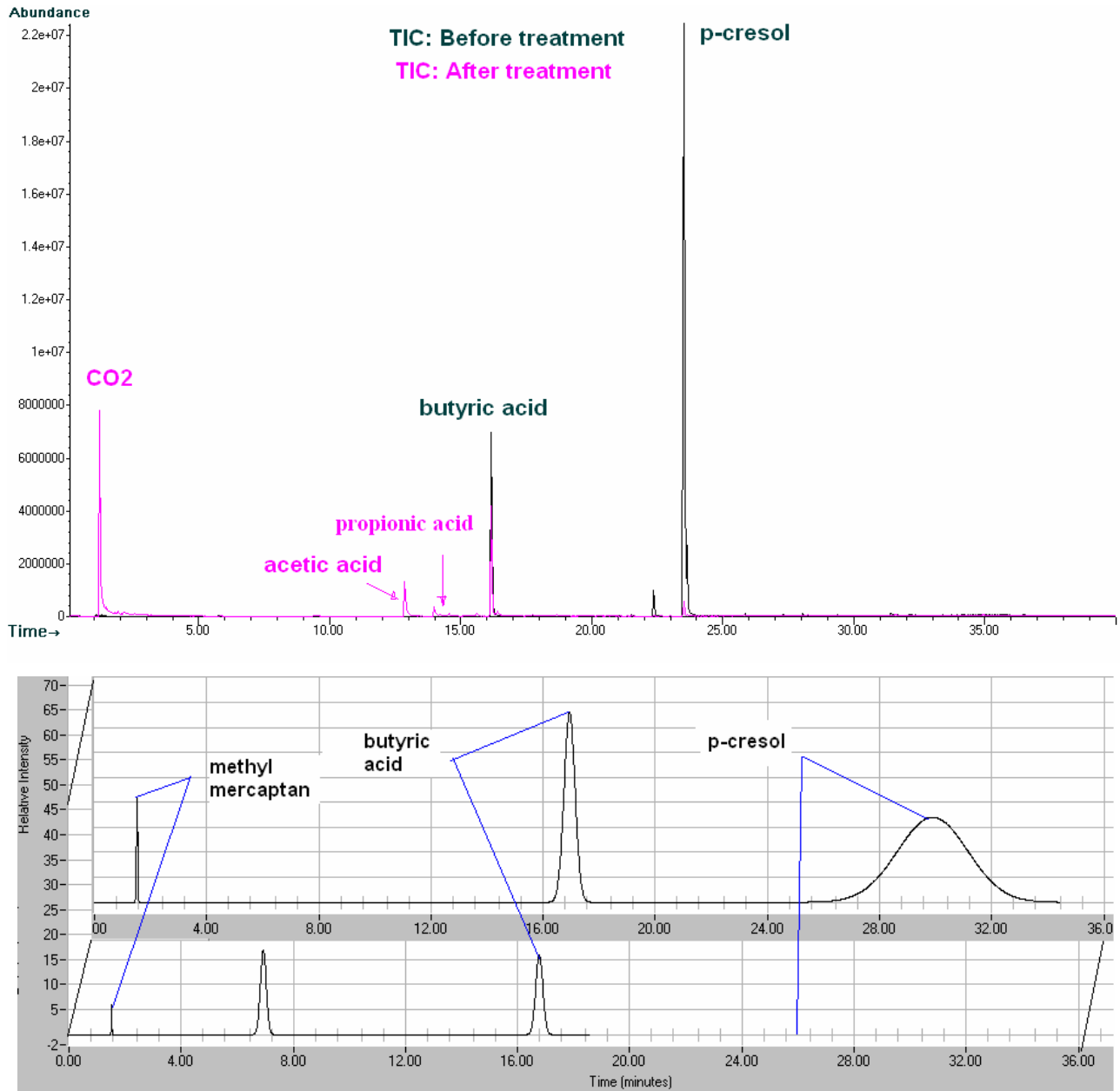


Fig. 8 UV effect on aromagrams of standard gas mixtures characteristic of swine manure odor

3.1.2 UV effect on chemical reduction

When the total flowrate was 400 ml/min, at 10min extraction, reduction rate for methylmercaptan, butyric acid and p-cresol was 96.2%, 48.15%, 92.16%, respectively, on chemical concentration. At 24hr extraction, reduction rate for methylmercaptan, butyric acid and p-cresol was 99.987%, 62.78%, 96.23%, respectively, on chemical concentration.

