Overview of Odor Measurement Techniques

M. Susan Brewer and Keith R. Cadwallader
Department of Food Science & Human Nutrition
University of Illinois
1302 W. Pennsylvania Ave.
Urbana, IL 61801

INTRODUCTION

"Odor" is elicited by chemicals in a gas phase which are detected via olfaction producing recognizable smells (cinnamon, lemon) and/or chemesthesis which mediates pungent sensations (tingling, burning, etc) in response to substances such as ammonia. Responses transmitted by the olfactory nerve elicit aroma. Many compounds are pungent at high concentrations. Many compounds detected by chemesthesis via trigeminal nerve stimulation are strong nasal, ocular and throat irritants (Cometto-Muniz et al., 1997, 1998). There are a number of factors which affect odor including the volatile compounds themselves, the number of olfactory receptors available to bind them, the degree to which the compounds become solvated for receptor binding, temperature, humidity, and the matrix in which the odor-producing chemicals are embedded. In addition, individual chemicals may interact (chemically). Odors vary in threshold, intensity and hedonic tone. Measuring odor intensity alone is insufficient to assess human perception of odor (Misselbrook et al., 1993).

The measurement of airborne volatile organic compounds (VOCs) within and surrounding livestock production facilities has been the subject of extensive research in the past decade (O'Neill and Phillips, 1992; Hobbs et al., 1995, 1997; Zahn et al., 1997; Burton et al., 1998; Kim-Yang et al., 2001). Of particular importance has been the characterization and measurement of key potent odorants responsible for the unpleasant odor associated with these facilities and their waste steams, including air emissions. Short-chain volatile fatty acids (VFAs), phenols, amines, indoles and sulfur-containing compounds are the predominant classes of VOCs associated with swine production facilities (Spoelstra, 1980; O'Niell and Phillips, 1992; Hobbs et al., 1997; Zahn et al., 1997; Mackie et al., 1998; Zhu et al., 1999). Accurate measurement of these compounds and their odor impact have been challenging because VOCs possess widely varying physical and chemical properties and are present at concentrations ranging from high parts-per-million (ppb) to low parts-per-billion (ppb). Furthermore, each odorant has a unique odor and odor detection threshold which means that compounds, even if present at the same concentration, may have markedly different odor impacts.

Monitoring odors can be accomplished in several ways: chemical analyses, electronic methods and dynamic dilution olfactometry which takes advantage of the human sensory response. With the current state of technology, the best way to measure odors from livestock facilities is through use of human panels and gas chromatography/mass spectrometry (NPPC, 1998). This paper discusses the use of various instrumental and objective sensory-based techniques for the measurement of VOCs and odors associated with swine production operations.

Air Sampling and Gas Chromatographic Analysis

Instrumental methods have relied mainly on the application of gas chromatography (GC), including gas chromatography-mass spectrometry (GC-MS), since this mature separation technology is capable of the efficient separation required for analysis of complex mixtures of VOCs. In gas chromatography a mixture of volatile substances is injected into a column which separates the compounds based on their relative vapor pressures and polarities. The compounds are then detected as peaks which have specific retention times and peak areas which can be used for qualitative and quantitative determinations, respectively.

The main problem or consideration associated with use of gas chromatography has been the requirement of an extraction or preconcentration step. VOCs are most often isolated by taking advantage of their volatility and nonpolar nature. For analysis of airborne VOCs this generally means the use of an adsorbent trap, which allows for the selective enrichment (trapping) of the VOCs away from the bulk of the atmospheric gases and water vapor. The VOCs contained in the adsorbent trap are then transferred via thermal desorption, which releases the compounds from the trap and sends them to the gas chromatograph for analysis.

Over the past four years we have employed trapping techniques for analysis of air-borne VOCs emitted from swine finishing buildings. For in-the-field studies we have utilized portable air sampling devices in which the air is drawn through an adsorbent tube using vacuum pump at a fixed flow rate (e.g. 20 mL/min). In the literature various trapping agents, e.g. Tenax™ and graphitized carbons, have been shown to be effective for the isolation of airborne VOCs (Krzymien et al., 1999; Smet et al., 1999; Kim-Yang et al., 2001; Zahn et al., 2001; Zhang et al., 2001). Based on our experience, mixed-bed graphitized carbon traps are an excellent choice, since they allow for isolation of VOCs having widely varying volatilities and polarities, while at the same time, these traps minimize water vapor absorption which can perturb the thermal desorption step by causing blockage (ice) of the cryogenic trap of the gas chromatograph. However, occasionally even these traps can have moisture problems, such as when field sampling is done under very humid or extremely cold conditions. To overcome this problem we now use Tedlar™ bags for the primary field sampling. The bag sample is then brought back to the laboratory where the airborne VOCs are transferred from the bag onto an adsorbent trap using a vacuum pump under controlled conditions which minimize moisture sorption on the trap. This approach had been previously reported by Zhang et al. (2001). The above method offers an additional advantage since the same bag samples can be used for dynamic dilution olfactometry.

