Comparison of Olfactometry, Gas Chromatography, and Electronic Nose Technology for Measurement of Indoor Air from Swine Facilities

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ASL-R683

Summary and Implications

Indoor air from swine finishing facilities was analyzed by olfactometry, gas chromatography (GC), and an electronic nose. Olfactometry used dynamic dilution triangular forced-choice. Air samples collected in Tedlar bags were analyzed using an AromaScan A32S electronic nose. Sixteen compounds, primarily nonsulfur protein metabolites were quantified by GC/mass spectrometry (MS) and an equation was generated to predict odor dilution threshold ($R^2 < .3$). Electronic nose evaluation of room air samples was not strongly correlated to olfactometry measures ($r < .2$). However, the equation developed from the GC/MS analyses was capable of predicting the electronic nose response to air samples ($R^2 > .8$).

The results suggest that human panelist responses may be based on detection of compounds that were not included in GC/MS quantification procedures and are not well detected by the electronic nose.

Introduction

For regulatory purposes there is a definite need for a means of accurate odor assessment that is available on-site. Currently, olfactometry using trained human panelists is the accepted method for determination of odor concentration (1). Unfortunately, olfactometry must be conducted in a controlled laboratory setting and a sufficient number of panelists must be available to conduct the analysis. Gas chromatography (GC) coupled to mass spectrometry (MS) is frequently used to identify and quantify odorous compounds. However, this does not represent the experience of odor sensation as perceived by a human being. Electronic nose analysis with a sensor array is a potential technology for odor evaluation. To date, relatively little research has been conducted with electronic noses in the area of agriculture manure odors.

The electronic nose is a technology for odor evaluation that has been developed in an attempt to mimic the human sense of smell. The sensor array of an electronic nose detects the chemicals that humans perceive as odors and records numerical results. The instrument generates a different pattern of response for different types of samples. Each sensor has an individual characteristic response and some of the sensors overlap and are sensitive to similar chemicals, as are the receptors in the human nose (2,7). A single sensor is partially responsive to a broad range of chemicals and more responsive to a narrow range of compounds (Osmetech, Crewe, UK). An array of sensors is responsive to a great number and many types of chemicals, with certain sensors in the array being moderately to extremely sensitive to specific compounds (6). Electronic noses have frequently been used in the food, beverage, and perfume industries, for product development and quality control (4). The technology is relatively new to the agricultural industry, although the potential for application is certainly great based on the limited research conducted (3,5).

The objectives of this study were to 1) analyze air samples from swine feeding facilities by using olfactometry and an electronic nose, 2) identify and quantify odorous compounds in the air by GC/MS, and 3) compare the three methods of odor evaluation and use GC/MS response to predict olfactometry and electronic nose response.

Materials and Methods

The experiment, conducted at the Iowa State University Swine Nutrition and Management Research Center west of Ames, was divided into six, 24-d periods. A total of 72 crossbred finishing pigs (average initial body weight = 86 kg) as used over the duration of the trial; 12 new pigs during each of the six periods. Two environmentally controlled, mechanically ventilated feeding rooms, 3.81 m × 3.96 m, were available for the experiment. Within the room, six finishing pigs were housed in a 2.44 m × 2.44–m pen with woven-wire flooring. Average room temperature during the course of the experiment was 22.3°C. Two 0.36–m exhaust fans provided the ventilation for each room. Each feeding room was equipped with a shallow manure storage pit under the pen. The pit sloped from 7.62 cm to 17.78 cm with a 30.48–cm–deep, 15.24–cm–wide gutter at one end. The pits were emptied by a pull-plug drain. Due to the limited manure storage that was available, the pits were drained and rinsed each Thursday (days 7).

Air samples were collected during the last 3 weeks of each 4-week period, thus allowing the first week for dietary acclimation. Samples were collected on Mondays and Thursdays (days 4 and 7) and were transported to the Iowa State University campus for analysis. A battery-powered Supelco 10 liter air sampler (Model 1062, Supelco, Bellefonte, PA,) was used to collect air samples in Tedlar bags. During sample collection, the air sampler was placed on the floor as close to the pit as possible.

