

ORIGINAL ARTICLE

Comparison on Usefulness of Sampling Methods of Indoles in Airs from Swine Facility by Tenax-TA and SPME

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Abstract

The purpose of this study is to compare the sampling methods for monitoring indoles (phenol, p-cresol, indole and skatole) in air of swine facility. As the collecting methods of indoles in air, Tenax-TA adsorption tube and solid phase microextraction (SPME) were examined. For the preparation of calibration curves of indoles concentrated in Tenax-TA, the standard indoles solutions were spiked in each of Tenax-TA tubes and thermally desorbed (ATD) into a gas chromatograph combined with mass detector (GC/MS). And for the preparation of calibration curves by SPME, indoles in the standard gaseous solution prepared by evaporating the aqueous solution that contained indoles into a polyester sampling bag were extracted with SPME fiber and subsequently analyzed by the GC/MS. Two sampling methods were evaluated for extracting indoles present in swine building environments. Results indicated that the SPME method using Polydimethylsiloxane/ Divinylbenzene (PDMS/DVB) fiber was more effective than Tenax-TA method in extracting indoles. The gas chromatographic analysis showed that the linearities of calibration curves and detection limits were useful for detection of indoles in swine air. The field tests also showed that considerably different levels of indoles were present in various parts of the swine building.

Key words : Swine odor, Indoles, Tenax-TA, SPME

1. Introduction

Odors from piggeries and slurry spreading operations have increased complaints among citizens in communities near livestock (Yu, 2004) and several measures for reduction of offensive odors had been proposed (Yu, 2012). It is generally accepted that the probiotic additive mixed in feed result in a reduction in excretion of substrate for production of odors (Kim, et al, 2003 ; Lee, 2008 ; Hong, 2007). But the debatement efficiencies of odors have been scarcely improved, probably due

to the complexity of analyzing the odorants such as ammonia, volatile nitrogen compounds like trimethyl amine, hydrogen sulfide, mercaptan and volatile fatty acids (Tanaka et al, 1991), whose odor threshold values are extremely low. Recently, emission of these odorants have been regulated by the offensive odor prevention law, and thus attempts to characterize the odors from swine facilities by analytical evaluation of odorants have been increased in literatures (Oh et al, 2006 ; Ko et al, 2013 ; Hobbs et al, 1995 ; Zhang et al, 2010).

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Although phenol, p-cresol, indole and skatole, which are named as indoles (Willig et al, 2004), are known to be the key odorants of swine wastes in addition to the volatile fatty acids (Hoob et al, 1999), few analytical examples of indoles from the airs of swine facility were found in literatures. And even now, their emissions are not regulated in the offensive odor prevention law. So far, we have studied the quantification methods of indoles in the airs of swine facilities.

As the method of analysis of airborne indoles which contribute to a varying degree to the malodor of swine slurry, adsorption of indoles in Tenax tube or carbon molecular sieve and subsequent analysis with a gas chromatograph are described in papers (Hoshika et al, 1978 ; Zahn et al, 1997). US EPA (Environmental Protection Agency) presents TO-01 and TO-02 for the official method of analysis of indoles in air (EPA, 1999). And also National Institute of Occupational Safety and Health (NIOSH, 1996) states the air sampling method of volatile organic compounds including indoles. But these have the problems such of poor separation efficiencies because of using a packed column and long sampling time for collecting the large volume of airs due to the very low odor threshold values of indoles.

Because of simplicity, easiness, sensitivity and no need of solvent, the extraction method of volatile organic compounds by SPME (abbreviation of solid phase microextraction), that was invented 1990, has been developed in a lot of application fields. And it was confirmed that SPME is effective for collecting indoles from the slurry such as cattle manure (Larreta et al, 2006). Though dynamic air sampling method for collecting indoles by SPME was suggested by Razote et al (2002), it is inconvenient to extract indoles in air onsite. And it would be not easy to evaluate the concentrations of odors from swine facilities that vary by the minute.


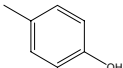
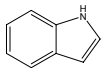

Thus, we attempted to compare the two sampling methods of indoles in airs from swine facilities ; one is the adsorption of indoles in airs to Tenax tube, desorption by automatic thermal desorber and consequently gas chromatographic analysis and the other is collection of indoles in airs desorption into gas chromatography, and suggest the usefulness of usefulness of each method.