A typical gas chromatogram of VOCs collected from a swine finishing chamber is shown in Figure 1. In this case, gas chromatography was performed using both a nonspecific, broad spectrum flame-ionization detector and a sulfur-selective flame photometric detector. Gas chromatography-mass spectrometry is applied during the early stages of method development to aid in compound (peak) identification. The use of duel detectors for routine monitoring allows for the simultaneous analysis of key swine odor components found in relatively high concentrations (e.g. volatile short-chain fatty acids and phenols by flame ionization detection) and those found at trace levels (e.g. sulfur-containing compounds by flame photometric detection). The trace level sulfur-containing compounds are of particular importance because they often have very low odor detection thresholds and possess noxious odor properties.

Gas Chromatic Analysis of Liquids and Solids

For liquid or solid samples a large number of sample preparation strategies may be employed prior to gas chromatographic analysis. These include direct solvent extraction, purge-and-trap and solid phase microextraction (SPME) among many other techniques. Purge-and-trap involves the continuous removal (entrainment) of VOCs from a thermostatted sample using a stream of inert gas (e.g. N_2). The VOCs contained in the gas stream are then enriched on an adsorbent trap and then analyzed by thermal desorption-gas chromatography as discussed above for air sampling. The relatively new solid phase microextraction represents a rapid, solventless technique that is based on the partitioning of the volatile components between the sample or the sample headspace and a polymer-coated fiber. For analysis, the volatiles are thermally desorbed from the fiber in the heated injector port of the GC. Solid-phase microextraction-gas chromatography offers the advantage of high sample throughput since this method can be performed by modern automated multipurpose samplers. The technique has been applied for the analysis of swine VOCs (Rizzuti et al., 1999; Yo, 1999).

Figure 2 shows a typical gas chromatogram of volatile constituents of a swine manure sample analyzed by solid-phase microextraction-gas chromatography. Prior to the analysis the sample was spiked with known amounts of two surrogate internal standards to aid in quantification of key odorants (i.e., 2-ethylbutanoic acid was used for volatile short-chain fatty acids; and 4-tert-amylphenol for phenolic and indolic compounds). In addition, the sample is mixed with a matrix modifier, which serves to stabilize the pH (necessary for analysis of volatile acids, phenols and indoles since their dissociation is affected by pH) and to minimize the protein or lipid binding of the volatile constituents by a salting out (high NaCl concentration) effect. Details of the analysis are given in the caption of Figure 2. Typical quantitative results for a manure sample are shown in Table 1. These concentration levels are in general agreement with other published reports on the volatile composition of swine manure and slurries (Chen et al., 1994; Zahn et al., 1997).

We also have applied the above methodology to the analysis of wastewater and dust samples originating from swine finishing buildings. A representative gas chromatogram of a dust sample is shown in Figure 3, which indicates the presence of several aldehydes (e.g. hexanal, heptanal, etc.) originating from the feed in addition to the usual volatile constituents of swine manure (Hammond et al., 1979).

Electronic Noses

The electronic nose is an instrument that consists of an array of electronic chemical receptors which detect volatile chemicals or categories of chemicals then usees the information to predict sensory-like properties. Electronic noses contain an array of sensors (sintered metal oxides, catalytic metals, conducting polymers, lipid layers, phtholocyanins, organic semi-conductors, surface acoustic wave or combinations) which respond to a wide variety of chemical classes (Strassburger, 1996). The sensors are based on conducting composites that change resistance on exposure to a vapor (Feast, 2000). The change in resistance (ΔR) of individual sensors from baseline resistance (R) produces a pattern of resistance changes ($\Delta R/R$) across the array (Misselbrook et al., 1997). The measured response is then converted to a signal using a

computer processor. To identify the type, quantity, and quality of the odor the computer uses changes in the pattern generated in the entire sensory array (Figure 4). Metal oxide arrays require very high temperatures to operate, and the polymer sensors don't detect small amines and thiols responsible for fishy, skunky and rotten-egg odors (really smelly substances). New sensors using inks based on organometallic compounds change color when bound by vapor molecules (like heme iron in hemoglobin which becomes bright red when it reversibly binds oxygen; Schmiedeskam, 2001).

All of these sensors (and their combinations) vary in the magnitude of response to any one compound giving them the discriminatory ability required to analyze odors. The volatile sample is injected, in combination with filtered air, such that it can flow over and interact with the sensors. An output signal is generated as a result of the change in resistance at the sensory surface as a result of its interaction with compounds in the gas phase. The binding and resistance change are rapid and temporary. Response data are exported to a computer which has been trained to use chemometric and "artificial neural network" computer software as a way to recognize the pattern of a mixture of compounds as a specific odor and to discriminate slight differences. Because very large amounts of data are generated, processing it into useful information requires statistical analysis software which can conduct principal component analysis and discriminant factor analysis.

Use of arrays of non-specific sensors allows for detection of many thousands of chemical species due to the broad selectivity of the sensory surfaces. The electronic nose can measure a complex group of substances (like the human olfactory system) very rapidly (10-120 seconds), and it can be trained to discriminate "good" from "bad" aromas. However, the electronic nose must be trained for each important component (grassy, smoky) for each application, it must be standardized by both chemical and olfactometric methods, and the "sensor array" is restricted. One of the biggest challenges for electronic noses is detecting complex odors against an intricate background matrix.