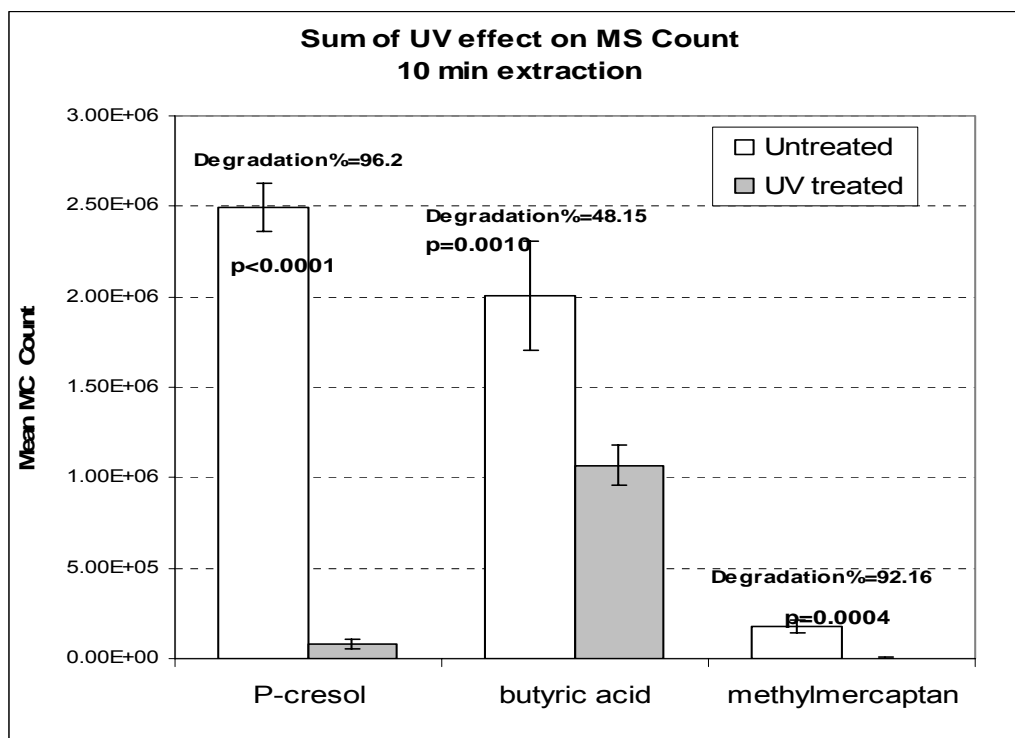


Fig. 9 UV effect on MS peak area count of standard gas mixtures characteristic of swine manure odor, Reaction time=5.81s

3.1.3 Effect of flowrate on reduction rate of p-cresol

To better simulate swine barn emissions and evaluate flowrate effect on UV degradation rate, gases were extracted at higher flowrate, 1150ml/min, 2150ml/min and 3150ml/min. The result showed reduction rate decreased as flowrate increased, but still a very good reduction rate of 79.07% on chemical concentration for p-cresol was obtained at flowrate 3150ml/min, which further verified the powerful treatment effect of UV light on VOCs and odor and feasibility of extending this technique to field applications.