2. Materials and methods

2.1. Chemicals and experimental equipments

Target compounds used in this study are characterized

Table 1. Characterization of the target odorous compounds

Substance	b.p.(°C)	Vapor pressure, p_o (hPa) ^a	Solubility in water ^a (g/100 mL)	M_r (gmol ⁻¹)	Structure
Phenol	181.7	0.351 (at 25 °C)	8.3	94.11	
p-Cresol	203	0.060 (at 25 °C)	2.4 (at 40 °C)	117.2	
Indole	254	0.016	0.19	108.1	
Skatole	266	0.020	Sparingly soluble	131.2	

M_r ; Molar mass

^a Vapor pressure and water solubility at 20 °C

in Table 1. Phenol and p-cresol are basically phenolic substances which was allocated to the category of indoles due to their similar physical/adsorption characteristics and the possibility of a simultaneous chromatographic determination together indole and skatole. They were obtained from Duksan Chemical in Korea (Junsei 99% GR, phenol) and Aldrich-Korea (p-cresol, indole and skatole), and 99.5% ethanol (Wako Pure Chemicals Industries, Ltd.) for dissolving indoles was obtained from Duksan Chemical (Seoul, Korea). All standards were used as received.

Polyester bags (manufactured at OMI Odor-Air Service, Japan) were used for collecting odorous airs in swine houses. Sampling bags were always cleaned by the clean air before use.

Preconditioned Tenax-TA tubes (Supelco Cat. No.: 25055) were purchased from Supelco for collecting indoles in airs from swine facilities. Before the first use, sorbent tubes were conditioned by thermal desorption under a 100 mL/min flow of N₂. For subsequent uses, pre-conditioning at 260°C for 30 min was tested as sufficient and applied for all tubes. The indoles obtained from Tenax tube were thermally desorbed by an automatic thermal desorber (Turbo-Matrix ATD 350, Perkin Elmer) and analyzed by a gas chromatograph combined with mass detector (Claus 500 Gas Chromatograph Mass Spectrometer, Perkin Elmer). Desorption temperature of ATD was set at 250°C. HT-8 (0.22 mm × 0.25 µm × 50 m, Supelco) was used for separation column. Temperatures of injection port, oven and detector were set at 250°C, 150°C, 280°C, respectively. The carrier gas was helium at 1 mL/min. The mass spectrum from each

chromatographic peak was compared with the spectra of indoles standards to identify the species of the compound. The TIC (total ion chromatogram) of each peak was integrated. The quantity of the compound was calculated by using a standard-calibration curve.

The SPME system, including reaction vials, extraction stand, holder, and fibers (100 mm Polydimethylsiloxane (PDMS), 75 mm Carboxen/Polydimethylsiloxane (CAR/PDMS), 65 mm Polydimethylsiloxane/Divinylbenzene (PDMS/DVB), Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS)) were purchased from Sigma-Aldrich Korea. The indole from SPME were analyzed by Varian 450 Gas Chromatograph equipped with mass detector (Varian 220MS). The compounds were separated on a fused silica SPB-608 capillary column (30 m × 0.25 mm × i.d. 0.25 mm; Sigma-Aldrich Korea). The carrier gas was helium at 1 mL/min. Desorption time was 3 min. The oven temperature was programmed as follows: initial temperature of 70°C, followed by a 4°C/min temperature increase to 250°C and held for 2.5 min. The injection port equipped with a 0.75 mm i.d. glass liner was set at 250°C, and MSD transfer line temperature was 280°C, respectively.

2.2. Experimental procedure

2.2.1. Preparation of standard solution

A standard stock solution consisting of 0.0078 g of phenol, 0.0136 g of p-cresol, 0.0132 g of indole and 0.0134 g of skatole was prepared at room temperature by dissolving the compounds in 1.0 mL of ethanol, diluting with distilled water and bringing the volume to 100 mL. To dissolve indole and skatole, the mixture

Table 2. Compositions of the Standard Working Solutions (ug/mL)

Compound	1.0 mL	2.0 mL	3.0 mL	4.0 mL	5.0 mL
Phenol	3.12	6.24	9.36	12.5	15.6
p-Cresol	5.44	10.9	16.3	21.8	27.2
Indole	5.28	10.6	15.8	21.1	26.4
Skatole	5.36	10.7	16.1	21.4	26.8

was heated to 70°C with intermittent shaking. Standard working solutions (25.0 mL) were prepared by diluting 1.0, 2.0, 3.0, 4.0 and 5.0 mL of the standard stock solution with 24.0, 23.0, 22.0, 21.0 and 20.0 mL distilled water (Table 2.), respectively. The standard working solutions were used for determining detector response factors and preparing calibration curves. All standard solutions were stored in a refrigerator (4°C) when not in use.