While the above instrumental methods do offer the potential for the accurate estimation of VOC levels in waste streams and air emissions associated with swine production facilities, they do not, however, allow for the direct measurement of odor intensity nor odor quality. For this purpose, researchers have relied on the use of subjective and objective sensory analysis using human panelists. Foremost among these techniques is dynamic dilution olfactometry.

Dynamic Dilution Olfactometry

Dynamic Dilution Olfactometry (DDO) is based on "dilution to threshold" of a gas sample containing multiple components. Odor threshold is a commonly used term. In general, it is the minimum concentration detectable or the minimum detectable difference between two concentrations (ASTM, 1997a). Because of additive / subtractive effects (of individual chemicals) in mixed systems, the threshold for a particular compound may not be useful. Thresholds for different substances can be several orders of magnitude different, and thresholds for different people can be several odors of magnitude different.

An odor threshold (minimum detectable amount) can be measured in "known" samples (standards) and expressed as "X ppm of compound Y" (in air). To conduct a dilution-to-threshold test, the gas containing the volatile chemical is collected in a bag, then a known volume is injected through a flow-splitter where air is used to dilute it to selected ratios. The dilutions are usually factors of 2 or 3. The more the gas must be diluted with pure air to lower it to the Detection Threshold, the stronger the odor of the gas. For a pure compound, the dilution corresponds to the concentration:

1 ppm = 1/1,000,000 = 10^{-6} dilution = dilution factor "6"

In this case, odor intensity is a function of concentration (Figure 5). "Stevens Power Law" (Stevens, 1957) states that the apparent magnitude of intensity grows as a power function of the stimulus magnitude which implies that equal ratio changes in sensation magnitude correspond to equal changes in the stimulus magnitude:

$$I = k (C)^n$$

where C is the odorant concentration, and k and n are constants that differ for each odor. Therefore, for a pure compound, if we know the power function and the concentration, we can determine the intensity. A derivative of this relationship is the log function of the concentration of the odorant.

Determining Detection Thresholds of "unknown" complex mixtures (barn air) is much more difficult because (1) we don't know what compounds are present, and (2) we don't know their concentrations. No instrument is available to quickly measure the concentration of odors consisting of many compounds. One way around this problem is to express the odor strength as "odor units". The odor unit is a calculated value based on the Threshold Dilution ratio and the concentration:

$$Z = C / Cs$$

where Z is the Threshold Dilution ratio measured by an olfactometer (as with a pure compound), C is the odor concentration and Cs is the theoretical minimum concentration of the odor for detection in 50% of the population. To calculate odor units, "Z" must be determined for the unknown sample while C and Cs are determined using a pure substance (standard; n-butanol). The "strength" of the odor is expressed in dimensionless "odor units" which are calculated as the -log of the dilution at which the odor can be detected which may be adjusted for the concentration and the detection threshold of a known substance. For example, if odor is detected at a dilution of 1 part barn air to 27 parts purified air:

Dilution Threshold (ratio) = Volume of pure air / Volume of odorous air

Dilution Threshold ratio = 27/1

DDO requires a panel of 3-10 people who determine how much a sample of air must be diluted before they can no longer smell it. An air sample, most often 10 L, is collected in a bag made of

relatively inert material (Tedlar). The odor mixture is diluted with purified air then presented to pre-selected sensory panelists at several dilutions. For each dilution, the panelist is presented with three samples two of which are the same. The panelist then makes a "forced choice" among three alternatives selecting the sample which is different Very dilute samples are presented at the beginning of the test, increasing in concentration after every set of three. At some point in the series of concentrations, each panelist will become able to detect the odor. The Best Estimate Threshold (BET), the halfway point between the dilution where odor can be detected and that where it can't be detected, is calculated as the square root of the product of those two dilution factors m=(ASTM 1990, 1997b). If the odor is detected at the 27/1 dilution but not at the 81/1 dilution, then:

$$\mathbf{BET = \sqrt{(27 \times 81)} = 46.77}$$

The BET value for each panelist is determined. The log of each value is calculated. The logs of the individual BETs are averaged to produce a "geometric mean". This geometric mean is similar to the log of the dilution factor for a pure compound (such as n-butanol). The antilog of the BET geometric mean is the average "concentration" (or average Dilution Threshold ratio for mixed samples) at which the group can "detect" the odor (Figure 6).

The panel response to the mixed sample may be expressed in Odor Units (OU) which are simply the Dilution Threshold Ratio, the Dilution Threshold Ratio adjusted for the concentration at the Detection Threshold for a known amount of a pure standard, or the amount of odorant in one cubic meter (OU/cm3). The European Odor Unit (OU_E) is defined in terms of N-butanol (AWME EE-6, 2002)

To calculate the European Odor Units:

1. Determine concentration of n-butanol at its Odor Detection Threshold (ODT_b). This is the Odor Detection Concentration for n-butanol (ODC_b).