Olfactometry

Air samples (11 liter) were collected from each room for analysis by olfactometry. Room air samples were analyzed using the Ac'scent International Olfactometer (St. Croix Sensory, Stillwater, MN) located in the Olfactometry and Air Quality Laboratory on the Iowa State University campus. The method of dynamic dilution triangular forced-choice olfactometry with an ascending concentration series was used to determine odor concentration.

Electronic Nose

Air samples (1 liter) were collected for analysis by the electronic nose. Air samples were analyzed using an AromaScan A32S electronic nose (Osmetech, Crewe, UK) located in the Iowa State University Department of Food Sciences and Human Nutrition. The AromaScan contains thirty-two semi-conducting polypyrrole sensors. Air that is drawn through activated charcoal is used as the baseline reference, and then the odorous air is analyzed. The sample data, in terms of the change in electrical resistance of each of the sensors, is recorded.

Gas Chromatography

GC/MS was used to identify and quantify odorous compounds in the feeding room air. A standard swine odor solution was formulated based upon the artificial slurry developed by Persaud et al. (6). Additional odorous compounds that were consistently present in the initial air samples were added to the standard solution. A total of 16 nonsulfur protein metabolites present in the ambient air were routinely quantified (Table 1). Standard solutions were prepared to generate a linear prediction curve.

Table 1. Components of the synthetic swine odor solution used for quantitation by GC/MS of 16 air analytes from air samples taken in feeding rooms housing finishing pigs

Acetic acid	3-methylphenol
Propionic acid	4-ethylphenol
Isobutyric acid	3-ethylphenol
Butyric acid	2,6-bis(1,1-dimethylethyl phenol)
Isovaleric acid	Indole
Valeric acid	3-methylindole
Phenol	2-methylindole
4-methylphenol	4-methylindole

GC/MS = gas chromatography coupled to a mass spectrometer detector.

Solid phase microextraction (SPME) fibers were used to absorb compounds in the air of the feeding rooms for analysis by mass spectroscopy (Supelco SPME portable field sampler; Supelco). The SPME field sampler was placed above the gutter end of the manure pit for 30 min to allow the fiber to be exposed to the headspace above the greatest amount of manure.

Statistical Analysis

Odor concentration, electronic nose response, and air composition were evaluated statistically using the mixed procedure of SAS version 6.01 (8). To analyze treatment effects (diet) room served as the experimental unit in the incomplete randomized block design. Fixed variables included room, day, and panelist. Period was included as a random variable. Stepwise regression procedures were used to generate an odor prediction equation from the 16 air analytes, considered as cubic terms. The GC/MS results were used to predict panelist response and were also compared with the electronic nose response. Correlation procedures were used to relate human panelist response to electronic nose response.

Results and Discussion

Odor Dilution Threshold

The log of odor dilution as measured by olfactometry was used to normalize the data because odor dilution was measured on an exponential scale. Normalizing the data provided a more uniform distribution of the data without affecting the results (Table 2). Odor dilution was affected by room ($P < .01$), Day ($P < .01$), and panelist ($P < .01$). The room effect was possibly due to differences in the ventilation systems. Room and period were confounded, therefore time or season may have influenced Room effect. Effects arising from the day of sampling and the human panelists involved in the olfactory evaluation were expected. Because the amount of manure in the storage pit increased from one sampling day to the next within a week, the odor generated from the manure would be expected to increase. As more manure was added to the pit each day, more substrate was available for breakdown by bacteria, thus more odorous compounds would have been generated. Also, the dissolved oxygen available would have decreased, and the resultant shift to anaerobic breakdown would have generated compounds of a more odorous nature, such as branched chain fatty acids. A panelist effect would be expected because of the inherent variability among human beings. Sensory perception of an odor is an individual response, differing from one person to the next.

GC

Day effects on the majority of the s16 air analytes measured by GC/MS (excluding acetic acid, butyric acid, and 3-ethylphenol) were observed ($P < .05$, Table 3). Room effects were noted for isobutyric acid, 3-methylphenol, 3-ethylphenol, and 2,6-bis(1,1-dimethylethyl)phenol ($P < .05$) as were room × diet interaction effects on acetic acid, propionic acid, butyric acid, valeric acid, 4-methylphenol, 3-methylphenol, 3-ethylphenol, and 2,6-bis(1,1-dimethylethyl)phenol ($P < .10$).