2.2.2. Calibration curves for the Tenax tube method

Compounds obtained from the standard solutions were tentatively identified first by their retention times with direct injection of 1.0 µl of each compound dissolved in the working solution. Calibration of sorbent tubes was performed as follows. 1.0 µl of each standard working solution was spiked into a sorbent tube and then pure N₂ gas was flowed in the tube at 50 mL/min for 5 min. The spiked tube was equipped in ATD and desorbed into GC/MS.

2.2.3. Selection of SPME fiber

Solid phase micro-extraction follows the principle of equilibrium extraction. The amount of chemical compounds in the sample matrix and the quantity of the compounds absorbed in the stationary phase on the SPME fiber is related to an equilibrium status at experimental condition. The combination of extraction time, reaction temperature and sample air are the essential factors determining the extraction conditions. Instead of finding the optimal extraction conditions, our goal for this experiment was to develop a feasible and reproducible extraction condition for indoles analysis of the air of swine facility. The equilibrium state of the SPME is described by the equation below (Yo, 1999).

$$N_i = KC^0V_i$$

Where N_i is the amount of i compound in the stationary phase. C^0 is the concentration of i compound in air, and V_i is the volume of the stationary phase. In

this study, V_i is constant. Therefore, the K value of each compound represents the adsorption efficiency of the fiber to extract the compound from the air. Variability of each K value from each experiment is related to the adsorption ability of SPME fiber and experimental condition.

To test the effectiveness of SPME fibers in extracting indoles of the standard solution in a 20 mL vial, four SPME fibers (100 mm PDMS, 75 mm CAR/PDMS, 65 mm PDMS/DVB and 65mm DVB/CAR/PDMS) were utilized in a preliminary investigation. The SPME fibers were conditioned as recommended by the manufacturer prior to their first use. In order to find the stability of each adsorption time period, we designed an experiment with fiber extraction time periods of 10, 20 and 30 minutes before thermal desorption. The results demonstrated that as time increased so did the amount of indoles extracted by SPME fiber, but prolonged extraction time decreased experimental efficiency. In this study, 30 minutes was chosen as the extraction time for indoles. Needle of each SPME assembly pierced the septum of the vial and the fiber was extended through the needle so that extraction took place in the head space of the standard working solution. The fiber was exposed to the solution for 30 minutes at 25°C in a water bath and then withdrawn into the needle. Once the extraction/derivation period was over, the fiber was withdrawn into the needle, removed from the vial and inserted into the hot injection port of GC. Since boiling points of indoles are very high (phenol, 181.7°C ; p-cresol, 203°C ; indole, 254°C ; skatole 266°C), we analyzed the fiber after desorption and found no compound remaining in the fiber after a 3 minute desorption period. Therefore, it was confirmed that a thermal desorption time of the 3 minutes is sufficient to force the compound out of the fiber. 5 point calibration curve for each fiber was made by directly injecting the fibers into the gas chromatography/mass spectrometer (GC/MS).

2.2.4. Calibration curves for the SPME method

The gaseous standard solutions were prepared by adding a few microliters of the liquid standard solutions into 10.0 L polyester bags, heating them at 80 °C for 20 minutes and leaving them to reach ambient temperature. Before SPME concentration in a fiber, the standard gas was warmed in a oven at 25 ± 1 °C for 15 minutes, and then the fiber inserted into the gas bag through the Teflon cock and remained for 30 minutes. The adsorbed fiber was then retrieved into the needle of the fiber assembly. Once desorption period was over, the fiber was baked in a hot auxiliary injection port for 3 minutes at the conditioning temperature of each fiber. The adsorbed fiber was then retrieved into the needle of the fiber assembly. The detection limit study was carried out by performing seven replications of samples at the concentration of the lowest calibration point. All laboratory and field sampling were carried using three replications.