2. Determine the Odor Units for the "mixed sample": this is the Odor Detection Threshold of the unknown sample adjusted to the Odor Detection Concentration for n-butanol

   $OU_E = (ODT \times ODC_b) / 40$ ppb

   OU_E = European Odor Units
   ODT = Odor detection threshold (ratio) of the sample
   ODC_b = Odor concentration of n-butanol at its detection threshold
   40 ppb= the "definition" of 1 OU_E in terms of n-butanol

European standards require that ODC_b be between 20 and 80 ppb for each panelist, so panelists are screened prior to their participation in an olfactometry panel. One "European Odor Unit" is 123 mg n-butanol (40ppb) by definition so, if we determine the ODC_b to be other than 40, we must adjust our ODT accordingly.

If we determined that our actual Odor Detection Threshold for n-butanol is 50ppb, we must adjust the Odor Detection Threshold of our unknown:

$$OU_E = (ODT) \times ODC_b / 40$$
$$OU_E = (25.7) \times 50 / 40$$
$$OU_E = 32.13$$

Dilution olfactometry will give an indication of the overall strength of the odor in terms of how much must be present to detect it, and it will give “numbers” for comparison (across time, intervention methods, etc.), however it gives no indication of odor strength at suprathreshold amounts. Dilution olfactometry will not identify individual odors, it will not give an idea of which compounds contribute most to a complex odor, and it will not give “hedonic” information (good / bad smell). Unless the DDO data are correlated with a sensory “intensity” reference scale (1 = very weak, 5 = very intense) using reference odorant concentrations, DDO data alone do not give an indication of how intense the odor is.

The primary advantage of DDO is that the human nose is the actual detector—it is the most sensitive detector for many compounds. The disadvantage is that is cumbersome for use outside a laboratory environment. It depends on using panelists who have (1) been selected for their sensitivity in a specific range, and (2) have been “standardized” to a specific concentration of a specific concentration of a specific compound (usually n-butanol). DDO determines odor threshold, not “odor quality” (smells like lemon, cinnamon, etc.).

The “odor unit” seems to be the most common index for odor emission control. A number of states in the US have a source emission standard. However, there are problems with using the odor unit as a standard: (1) because of the variability of people, who serve as the detectors for generation of the odor unit, data vary from laboratory-to-laboratory, and (2) the odor unit includes *no measure of the importance of the odor.*

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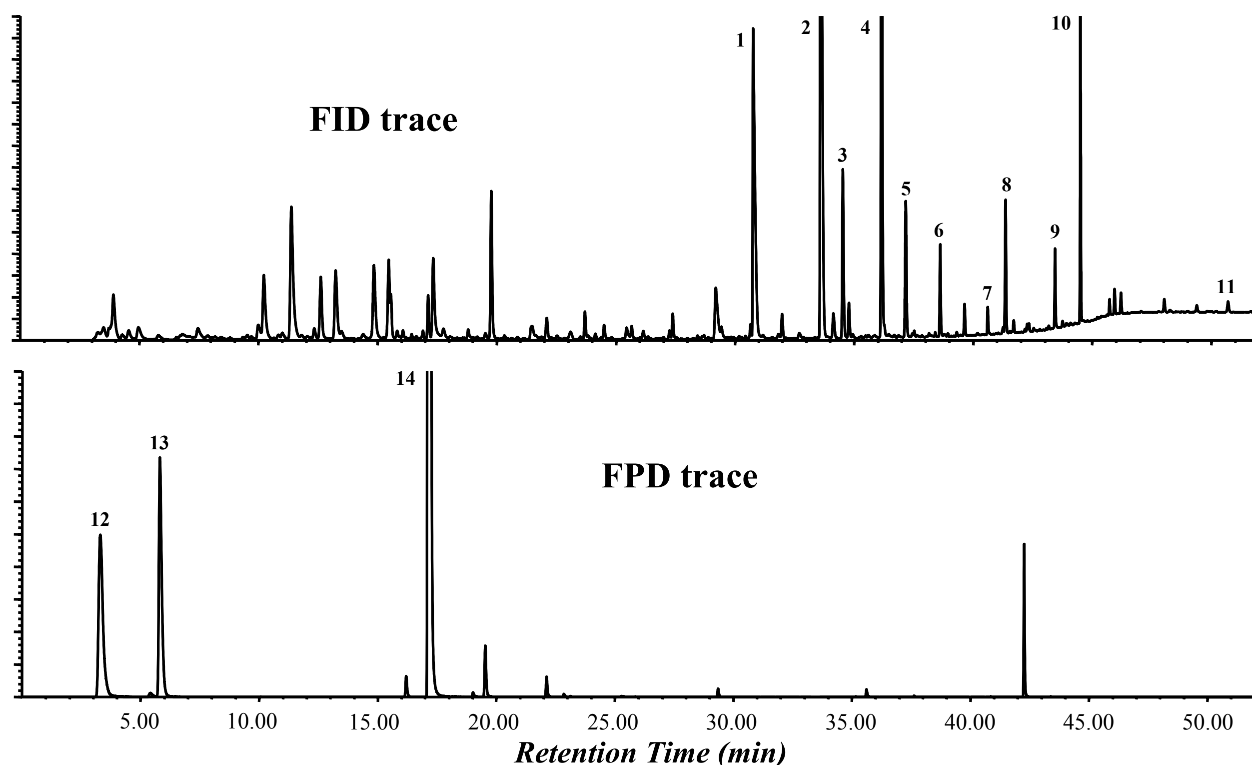