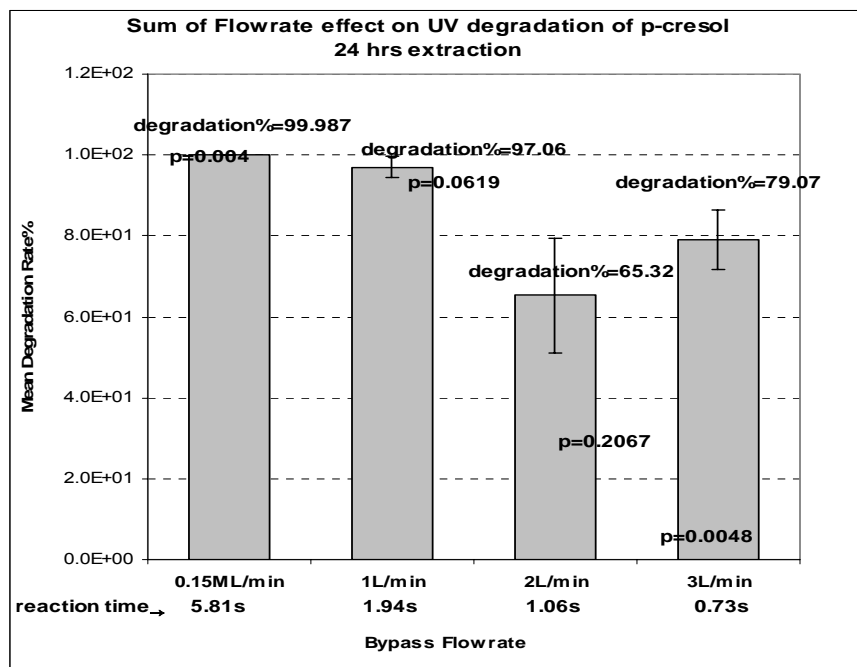


Fig. 10. Flowrate effect on reduction rate of p-cresol using UV light

3.2 UV EFFECT ON ODOR REDUCTION

When the total flowrate was 400 ml/min, at 10min extraction, reduction rate for methylmercaptan, butyric acid and p-cresol was 98.4%, 51.1%, 38.9%, on odor area count and 81.48%, 44.69% and 73.36% on odor intensity count. 24hr extraction gave reduction rate of 74.66%, 45.06%, 93.56%, on odor area count and 69.93%, 40.01% and 88.66% on odor intensity count.

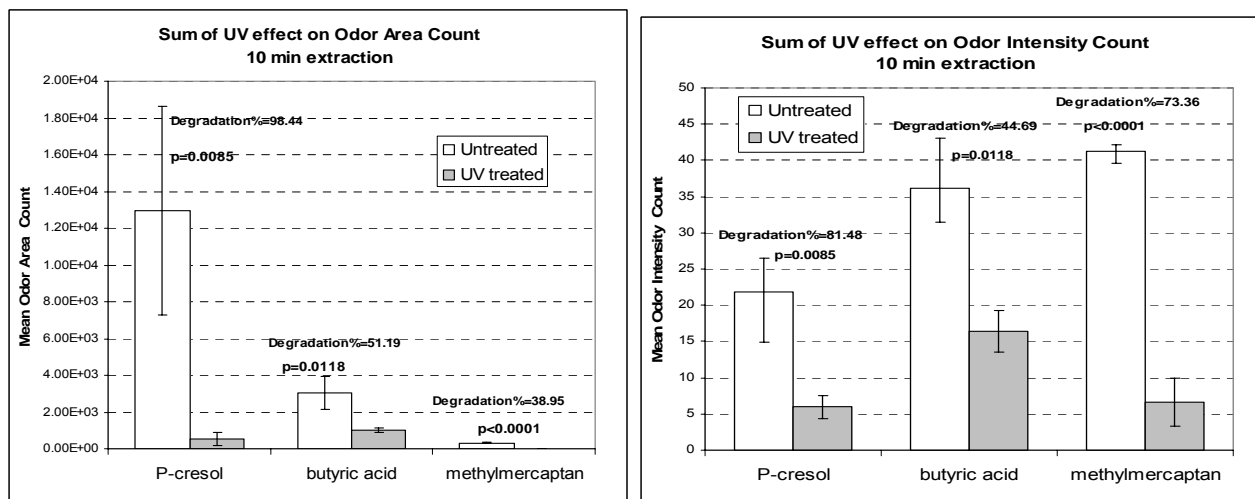


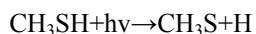
Fig. 11. UV effect on odor area count and odor intensity count of standard gas mixtures characteristic of swine manure odor,

Reaction time=5.81s

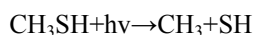
3.3 PRELIMINARY RESEARCH ON CHEMICAL MECHANISM INSIDE UV PHOTOREACTOR

Preliminary results have been drawn based on literature review on possible pathways of UV photolysis of methylmercaptan, butyric acid and p-cresol and match of reaction products identified by GC-MS. A 24 hr extraction of gases before and after UV treatment was performed and then analyzed by GC-MS. The compounds identified were listed in table 5.

The dominant reaction pathway for the photolysis of methylmercaptan with UV light is the breaking of the S-H bond (Segall et. al, 1993):

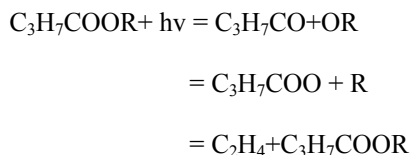


Followed by C-S bond breaking as the second dominant pathway:



Combination of free radicals then formed into dimethylsulfide (Vaghjian et.al, 1993), which was found in the treatment gas sample. Further oxidation of those free radicals will produce DMSO₂ (Tevault et.al 1981), which will probably further react with the free radicals and form into methyl sulfone as confirmed by GC-MS in this work.

