Technical note: Fourier transform infrared (FTIR) spectroscopy as an optical nose for predicting odor sensation

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ABSTRACT: Quantifying odor is important for objectively assessing the impact of animal production systems on surrounding areas. A possible method that has received little attention is Fourier transform (mid) infrared spectroscopy (FTIR). Gases that contribute to odor have unique infrared spectra, and the advantage of FTIR over electronic nose technology or gas chromatography is that theoretically all these gases can be analyzed instantaneously. To determine the feasibility of FTIR for predicting odor, 71 air samples analyzed by olfactometry were scanned in a spectrometer using an 84-m path-length gas cell. Scans were obtained over a period of about 1 min and from 4,000 to 740 cm\(^{-1}\) with a resolution of 0.5 cm\(^{-1}\). Calibrations for predicting odor were developed using partial least squares regression with full cross-validation. Air samples were obtained from experiments with pigs fed diets formulated to alter odor emission or from stored manure. Odor threshold dilution ratios averaged 676 ± 491 units, with a range from 120 to 2,161. Using these samples, a prediction error for odor sensation of 344 units (\(R^2 = 0.51\)) was obtained. Log transformation of the odor data improved the \(R^2\) to 0.61. Based on the olfactometry data, it is estimated that the measurement error of olfactometry is 250 units, which limits the \(R^2\) of any method to approximately 0.74. Thus, this calibration is very encouraging. In conclusion, FTIR shows promise as a practical means for objectively assessing swine odor.

Key Words: Infrared Spectrophotometry, Nose, Odors, Pigs


Introduction

The production of livestock is invariably associated with emission of odor. These odorous emissions are not always well received by neighbors and passers-by. Worse, there are even indications that these odors can lead to health problems (Schiffman, 1998). Methods for objectively measuring odors are thus urgently needed.

Odorants can be measured using chemical methods, but extrapolation of these data to an odor measurement has not been very successful (Lunn and van de Vyver, 1977). A method that attempts to bypass this difficulty is the electronic nose. In this instrument, sensors react with specific chemical groups of airborne chemicals, changing their conductivity. In principle, these sensors mimic the action of odor receptors in the human nose, and with carefully chosen and sufficient sensors, it may be possible to predict odor sensation (Gardner and Bartlett, 1992). Possible shortcomings of the electronic nose are a limited number of sensors, drift and distortion of sensor response due to moisture, and the use of a very small sample of air (milliliters).

Fourier transform infrared spectroscopy (FTIR) could provide an alternative method for predicting odor sensation. In the mid-infrared range, the region in which FTIR typically operates, all organic compounds interact with infrared radiation, yielding compound-specific absorption characteristics whose intensity follows Beer’s law (ASTM, 1997). Using open-path FTIR, it is possible to measure organic compounds on property boundaries over a distance of several hundred meters, analyzing the air as it transverses across the landscape. Indeed, FTIR (both open- and closed-path) is used for measuring air pollutants such as methane and ammonia (e.g., Childers et al., 2001). Whether this method is suitable for predicting odor sensation, though, has not been investigated. The objective of this study was to determine whether FTIR data could be used for predicting odor sensation as determined using olfactometry.

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Table 1. Olfactometry data (odor threshold dilution ratios) and calibration statistics for North Carolina State University (NCSU), Purdue University, and the combined data set

<table>
<thead>
<tr>
<th>Parametera</th>
<th>NCSU</th>
<th>Purdue</th>
<th>Combined</th>
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<tbody>
<tr>
<td><strong>Sample characteristics</strong></td>
<td></td>
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<tr>
<td>n</td>
<td>41</td>
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</tr>
<tr>
<td>Mean</td>
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<tr>
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<tr>
<td>Minimum</td>
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<tr>
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<td>1,511</td>
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<tr>
<td><strong>Calibration statistics</strong></td>
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<tr>
<td>Conversionb</td>
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<td>RMSEP</td>
<td>381</td>
<td>240</td>
<td>344</td>
</tr>
<tr>
<td>R²</td>
<td>0.57</td>
<td>0.31</td>
<td>0.51</td>
</tr>
<tr>
<td>PC</td>
<td>7</td>
<td>2</td>
<td>10</td>
</tr>
</tbody>
</table>

aRMSEP is the prediction error for the calibration determined using full cross-validation, R² is the resulting explained variation, and PC is the number of principal components used for the regression.
bCalibrations were based on the olfactometry data as is, or after log transformation for the combined data set.