Figure 1. Gas chromatograms of air-borne volatile organic compounds collected via a Tedlar™ bag from air emitted from a swine finishing building; FID trace = flame ionization detector, FPD trace = flame photometric detector. (**1** = acetic acid, **2** = N,N-dimethylacetamide {artifact from Tedlar™ bag}, **3** = 2-methylpropanoic acid, **4** = butanoic acid, **5** = 2-/3-methylbutanoic acid; **6** = pentanoic acid, **7** = hexanoic acid, **8** = heptanoic acid, **9** = phenol, **10** = 4-methylphenol {*p*-cresol}, **11** = indole, **12** = methanethiol, **13** = dimethylsulfide, **14** = dimethyldisufide). [***Purge and Trap-Thermal Desorption-GC.*** VOCs were collected on 1/4 in. glass Carbotrap 300 multi-bed adsorbent tubes (Supelco, Bellefonte, PA) by drawing air through trap at a rate of 100 mL/min using a vacuum pump for 20 min. Gas chromatographic (GC) analysis was performed using a TDSA automated thermal desorption system (Gerstel, Germany) connected to an Agilent 6890 GC (Agilent Technologies, Inc.) system equipped with flame ionization (FID) and flavor photometric (FPD) detectors. Each trap was dry purged for 20 min (helium at 50 mL/min) at 30ºC to remove moisture from the trap and then the VOCs were thermally desorbed (300ºC for 5 min; 50 mL/min, helium flow) and subsequently cryofocused (-150ºC) in a CIS 4 programmable temperature vaporizer inlet (Gerstel). Cryofocused volatiles were thermally desorbed (280ºC) directly into the analytical GC column. Between analyses traps were reconditioned at 300ºC for 30 min under a flow of helium (100 mL/min). Separations were performed on a DBWAXetr column (50 m length x 320 µm i.d. x 1 µm film thickness; J&W Scientific, Folson, CA). GC column effluent was split 1:1 between FID and FPD using deactivated fused silica tubing (1 m length, 250 µm i.d.). Oven temperature was programmed as follows: 40ºC (5 min initial hold), ramped at 4ºC/min to 155ºC, ramped at 8ºC/min to 250ºC (21.5 min final hold). GC peak identifications were made by comparing data from GC-mass spectrometry and retention indices (Van den Dool and Kratz, 1963) with those of authentic standard compounds. GC peak areas were determined using HP Chemstation software.]