The photolysis of n-butyric acid was found to have the following primary reactions (Borrell et al, 1961):



It is well known that solar radiation with wavelength < 242 nm can break the molecular oxygen back into oxygen atoms, $\text{O}_2 \rightarrow \text{O} + \text{O}$. One of these oxygen radicals in turn can combine with O_2 to form ozone, $\text{O}_2 + \text{O} \rightarrow \text{O}_3$, which will in turn react with VOCs. The identification of many new compounds by GC-MS showed there was great possibility these three compounds reacted with each other even before UV light on. That will make the whole chemical mechanism more complicated. To our best knowledge, there's no literature about the breakdown of p-cresol in gas phase without presence of catalyst and OH radicals so far. Further experiment will be designed to figure out the mechanism for photolysis of only one compound each time.

Table 4 List of compounds identified from 24 hr extraction

RT	RT(MSL)	compound	MS Match		MS Count	
			control	treat	control	treat
1.32	1.38	methylmercaptan	83		2,395,008	
1.80	1.88	acetone		74		937,829
2.15	3.18	sulfur dioxide	83	76	1,064,023	937,829
2.47	2.51	butanal		76		19,268,576
2.51		tetrahydro,furan		76		216,876
3.60	3.66	diacetyl		50		509,275

4.38	4.32	butanoic acid,methyl ester	74	81	68,369	251,180
5.35	5.23	ethenyl-cyclohexane	85		63,459	
5.42	5.60	toluene	88	68	149,097	154,166
5.70	5.83	dimethyl disulfide	68	83	1,972,352	130,308
8.36		butanoic acid,propyl ester		72		41,354
9.15	9.03	butanethioic acid,S-methyl ester	63		39,364	
10.01	10.06	styrene	88		24,948	
10.58		cyclohexanone	74		35,349	
10.88		butanoic acid,butyl ester	72		39,976	
12.54	12.56	dimethyl trisulfide	75		37,413	
12.92	13.18	acetic acid	83	86	365,641	22,921,948
14.54	14.88	propanoic acid		93		1,084,282
15.63		2-cyclopentene-1,4-dione	85	93	99,216	856,249
16.17	16.51	butyric acid	93	94	147,613,702	56,093,052
16.32		2-propenoic acid		63		827,026
16.41		dihydro-2[3H]-furanone		83		2,346,666
16.94	16.81	methanesulfonic acid,methyl ester	86	88	72,943	591,840
17.31		methanesulfonic acid,ethyl ester		68		106,359
17.57		2-butenic acid		81		219,443
18.07		pentanoic acid		54		459,083
18.18		3-butenic acid		85		129,991
18.62		acetic acid,4-methylphenyl ester	94		514,536	
18.63		2-butenic acid,[E]-		85		806,487
18.98		2-pentanol		59		706,740
19.04	18.88	naphthalene	75		35,786	
20.73		3-methyl-2-cyclohexen-1-one		83		134,289
20.89	21.06	Methyl Sulfone		93		276,423
21.40		butanoic acid,4-methylphenyl-ester	88		176,034	
21.53		2-methyl-4-methylphenyl-ester-propanoic acid	91	63	6,092,264	56,829
22.35		2-methylphenol	93		6,832,205	
22.43		4-hydroxy-benzenesulfonic acid		58		171,926
23.49	23.85	p-cresol	95	95	307,871,578	4,324,391
23.53		2,6-dimethylphenol	95		2,248,215	

4. CONCLUSIONS

A novel method has been built up for treatment of livestock odor and VOCs by UV photolysis. VOCs associated with swine odor, including sulfuric compounds, volatile fatty acids and phenolic compounds, were generated by a standard gas generation system at a constant temperature and then treated by UV light. SPME as a very effective gas sampling method was used, and gas samples were sent to GC-MS-Olfactory system for simultaneous chemical and olfactory analyses.

Carboxen/polydimethylsiloxane (PDMS) 85µm fiber and 10 min extraction was used. The comparison between the MS area from GC response of samples with UV light off and on showed that UV photolysis resulted in a reduction rate of

96.2%, 48.15%, 92.16% for methylmercaptan, butyric acid and p-cresol respectively on chemical concentration, and 98.4%, 51.1%, 38.9%, on odor area count and 81.48%, 44.69% and 73.36% on odor intensity count when the total flowrate was 400 ml/min, at 10min extraction. At higher flowrate, UV photolysis still showed a very good degradation rate 79.07% for p-cresol on chemical concentration at flowrate 3150ml/min. Thus, UV photolysis is powerful for treatment of livestock odor and VOCs, and could be very potentially extended to field applications.



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