Materials and Methods

Fourier Transform Infrared Spectrometer

The FTIR instrument used was a Magna 760 FTIR equipped with a mercury-cadmium-telluride (MCT) detector and a KBr beam splitter (Nicolet, Madison, WI). Air was sampled using a Saturn variable path-length gas cell set to 84 m in length (Gemini, Anaheim, CA). This cell has an internal volume of 18 L and a length of 1 m but uses gold-coated mirrors to reflect the infrared beam such that an internal path length of, for example, 84 m is obtained.

The FTIR spectra were recorded from 4,000 to 740 cm⁻¹ at a resolution of 0.5 cm⁻¹ such that a total of 13,524 data points were obtained per spectrum. This resolution is a good compromise for achieving resolution of the absorption bands of organic molecules at a desired signal-to-noise ratio for a given total scan time. The interferograms were coscanned a minimum of 64 times to achieve the desired signal-to-noise ratio. Total scan time was approximately 1 min. Absorbance spectra were calculated based on background spectra collected using identical instrument settings immediately preceding the analysis of the test air samples but using clean air.

Air samples (Table 1) were obtained either from experiments carried out in two environmental chambers at North Carolina State University (NCSU) adjacent to the FTIR instrument (n = 41) or from Purdue University (n = 30). The environmental chambers at NCSU typically housed 10 pigs each that were fed diets manipulated to affect odor and(or) ammonia emission and(or) their manure. Pig size varied from growing to finishing pigs. Chambers were operated with a pit recharge system. Air samples from these chambers were collected semicontinuously from the exhaust air stream through Teflon-coated tubing at a rate of 65 to 100 L/min and drawn through the gas cell. In these experiments, a large variation in odor intensity was observed (Table 1).

Two identical environmental rooms with independent and identical ventilation, temperature control, and manure handling systems at Purdue University were used to house finishing pigs (25 pigs per room) for group feeding studies. Experimental diets were formulated to affect the odor, ammonia, and hydrogen sulfide emissions. Air samples from each separate room and locations within the rooms (0.3 m above the woven wire floor and at the exhaust duct) were collected in replicate in two 10 l Tedlar bags (eight total samples each collection) and shipped overnight to NCSU. Tedlar bags were used for all air shipments because they are gas-impermeable and chemically virtually inert (bags manufactured at Iowa State University). These samples represent data collected from more conventional animal housing in which ventilation rate was dictated by heat production in the facility and outdoor climate. After arrival at NCSU, these samples were introduced after evacuating the cell and this air was analyzed while statically contained in the cell.

Olfactometry

At the same time that air samples were collected for FTIR analysis, air samples were also collected in Tedlar bags that were shipped overnight to Iowa State University, where they were analyzed using dynamic forced-choice olfactometry (Huang et al., 1996). Laboratory procedures are fully described elsewhere (Gralapp et al., 2002).

Animal Experiments

Air samples were obtained from experiments assessing the impact of diet composition on odor emission. All experiments employed corn-soybean meal diets as a control. Test diets included diets to which feed-grade antibiotics, alternative calcium and phosphorus salts fiber synthetic amino acids, and low-sulfur mineral sup-
Figure 1. Infrared absorption spectra of water vapor and several gases that may contribute to swine odor. Spectra are offset relative to each other to facilitate interpretation.

Data Analysis

Absorbance spectra were imported into The Unscrambler (Camo, Trondheim, Norway), a chemometrics package. Olfactometry data were subsequently linked to the spectral data. These data were analyzed by partial least squares regression with full cross-validation (Esbensen et al., 1996). In brief, this method restructures the data to emphasize variation between the different spectra in such a way that this variation maximally correlates with variation in the response variable, in this case the olfactometry data. Models to correlate the reorganized spectral data and the response variable are subsequently developed for n-1 samples, after which the deleted sample is predicted with this model. This is repeated for all samples such that an accurate prediction error can be calculated.

Results and Discussion

Infrared spectroscopy relies on the fact that all organic gases interact with infrared light in a compound-specific manner. Thus, acetic acid, ammonia, methyl mercaptan, and p-cresol, to name a few, all have unique infrared spectra (Figure 1). Not only are their spectra unique, but, because absorption is a function of concentration and path length as described by Beer’s law, the concentration of gases can be quantified (ASTM, 1997).