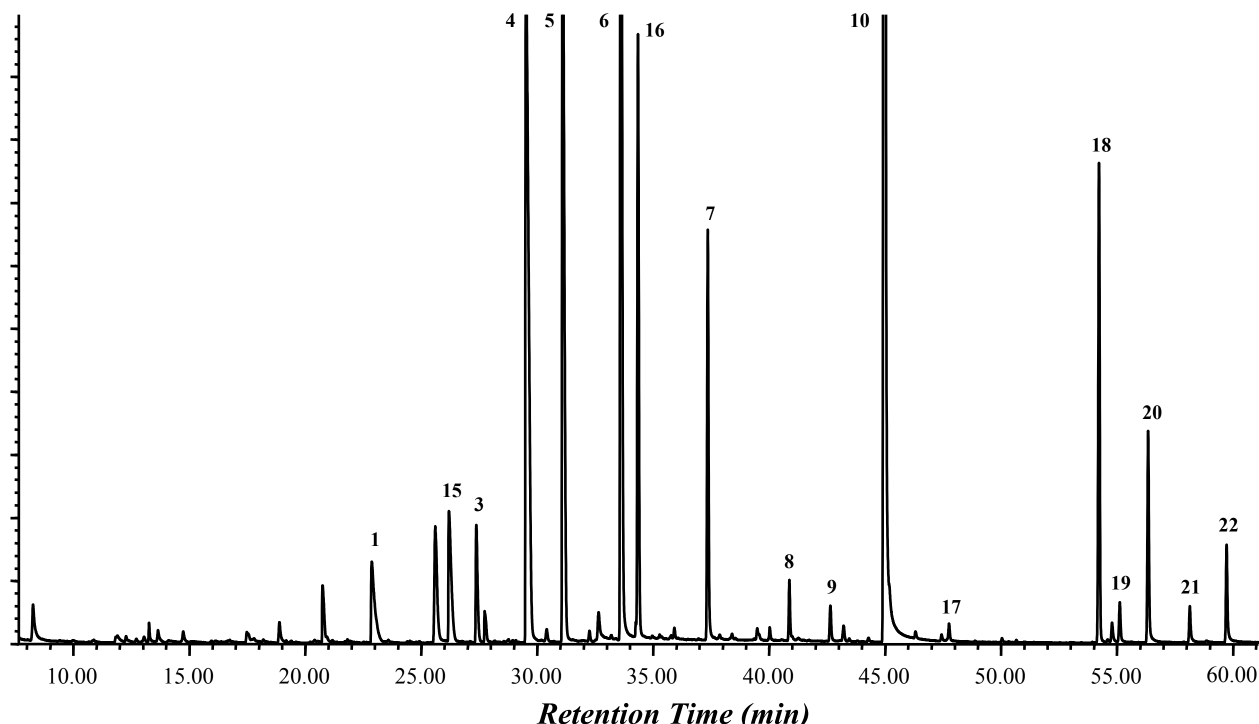

Figure 2. Headspace SPME-GC-MS profile of a swine manure sample. (**1** = acetic acid, **15** = propanoic acid, **3** = 2-methylpropanoic acid, **4** = butanoic acid, **5** = 2-/3-methylbutanoic acid; **6** = pentanoic acid, **16** = IS_1 = 2-ethylbutanoic acid, **7** = hexanoic acid, **8** = heptanoic acid, **9** = phenol, **10** = 4-methylphenol {*p*-cresol}, **17** = 4-ethylphenol, **18** = IS_2 = 4-*tert*-amylphenol, **19** = indole, **20** = 3-methylindole {skatole}, **21** = benzeneacetic acid, **22** = benzenepropanoic acid). [***Sample Preparation.*** Sample (1 g) plus 5 mL of a matrix modifier solution (deodorized 2 M aqueous citrate-phosphate buffer, pH 5, saturated with NaCl) and 5 µL of internal standard solution (1.19 mg/mL of *tert*-amylphenol and 13.4 mg/mL of 2-ethylbutanoic acid in methanol) was transferred to a 22-mL glass headspace vial and the vial was sealed with a Teflon-faced silicon septum. ***Headspace-Solid Phase Microextraction-Gas Chromatography (H-SPME-GC).*** Analysis system consisted of an Agilent 6890 GC (Agilent Technologies, Inc., Palo Alto, CA) equipped with a flame ionization detector (FID) and MPS2 (SPME mode) autosampler (Gerstel, Germany). For SPME, vial was preinclubated at 60°C for 10 min with agitation (500 rpm, 5 s on, 2 s off). Then a SPME fiber (Carboxen/polydimethylsiloxane fiber, Supelco, Bellefonte, PA) was exposed to the vial headspace for an additional 20 min. Immediately after sampling, the fiber was desorbed by splitless injection (injector temperature 260°C; splitless time 4 min; split vent flow 50 mL/min) into a Stabilwax® DA GC column (15 m x 0.32 mm i.d. x 0.5 µm film; Restek, Bellefonte, PA). GC oven temperature was programmed from 35 to 225°C at a rate of 10°C/min with initial and final hold times of 5 and 10 min respectively. For qualitative analysis an Agilent 5973 mass selective (MS) detector was used as the GC detector. Compounds were identified by comparison of their mass spectra and retention indices (Van den Dool and Kratz, 1963) with those of reference standards.]