2.2.5. Field sampling

Field sampling were done at a pig house, in Geochang of Kyongnam Province, Korea, containing 40 growing pigs on area of 80 m² and a room height of 2.5 m, consequently the air volume was 5.0 m³ per pig. This volume is therefore in the normal range for pigs under fattening conditions in Korea. Fresh air

was provided by forced ventilation fans. Three locations at the facility were chosen for sampling sites: 1.5 m above the floor in the house (sampling point A), at the outlet of the exhaust fan (sampling point B) and at the borderline of the pig house (sampling point C). Temperatures, humidities and wind speeds at sampling sites are presented in Table 4.

In order to study the usefulness of Tenax-TA for analyzing indoles in swine facility, 50 L, 100 L and 200 L of the air of the pig house (A) were passed through the Tenax tubes by use of a portable vacuum pump with a set flow rate of 5.0 Lmin⁻¹. Total amount of air passing the tube was measured with a dry gas meter (DC-1 Kawasaki, Japan) that was connected to the outlet of the sorbent tube. Simultaneously, several polyester bag (10 L) for SPME analysis were fulfilled with the air taken at same sampling point using a handy pump (Flex-Pump DC-NA, OMI Odor-Air Service, Japan). The handy pump was connected with Teflon tubing to minimize VOC adsorption on their walls. The airs of the other two sampling points (B and C) were collected for the analysis. All sample tubes and bags were delivered to the laboratory and followed by storage 4 °C, and analysis within 7 days. The sampled tubes were equipped in ATD and desorbed into GC/MS.

Table 3. Gaseous standard solutions of indoles in PET bag ($\mu\text{g/L}$)

Compound	10.0 uL	20.0 uL	30.0 uL	40.0 uL	50.0 uL
Phenol	128	256	384	512	640
<i>p</i> -Cresol	131	262	393	524	655
Indole	147	294	441	588	735
Skatole	135	270	405	540	675

Table 4. Weather condition at sampling sites

Sampling site	Temperature(°C)	Humidity(%)	Wind speed(m/s)
Inside the pig house (A)	24.1	62.4	0.2
Outlet of the exhaust fan (B)	25.1	57.0	3.7
Borderline of the pig house (C)	26.3	50.1	0.4

To extract the indoles in sample bags with the SPME fiber (PDMS/DVB coating), the SPME needle was inserted into the sampling bag through the Teflon cock and the fiber was exposed for 30 minutes. The exposure depth of the SPME fiber in the sampling bag was maintained for all sampling by keeping the holder needle to 1 cm below the Teflon cock. After concentration on the fiber, the fiber was retracted in the holder and the whole SPME assembly was wrapped in a plastic film, placed in a small box with ice until GC analysis.

3. Results and discussion

3.1. Analysis with Tenax-TA

One of total ion chromatograms from the Tenax-TA tubes spiked with standard aqueous solutions analyzed by GC/MS is shown in Fig. 1. It is confirmed that 4 target compounds are clearly separated for quantification. Calibration equations, correlation coefficients and detection limits of 4 compounds by Tenax-TA are in Table 5. That all of correlation coefficients are over 0.99 means high linearity of calibration curves. Detection limits of this method that used a capillary column is lower than 1 ng described in the paper by Hoshika and Muto (1978) that used a packed column for analysis of indoles in Tenax-GC tube, so this method is found to be more sensitive than better than the their method. On the other hand, the method using HPLC (High Performance Liquid Chromatography) published by Willig (2004) presented 0.01 ng of detection limits of indole and skatole. Thus, this method that used GC/MS is less sensitive than that of

HPLC. And indole and skatole, boiling points of which are higher than those of phenol and p-cresol, showed higher sensitivities than those of phenol and p-cresol and this is similar to Willig's measurements.

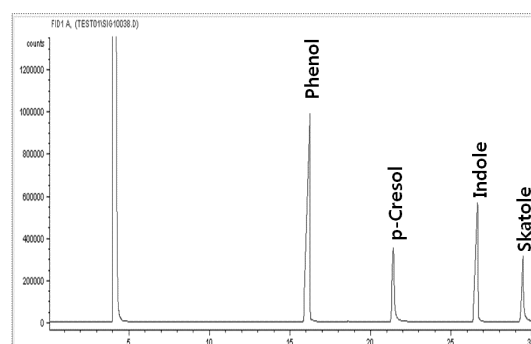


Fig. 1. Typical total ion chromatogram of indoles standard solution.