Using infrared spectroscopy, it is thus, in principle, possible to identify and quantify all the gases present in air, presuming their concentration exceeds the detection limit of the instrument and presuming that the spectral features of different compounds can be adequately separated. The detection limit of an instrument is a function of the path-length and the quality of detection (signal-to-noise ratio). For this study, a path-length of 84 m was used and a highly sensitive MCT detector. This combination can yield theoretical detection limits in the order of 10 ppb (ASTM, 1997). Practically, the detection limit is also dependent on interfering compounds, most noticeably water, which affects virtually the entire infrared spectrum.

Because the NCSU samples covered a wide range of odor dilution threshold ratios without distinct stratification, this data set was well suited for evaluating the feasibility of calibrating for odor. Using partial least squares regression and full cross-validation, a calibration could be developed that explained 57% of the variation in odor intensity and yielded a prediction error of 381 (Table 1). Given the small size of the data set no outliers were removed to further improve this calibration.

The Purdue samples were less suited for developing a calibration, likely because sampling day effects were strong. Thus, specific clusters of samples could be identified, with up to eight samples per cluster. Using only the Purdue samples, a calibration could be developed with a prediction error of 240, which explained only 31% of the variation in that population.

Combining both data sets yielded a total of 71 samples, based on which a calibration could be developed that explained 51% of the variation and which yielded a prediction error of 344 (Table 1 and Figure 2). Log transformation of the odor intensity data yielded a calibration that statistically was stronger, with 61% of the variation in odor intensity explained. This calibration had a prediction error of 0.19 (log odor intensity). Log transformation of the data resulted in a more uniform spread of data points, thus de-emphasizing samples with a high odor intensity by decreasing their leverage (distance to the center of the population). Theoretically, the log-based calibration also results in a prediction error, after converting results back to the original odor units, which is more proportional to the actual odor values. This results in smaller prediction errors for samples with low odor intensity and larger prediction errors for samples with high odor intensity. Statistically, this could not be proven for the current data set.

The actual regression coefficients assigned were difficult to interpret because a large number of gases that absorb infrared light were present for which standard spectra were not available at the 0.5 cm$^{-1}$ resolution. Methane (data not shown) and ammonia both received a strong negative regression coefficient, indicating that these gases were negatively correlated with odor (Figure 3). Volatile fatty acids, observable between 1,200 and 1,100 cm$^{-1}$, received a positive coefficient, indicating that volatile fatty acids apparently contribute positively to odor. Fourier transform infrared spectroscopy not only can predict odor intensity, but with the proper reference spectra it can also be used to study which
Infrared optical nose to predict odor

Figure 2. Predicted vs true odor intensity for the data set containing both North Carolina (NCSU) and Purdue samples. Top panel: data as is, yielding a prediction error of 344 and a $R^2$ value of 0.51. Bottom panel: log-converted data, yielding a prediction error of 0.19 and a $R^2$ value of 0.61.

Figure 3. Regression coefficients (multiplied by 1,000) and a typical spectrum. The region displayed is where ammonia and volatile fatty acids absorb strongly. Ammonia, however, receives negative regression coefficients whereas volatile fatty acids receive positive regression coefficients.

In summary, these data demonstrate that making a FTIR calibration for predicting odor appears feasible, and such calibrations may actually provide valuable insight into what constitutes odor. Practically, FTIR, especially open-path, is well suited for field measure-

compounds contribute and do not contribute strongly to odor sensation.

The quality of any calibration is limited by the quality of the reference method, in this case, olfactometry. Based on the olfactometry data collected, it was estimated that the measurement error of olfactometry was approximately 250 units, which would limit the variation explainable by a calibration to approximately 74%. The quality of these calibrations, therefore, has to be judged as reasonable to good. This measurement error also indicates that one of the major challenges for developing indirect techniques for predicting odor intensity is the quality of the reference data.

In summary, these data demonstrate that making a FTIR calibration for predicting odor appears feasible, and such calibrations may actually provide valuable insight into what constitutes odor. Practically, FTIR, especially open-path, is well suited for field measure-

Implications

Fourier transform infrared spectroscopy seems to be well suited both practically and technically for predicting odor from livestock facilities or on property boundaries.

Literature Cited