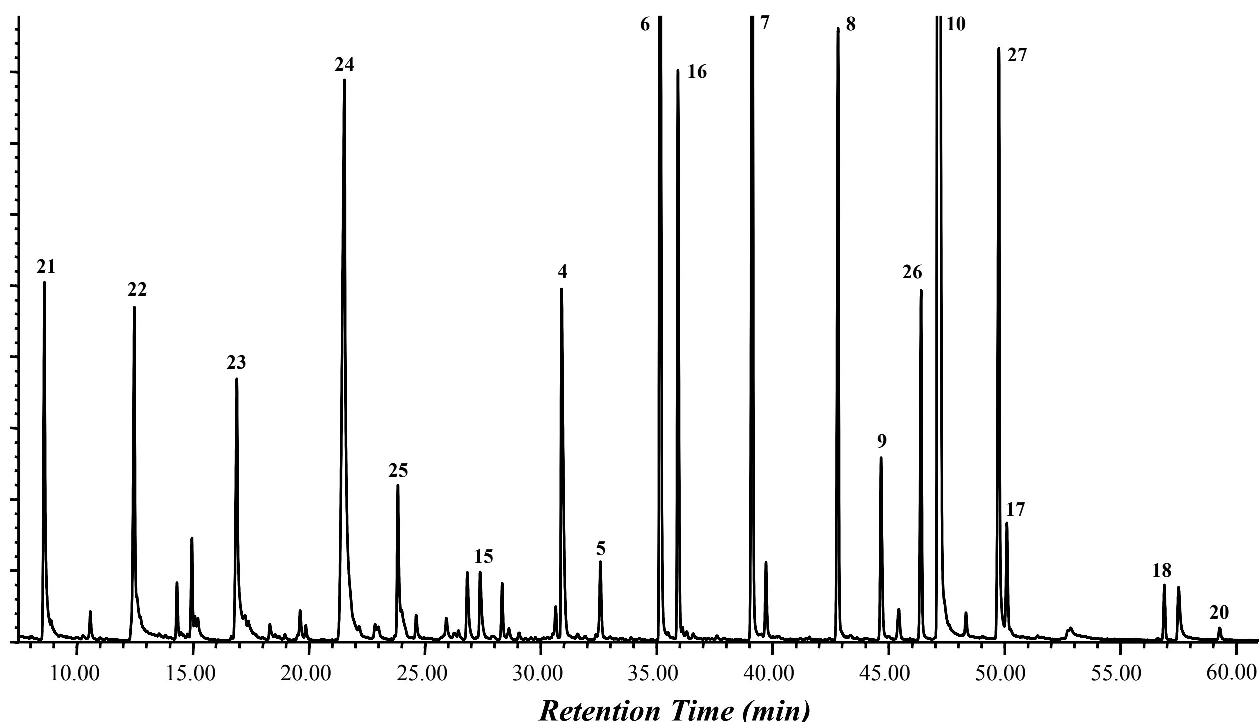

Figure 3. Typical headspace SPME-GC-MS profile of dust collected from a swine production facility. (**21** = hexanal, **22** = heptanal, **23** = octanal, **24** = nonanal, **25** = 1-octen-3-ol, **15** = propanoic acid, **4** = butanoic acid, **5** = 2-/3-methylbutanoic acid; **6** = pentanoic acid, **16** = IS_1 = 2-ethylbutanoic acid, **7** = hexanoic acid, **8** = heptanoic acid, **9** = phenol, **26** = octanoic acid**, 10** = 4-methylphenol {*p*-cresol}, **27** = nonanoic acid, **17** = 4-ethylphenol, **18** = IS_2 = 4-*tert*-amylphenol, **20** = 3-methylindole {skatole}). [One gram sample analyzed by the method described in Figure 3 caption.]