Result of measuring the concentrations of indoles in indoor airs using Tenax-TA is represented in Table 6. In cases of 50 L or 100 L of sampling volume, the concentrations of indole and skatole were found to be lower than their detection limits, but increasing sampling volume up to 200 L made the concentrations of indole and skatole to be 0.34 ppb that is almost equal to their detection limits. The chromatogram obtained from 200 L of sampling volume is shown in Fig. 2. As confirmed from Fig. 2, peaks of indole and skatole are very small in comparison to those of phenol and p-cresol. This result means that adsorption volume of air into a Tenax tube affects the concentrations of indoles and more than 200 L of sample air must be needed in order to analyze the indoles in swine

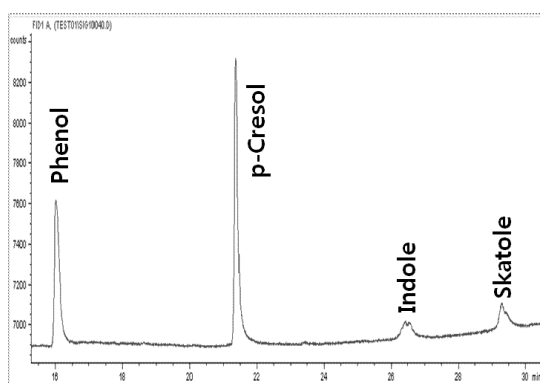
Table 5. Calibration equation from standard solutions of indoles

Compounds	Calibration Equation	R ²	Detection Limit(ng)
Phenol	$y = 1.12x - 0.125$	0.990	0.80
p-Cresol	$y = 1.34x - 0.117$	0.995	0.66
Indole	$y = 1.89x - 0.043$	0.999	0.30
Skatole	$y = 2.57x - 0.046$	0.998	0.43

Table 6. Measured concentrations of indoles in airs of swine house and expected dilution factors

Compound	Odor threshold value (ppb)	Concentration (ppb)			Expected dilution factor		
		50L	100L	200L	50L	100L	200L
Phenol	5.60	0.98	0.82	1.02	0	0	0
p-Cresol	0.054	0.79	2.22	5.93	17	41	110
Indole	0.30	n.d.	n.d.	0.34	-	-	1
Skatole	0.0056	n.d.	n.d.	0.34	-	-	14

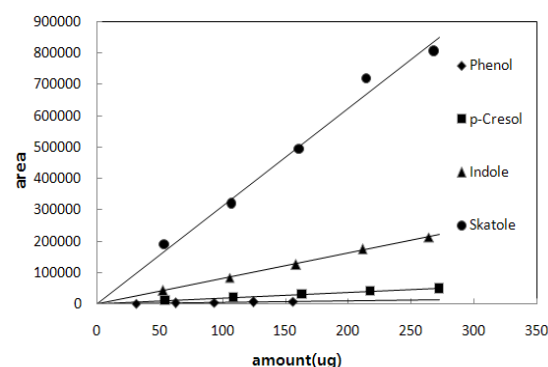
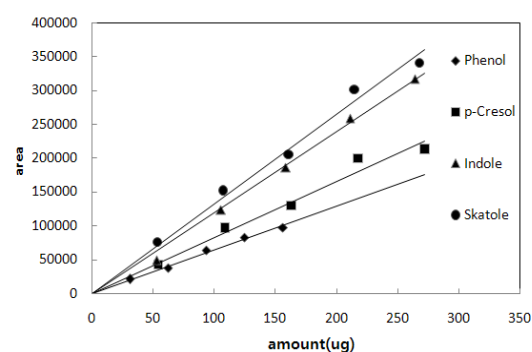
facilities over the concentrations of odor threshold values. If sample volume of air being collected in a Tenax TA tube is set to 200 L, detection limits of indole, skatole, p-cresol and phenol are 0.190 ppb, 0.190 ppb, 0.034 ppb and 0.033 ppb respectively. As Hoshika and Muto described in their paper, we suggest that the reason of low reproducibility of this method is due to the high boiling points of indoles (in case of skatole, 265°C), i.e., indoles that condensed in wall of the bag after sampling airs are hardly evaporated in the Tenax tube.