The 16 air analytes were individually correlated with the log of the odor concentration by using simple correlation procedures, both before and after removing the seven panelists with a standard error greater than .70. A large standard error indicates variability in a panelist's responses. Panelists with a

large standard error were removed in an attempt to improve the correlations. All of the correlations were fairly low and removing the panelists with the greatest standard error did not result in much improvement. The analytes best correlated with odor concentration were 3-methylphenol (r = .23), 2,6-bis(1,1-dimethylethyl)phenol (r = .14), 4-methylphenol (r = .12), and indole (r = .11).

Electronic Nose

The principal component for the response of each sensor was generated. Using the AromaScan software, a two-dimensional principal component analysis (PCA) map was made (Figure 1). The lack of clustering on the PCA map indicates that the electronic nose sensors did not differentiate among air samples taken from the rooms housing pigs fed the three diets.

Odor Prediction

An equation was generated from the air analytes to predict odor dilution threshold. With all terms considered as cubic terms an R^2 value of .27 was obtained. Removing the insignificant (P > .10) terms and including them as quadratic or linear variables reduced the R^2 value to .21. The poor prediction capability indicates that additional analytes may require consideration, although the repeated occurrence of other analytes in the air samples was not evident from GC/MS analyses using the method developed.

The principle component for the response of the 32 electronic nose sensors was generated. The eigenvector value was then correlated to the log of odor dilution threshold. The electronic nose evaluation of the air samples was not strongly correlated to the olfactometry measures (r = .18). The equation generated from the GC/MS analysis predicted the electronic nose response with an R^2 of .81. Thus, the two instrumental methods of odor analysis were fairly compatible, but the instrumental methods were not highly related to organoleptic analysis.

References

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Table 2. Least squares means of detectable dilution ratios of collected room air samples when finishing pigs were fed one of three diets.

	Log odor dilution		
	Diet 1	Diet 2	Diet 3
Period 1[a]			
Day 4	5.08	4.80	
Day 7	5.21	5.02	
Period 2			
Day 4		5.68	5.37
Day 7		5.81	5.59
Period 3			
Day 4	4.70[1]		5.28[1]
Day 7	6.13[2]		6.03[2]
Period 4			
Day 4		5.27	5.16[1]
Day 7		5.40	6.09[2]
Period 5			
Day 4	5.39[1]		5.35
Day 7	5.82[2]		5.66
Period 6			
Day 4	5.11[1]	5.11[1]	
Day 7	5.78[2]	6.01[2]	

[a]Empty cells reflect not all diets fed during each Period due to facility limitations.

[1,2]Different superscripts indicate within diet, day was significant (P < .10).

Table 3. Least squares means of air analyte concentrations collected from experimental rooms housing finishing pigs fed one of three diets.

Analyte	Diet 1		Diet 2		Diet 3	
Concentration (ppb)	Day 4	Day 7	Day 4	Day 7	Day 4	Day 7
Acetic acid	176,818	166,366	113,415	143,290	174,579	147,701
Propionic acid	52,278	67,679	49,667	55,765	63,669	59,840
Isobutyric acid	23,115	55,220	25,779	38,105	24,585	25,811
Butyric acid	27,850	31,758	27,259	27,901	32,060	29,289
Isovaleric acid	17,706[1]	26,444[2]	20,221	26,123	21,151	22,371
Valeric acid	8,289	12,895	9,249	10,859	9,296	11,188
Phenol	2,601[1]	6,171[2]	2,196[1]	5,483[2]	2,817[1]	5,222[2]
4-Methylphenol	24,075	24,956	20,925	30,033	26,729	28,038
3-Methylphenol	3,659	5,528	2,711	3,446	3,447	4,146
4-Ethylphenol	1,368	3,517	1,266	1,643	1,925	1,665
3-Ethylphenol	491	639	344	338	759	566
2,6-bis(1,1-dimethylethyl)phenol		247			64	127
Indole	411	477	596[1]	1,186[2]	416	668
3-Methylindole	250	120	6,925[1]	8,689[2]	1,475	2,460

[1,2]superscripts indicate differences between samples collected on d 4 and d 7 ($P < .05$); no diet differences were observed.

Figure 1. Two dimensional principal component analysis (PCA) map of electronic nose response to air samples from rooms housing finishing pigs fed one of three diets