Figure 4--Electronic Nose Sensor Response to Odorant

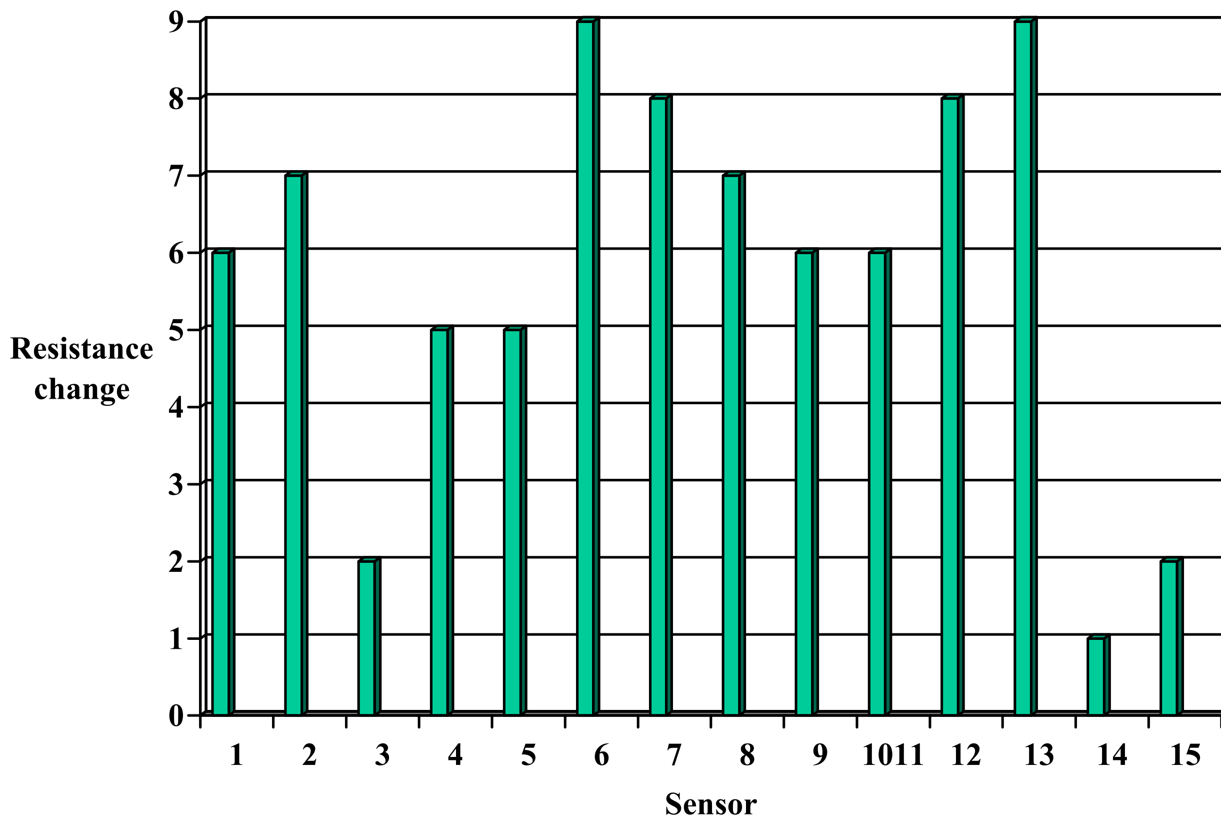

Figure 5--Relationship of Odor Strength of a Pure Compound to Dilution Factor

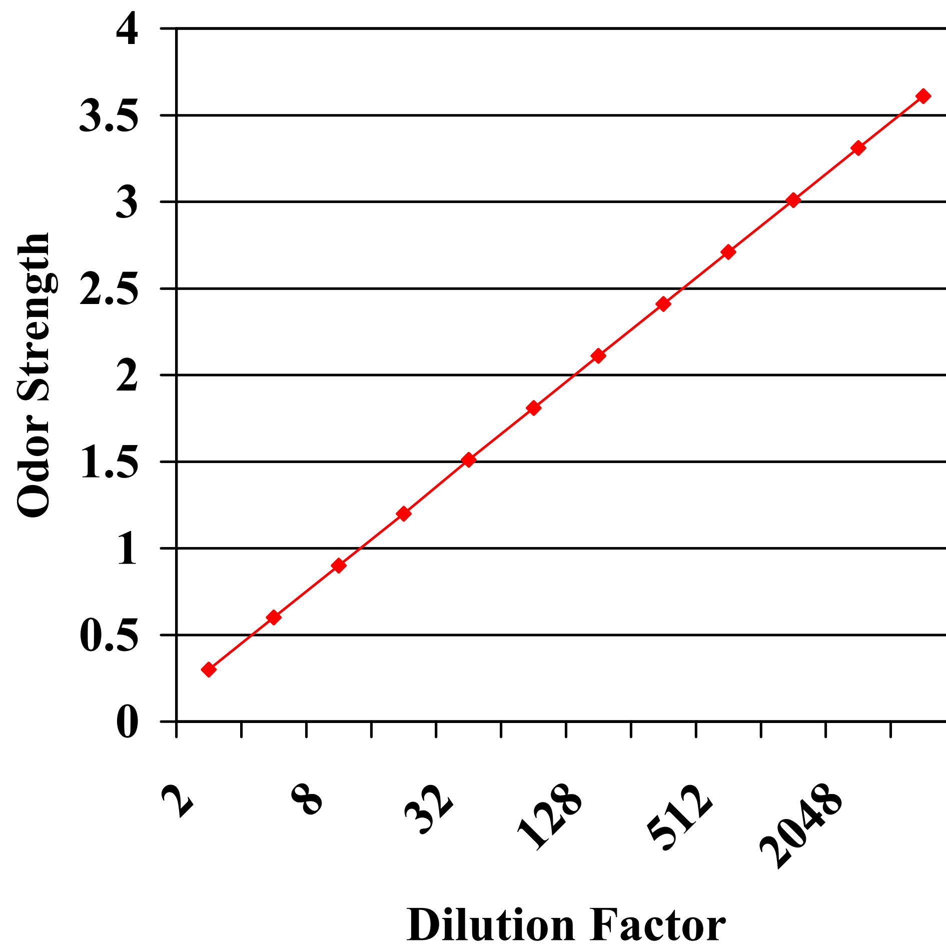

Figure 6--Calculation of Odor Threshold from 3-Alternative Forced Choice Data Determined by Olfactometry

Judge	Dilutions									
	Dilution Factors (concentrations increase →)								**Best Estimate Threshold (BET)**	
	8	7	6	5	4	3	2	1		
	256	128	64	32	16	8	4	2	Value	**$\log_{10}$ of value**
1	0	0	0 *	+	+	+	+	+	45.25	1.65
2	+	0	+	0 *	+	+	+	+	22.62	1.35
3	0	+	0	0	0 *	+	+	+	11.31	1.05
4	0	0	0 *	+	+	+	+	+	45.25	1.65
5	0	0	0	0	0	0 *	+	+	5.65	0.75
6	0	0 *	+	+	+	+	+	+	90.51	1.96
									$\Sigma\log_{10}$	8.41
									Mean	1.41
Group BET Geometric Mean									**25.70** ←	Antilog 1.41

"0" indicates that judge selected the wrong sample from the set of three
"+" indicates that judge selected the correct (different) sample
"Value" is the half-way point between the dilutions where the judge was and was not (*) able to select the correct sample
"BET" is the Best Estimate Threshold = √([+] x [-])

Table 1. Concentrations for Selected Odorants in a Swine Manure Sample

No.[a]	Compound	Concentration (ug/g)[b]
1	Acetic acid	561
15	Propanoic acid	1080
3	2-Methylpropanoic acid	167
4	Butanoic acid	2010
5	2-/3-Methylbutanoic acid	587
6	Propanoic acid	740
7	Hexanoic acid	158
9	Phenol	111
10	4-Methylphenol (p-cresol)	1180
17	4-Ethylphenol	13.2
19	Indole	1.8
20	3-Methylindole (skatole)	10.8
21	Benzeneacetic acid	6.1
22	Benzenepropanoic acid	14.1

[a] Numbers correspond to those in Figures 1-3. [b] Average (n = 2) concentration by H-SPME-GC [***Quantification of Volatile Compounds.*** GC-FID response factor (f_i) for each compound was determined by addition of known amounts of reference standards into 5-mL of matrix modifier solution containing 1 mL of deodorized water prior to analysis. Sample preparation and GC-FID analysis were performed in the same way as described above for samples, with the assumption that the extraction recoveries of individual volatile compounds in this matrix were similar to those in the sample matrix. FID response factors (f_i) were used to calculate actual concentrations according to Zhou et al. (2002). Internal standard *tert*-amylphenol was used to determine f_i values for phenol, 4-methylphenol and 4-ethylphenol, indole and 3-methylindole, and internal standard 2-ethylbutanoic acid was used for acetic, propanoic, isobutyric, butyric, 3-methylbutyric, pentanoic, hexanoic, phenylacetic and 3-phenylacetic acid.]