**Fig. 2.** Extracted chromatogram of a sample taken at the indoor air in pig house.

3.2. Analysis with SPME

The calibration curves, correlation equations and coefficients of four fibers obtained from the experiments of standard aqueous solutions of indoles are shown in Fig. 3. ~ Fig. 6. and Table 7. In the case of phenol and p-cresol, sensitivities (defined as the slope of the calibration curve) were relatively lower than those of indole and skatole. On the contrary, the sensitivity of

skatole was indicated to be highest. Even though CAR/PDMS fiber was seen to be most effective for all target compounds (Cai et al, 2006), the standard deviation of concentrations obtained with CAR/PDMS was unacceptably high. The reason of high deviation of CAR/PDMS was the tailing phenomenon of the indole peak observed in the total ion chromatogram. So in this study, PDMS/DVB fiber was selected for the extraction of indoles.

**Fig. 3.** Calibration curve of PDMS.**Fig. 4.** Calibration curve of CAR/PDMS.

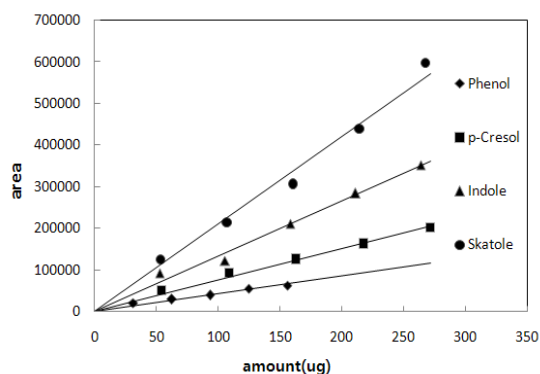


Fig. 5. Calibration curve of PDMS/DVB.

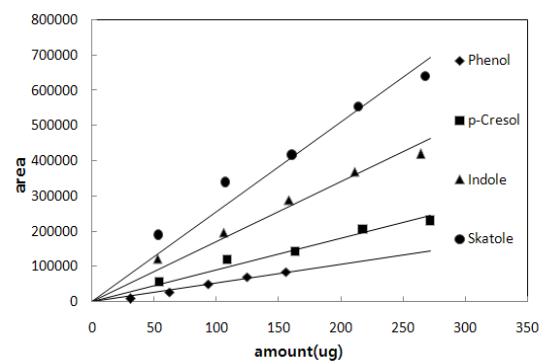


Fig. 6. Calibration curve of DVB/CAR/PDMS.

Calibration curves of indoles obtained from the evaporated standard solutions in 10 liters PET bag were depicted in Fig. 7. Slopes of calibration lines of

phenol and p-cresol are higher than those of indole and skatole. The reason of higher slopes of phenol and p-cresol in PET bags is supposed that volatilities of phenol and p-cresol are higher than those of indole and skatole, but slopes of phenol and p-cresol are lower than those of indole and skatole because of higher solubilities of phenol and p-cresol in water than those of indole and skatole.

Detection limits, calibration curves and correlation coefficients using PDMS/DVB fiber for the evaporated indoles obtained from PET bags are given in Table 8. Because of the same reason of high volatilities of phenol and p-cresol, it was observed that phenol and p-cresol are more detectable than indole and skatole.

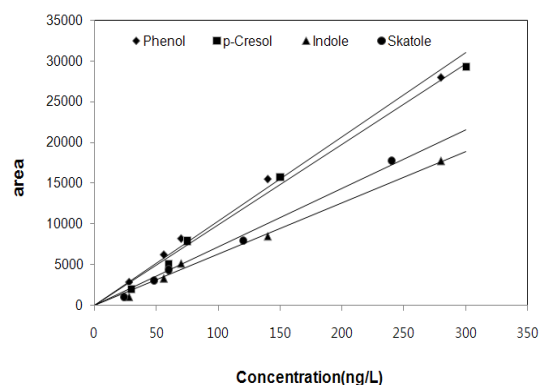


Fig. 7. Calibration curves of standard indoles in PET bags.

Table 7. Correlation equations and coefficients of four fibers

SPME fiber	Phenol	p-Cresol	Indole	Skatole
PDMS	$y = 60.2x$ $R^2 = 0.992$	$y = 189x$ $R^2 = 0.989$	$y = 813x$ $R^2 = 0.998$	$y = 3130x$ $R^2 = 0.985$
CAR/PDMS	$y = 645x$ $R^2 = 0.991$	$y = 830x$ $R^2 = 0.971$	$y = 1200x$ $R^2 = 0.995$	$y = 1320x$ $R^2 = 0.988$
PDMS/DVB	$y = 427x$ $R^2 = 0.931$	$y = 758x$ $R^2 = 0.984$	$y = 1330x$ $R^2 = 0.982$	$y = 2110x$ $R^2 = 0.981$
DVB/CAR/PDMS	$y = 536x$ $R^2 = 0.966$	$y = 901x$ $R^2 = 0.958$	$y = 1710x$ $R^2 = 0.955$	$y = 2560x$ $R^2 = 0.926$

Table 8. Detection limit and linearity determination for the indoles in PET bag PDMS/DVB

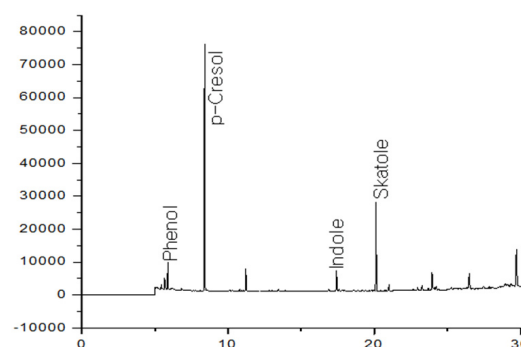
	Phenol	p-Cresol	Indole	Skatole
Detection limit (ng/L)	0.031	0.025	1.12	0.87
Calibration equation	$y = 10329 x$	$y = 9879 x$	$y = 6308 x$	$y = 7200 x$
Correlation factor	$R^2 = 0.992$	$R^2 = 0.995$	$R^2 = 0.994$	$R^2 = 0.994$

3.3. Analysis of field samples

One of total ion chromatograms of volatile organic compounds taken at the swine facility is shown in Fig. 8. It is confirmed that chromatographic peaks of indoles are not overlapped with other peaks and separated clearly. Concentrations of indoles collected in the PET bags sampled in the pig house, at the outlet of exhaust fan and border of the swine facility are summarized in Table 9. And the data measured by Willig et al. (2004) are added in the lower lines in Table 9.

Measured concentrations of phenol and indole are confirmed to be lower than those of p-cresol and skatole. In the pig house, where feces and slurry had been deposited beneath the floor, concentrations of indoles were higher than those of indoles taken at the outlet of exhaust fan and border of the swine facility. The expected dilution factors of indoles (concentration of compound/odor threshold value of odorant) indicate p-cresol and skatole contribute to the cause of offensive odor of swine facilities. And the measured concentrations of indoles with SPME

sampling and GC/MS analysis are similar to those from cartridges sampling and HPLC analysis.

**Fig. 8.** Total ion chromatogram of indoles in air of a swine facility.

4. Conclusions

In conclusion, the polyester bag sampling of swine airs and SPME extraction of indoles is simple and effective, compared to adsorption in Tenax-TA tube. For SPME fiber, PDMS/DVB is adequate for extracting indoles in a swine facility. By extraction of

Table 9. Average concentrations of indoles measured at the pig house and

Sampling Site	Phenol	p-Cresol	Indole	Skatole
Inside the house	5.7 ^b (0) ^c	71.7 (300)	2.5 (2)	26.6 (886)
Outlet of exhaust fan	6.7 (0)	51.4 (215)	2.1 (1)	18.0 (598)
Border of pig house	4.7 (0)	24.1 (101)	1.8 (1)	8.9 (295)
Slurry duct ^a	no data	191 (800)	7.3 (5)	19.9 (663)
Middle of room ^a	no data	126 (528)	4.9 (3)	6.3 (210)
Exhaust duct ^a	no data	113 (473)	4.1 (3)	5.7 (190)

^a Data from the previous work by Willig et al. (2004)

^b Number in parenthesis indicates the expected dilution factor of odor calculated from concentration/odor threshold value (phenol 21.55 ng/L, p-cresol 0.239 ng/L, indole 1.437 ng/L, skatole 0.030 ng/L)

^c Expected dilution factor

indoles in 10 liter air sample collected from the swine facility, SPME fiber could gain the detection limits of phenol, p-cresol and indole which are below the odor threshold of each compound. But the odor threshold value of skatole was lower than its detection limit. The SPME method showed acceptable ranges of reproducibility with standard chemical odor mixtures. We recommend use of an 10 liters polyester bag and PDMS/DVB-coated SPME fiber rather than Tenax-TA tube for collection of indoles in swine facility.

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